Electro-Remediation in The Presence of Ferrous Sulfate as an Ex-Situ Alternative Treatment for Hydrocarbon Polluted Soil

R. Flores[1,2], M. G. García[2], J. M. Peralta-Hernández[3], A. Hernández-Ramírez[4], E. Méndez[1], E. Bustos[1,*]

[1] Laboratory of Treatment of Soil, Centro de Investigación y Desarrollo Tecnológico en Electroquímica, CIDETEQ, S. C. Parque Tecnológico de Querétaro, Safandila Pedro Escobedo, Qro. C.P. 76703, México.
[2] Department of Chemistry, Universidad de Guanajuato. Lascuráin de Retana No. 5, Centro, 36000, Guanajuato, Gto. México.
[3] Centro de Innovación Aplicada en Tecnologías Competitivas, CIATEC, A. C. Calle Omega 201, Fracc. Ind. Delta, 37545, León, Guanajuato, México.
[4] Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Av. Guerrero y Progreso, Col. Treviño, 64570, Monterrey, Nuevo León, México.
[*]E-mail: ebustos@cideteq.mx

Hydrocarbons in soil have become a growing concern due to their chronic toxicity and their impact on human health and the environment. Various conventional physical, chemical and biological technologies are available for the treatment of contaminated sites; however, they are unsuccessful in the remediation of soils that contain compounds with low solubility, such as hydrocarbons. Electrokinetic remediation is one of the most promising technologies for the remediation of soils. In this process, application of an electric field between two electrodes inserted in the contaminated mass allows the separation of contaminants, with or without the addition of chemical reagents. This study investigates the feasibility of using an enhanced electrokinetic process in the presence of $FeSO_4$ under acidic conditions for the remediation of hydrocarbons contained in Vertisol pelic and Gleysol soil. Hydrocarbon removal was more efficient in Vertisol than in Gleysol soil when this electrochemical treatment was applied.

1. INTRODUCTION

There are numerous polluted sites requiring efficient methods for removal of organic contaminants that pose a serious threat to the environment. In this context, the development and

implementation of environmentally friendly and cost effective technologies are needed for organically contaminated soil remediation [1].

Currently, conventional techniques for soil remediation, such as solidification / stabilization and soil washing / flushing, have been the most common technologies used to treat soils contaminated with hydrocarbons [1]. In some cases, bioremediation has also been used to treat contaminants in soil [2].

However, these technologies have difficulty treating heterogeneous subsurface environments that contain clay and/or organic soils with low permeability. *In-situ* soil flushing with surfactants / cosolvents has shown great promise for polyaromatic hydrocarbon (PAH) contaminated soils with hydraulic conductivities of at least 10^{-5} cm s^{-1} in magnitude, but the likelihood of success decreases when lower permeability soils are present [3].

For the remediation of soils polluted with organic compounds, incineration is the most widely used method. This method is very expensive and generates problems with air emissions and noise [4]. In contrast, *in-situ* bioremediation technologies [5] are being sought as alternatives that are less expensive and more energy efficient.
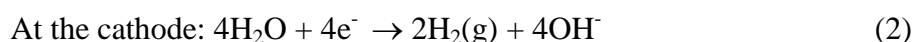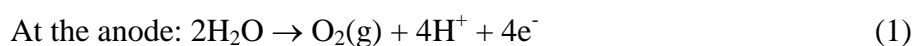
Bioremediation, however, is often slow and may be incomplete because of electron-withdrawing organic compounds that inhibit electrophilic attack by oxidative enzymes of aerobic bacteria [6]. To cope with limitations of bioremediation, *in-situ* chemical oxidation / reduction methods have also been studied [7-8].

The electrokinetically enhanced *in-situ* flushing process basically involves the installation of electrodes into injection and extraction wells, along with the application of a low voltage gradient across designated anode and cathode electrodes.

The electrically induced contaminant transport mechanism of electroosmosis greatly improves soil–solution–contaminant interaction through low permeability soils. Low pH conditions occur in low buffering soils, however, as a result of migration of the acid generated at the anode of the electrolysis reaction. The low pH soil conditions inhibit electroosmosis and, hence, removal efficiency [3].

Although electrokinetics is commonly used for toxic metal contamination, this procedure can be successfully used for the remediation of soluble organic contaminants, such as benzene, toluene, and phenol [3].

When an electric potential is applied during this electrochemical process, electrolysis of water occurs at the electrodes according to the following reactions:

$$\text{At the anode: } 2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \qquad\qquad (1)$$

$$\text{At the cathode: } 4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^- \qquad\qquad (2)$$

As can be seen from these equations, the electrolysis reactions cause an acidic solution to be generated near the anode and an alkaline solution near the cathode.

The primary contaminant transport mechanisms that occur during electrokinetics are electromigration, electroosmosis, and electrophoresis. Electromigration describes the transport of ionic

species present in the pore fluid. This process is largely responsible for generating the electrical current, and it includes the migration of H^+ and OH^- towards the oppositely charged electrode.

Moreover, under an electric field, electroosmotic flow (electroosmosis) is produced because the locally existing excess ions migrate parallel to the particle surface towards the oppositely charged electrode, transferring momentum to the surrounding fluid molecules via viscous forces. Electroosmosis depends on the net amount of ionic migration towards an electrode location, and, in low permeability clayey soils, the net ion migration may be high and significantly affect the decontamination process.

The electrolysis reactions affect the remediation process because of the ionic products (H^+ and OH^-) that may migrate and/or be transported by electroosmotic advection towards the oppositely charged electrode location. Thus, an acidic front of solution may move from the anode towards the cathode, and/or an alkaline (OH^-) front of solution may move from the cathode towards the anode.

The rate of electromigration could be affected by ionic mobility, and, since hydrogen ions are smaller and have 1.76 times the ionic mobility of hydroxyl ions, the acidic front generally moves faster through the soil. In addition, the reaction kinetics, or the rate of the electrolysis reactions at the electrodes, could affect the generation and migration of the hydrogen and/or hydroxyl ions [3].

On the other hand, considerable attention has been given to various applications in the environmental remediation of ferrate ion Fe(VI) as a potassium salt due to its great oxidizing power, selective reactivity, stability as a salt, and non-toxic decomposition of ferric ion byproducts. Due to the chemical properties mentioned before, Fe(VI) has been proposed as a green oxidant, coagulant, disinfectant, and anti-flocculent to treat different organic and inorganic contaminants found in wastewater and soil [9].

An important property of the ferrate ion is the ability to carry out oxidation reactions faster than other oxidant species, such as permanganate and chromate [1, 10]. Consequently, the ferrate ion is an emerging soil and wastewater oxidant. The principal reactions that can occur with Fe(VI) are as follows:

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad \text{acidic conditions, 2.20 V}$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \qquad \text{basic conditions, 0.70 V}$$

In previous work, Villanueva and col. [11] reported the electrochemical degradation of an azo dye solution enhanced by the addition of a ferrous salt. In this context, it was suggested that the reaction rate was increased by the addition of Fe^{2+} (as ferrous sulfate) to the system, assuming generation of ferrate ion [Fe(VII)] over the electrode.

In this paper, electrokinetic assays were conducted for electro-remediation of two different kinds of polluted soils, Vertisol pelic and Gleysol. The electro-oxidation of the organic matter was carried out in the presence of $FeSO_4$ in acidic conditions to evaluate the effect of this ferrous salt in the electrokinetic process.

2. MATERIALS AND METHODS

2.1. Sampling of Clean and Polluted Soils

Samples of clean and polluted Vertisol pelic soil of Salamanca, Guanajuato, Mexico (20º36'07 N 101º10'43 O 5640), and Gleysol of Nuevo Teapa, Veracruz, Mexico (15Q0359514 SO 1998831 UTM 28M) were studied in this investigation. The soil was collected from the A - horizon (0 – 10 cm) using 135 stainless steel shovels according to NMX2–12 / 1-1987 and chapter 9 of EPA SW 846. The climatic conditions during sampling were at 136 to 293 K, with a 30 Km/h wind speed.

2.2. Chemicals

The salt used as source of ferrous ions was 97% $Fe(SO_4) \bullet 7H_2O$, along with $HClO_4$ from J. T. Baker of high purity grade. All other reagents were analytical grade and used without further purification.

2.3. Electrochemical Apparatus and Procedures

Experiments were performed in an electrochemical cell reactor with about 35 g of soil at room temperature (297 ± 2 K). The experiments were conducted at 20 V with a DC Power Supply GP-4303DU potentiostat, recirculating 12 mM $Fe(SO_4) \bullet 7H_2O$ in 0.1 M $HClO_4$ with a Master Flex L/S peristaltic pump for 4 h. The current across the system was measured with a Fluke digital multimeter.

2.4. Analytical Procedures

For the physicochemical characterization of the polluted soils, NOM–027–REC–NAT-2008 was followed to determine pH, electric conductivity, percent humidity, real density and hydrocarbon quantity.

The pH was determined with a glass pH electrode (BECKMAN) using 10 g of soil and 25 cm^3 of water. Density measurements were obtained with a pycnometer with 10 mL of water in 0.50 g of soil. Electric conductivity (EC) was measured using an ORION conductivity meter (NMX–AA–093-SCFI).

For metal quantification, each sample of 30 g of soil was digested in 50 mL of solution with 5 mL of 2% HNO_3 and characterized using a Perkin Elmer model Optima 3300 Inductively Coupled Plasma (ICP).

Gas chromatography with mass detection was employed using an HP-5 MS column, with temperature control in the injector and detector of 543 and 573 K respectively. The carrier gas was helium UHP at a constant flow of 0.8 mL min^{-1}. Initial oven temperature was 318 K for 4 min and 282 K min^{-1}. The rate was 282 K min^{-1} from 318 to 573 K.

To evaluate pollutant removal, absorbance was measured at 300 nm using an Ocean Optics UV-Vis spectrophotometer to verify the double bond π - π^* electronic transitions of HC aromatic rings.

To verify the removal of HC following electrochemical treatment of polluted soil, the pollutant was obtained in liquid phase by Soxhlet extraction using CH_2Cl_2 and the calculation: % efficiency = $((([HC]_{t = 0 h} - [HC]_{t = 4h}) / [HC]_{t = 0 h}) * 100)$, where $[HC]_{t = 0 h}$ is the HC extracted from polluted soil, and $[HC]_{t = 4h}$ is the HC extracted from electro-remediated soil after 4 h of electrochemical treatment.

3. RESULTS AND DISCUSSION

The characterization of the different kinds of polluted soils is presented in Table 1. In the case of pH value, the Gleysol polluted soil (PS) showed a pH close to 6, with the Vertisol PS showing a pH of 4.98.   The behavior of the last sample is of consequence in that it contains mostly 1,2-benzenedicarboxilic acid, an organic acid with a pKa around 3.5 [12]. The same hydrocarbon effect was evident in the percent humidity, with that of the polluted Vertisol lower than Gleysol soil, showing 11 and 31 % respectively.

On the other hand, conductivity was higher in the Vertisol, as compared to the Gleysol PS with a high clay content [12]. Density was the same for all cases, eliminating texture and porosity effects, although the polluted Vertisol soil had the major concentration of hydrocarbons, explaining the lower pH and humidity seen [12].

Table 1. Data of physicochemical characteristics of Vertisol and Gleysol soils polluted with hydrocarbons.

Characteristic	Vertisol	Gleysol
pH	4.98	6.44
Conductivity / μS	1.36	0.52
Humidity / %	10.99	30.64
Density / g cm^{-3}	1.70	1.71
Hydrocarbons / g Kg^{-1} soil	1.64	0.21

Once the different soils were analyzed physicochemically, the electro-remediation process was developed. According to the literature, Ti modified with IrO_2 - Ta_2O_5 was probed as an anode to increase the window of potential to remove hydrocarbons during electrolysis in a soil matrix, in comparison with a naked Ti electrode.

In this manner, two combinations of electrodes, Ti | Ti and Ti | Ti / IrO_2 - Ta_2O_5 , were compared during electro-remediation with the experimental set up of the electrochemical reactor. After 20 min, a sample of the output flow was taken and analyzed with UV-Vis spectroscopy. The pH, conductivity and current were measured at the same time.

All final solutions had an acidic pH, at around 4. This behavior was in accordance with the input of solution to electrolytically eliminate the soil hydrocarbons with 0.1 M $HClO_4$.

The current density generated in the Vertisol soil was slightly higher than in Gleysol soil, at 0.03 and 0.01 mA cm^{-3} respectively. This is a consequence of the major metallic ions shown by ICP analysis (Table 2), mainly K, S and Na, which were lixiviated in acidic conditions.

Table 2. ICP analysis by particle size of polluted Vertisol and Gleysol soil. Metallic ion concentrations are in ppm.

Element	Particle Size / mm					
	Vertisol Pelic Soil			Gleysol Soil		
	1.60	0.25	0.0625	1.60	0.25	0.0625
C	17.15	21.4	23.41	9.54	10.78	7.23
O	40.33	39.08	39.12	45.3	44.59	31.36
Na	1.59	1.19	1.08	1.09	1.09	0.8
Mg	1.09	1.07	1.13	1.15	1.09	1.01
Al	6.89	6.61	6.47	8.64	8.8	6.01
Si	22.99	21.93	19.95	26.49	25.8	14.72
S	0.53	0.68	0.86	0.29	0.27	0
K	2.08	1.84	1.53	0	0.3	0
Ca	2.36	1.25	1.21	1.66	1.65	1.18
Ti	0.45	0.47	0.5	0.88	0.9	1.06
V	0.23	0.42	0.55	0.56	0.48	0.53
Fe	4.32	4.06	4.2	4.39	4.25	5.41

For conductivity, the highest value of 50 mS was obtained in Gleysol soil after 4 h to the end of the experiment using the combination of Ti │ Ti / IrO_2 - Ta_2O_5 electrodes. The other cases showed a conductivity of around 30 mS after 2 h, which remained constant for the 12 h of monitoring (Figure 1). This behavior is a consequence of the Dimensional Stable Electrode (DSA) of Ti / IrO_2 - Ta_2O_5, which has a greater roughness and is more stable and active than Ti when used as an anode.

Figure 2 shows a comparison of the different absorbances of the output of the electrochemical reactor, obtained from UV-Vis absorbance ($\lambda = 300$ nm) indicated for each solution after crossing the reactor.

In verifying removal efficiency with Soxhlet extraction of grease and fats, the Vertisol and Gleysol soils showed the same efficiency at 84% pollutant removal. This was very interesting, as these soil types were electro-remediated with only water, applying 20 V during 4 h and showing a removal efficiency of 33% for Vertisol and 62 % for Gleysol soil.
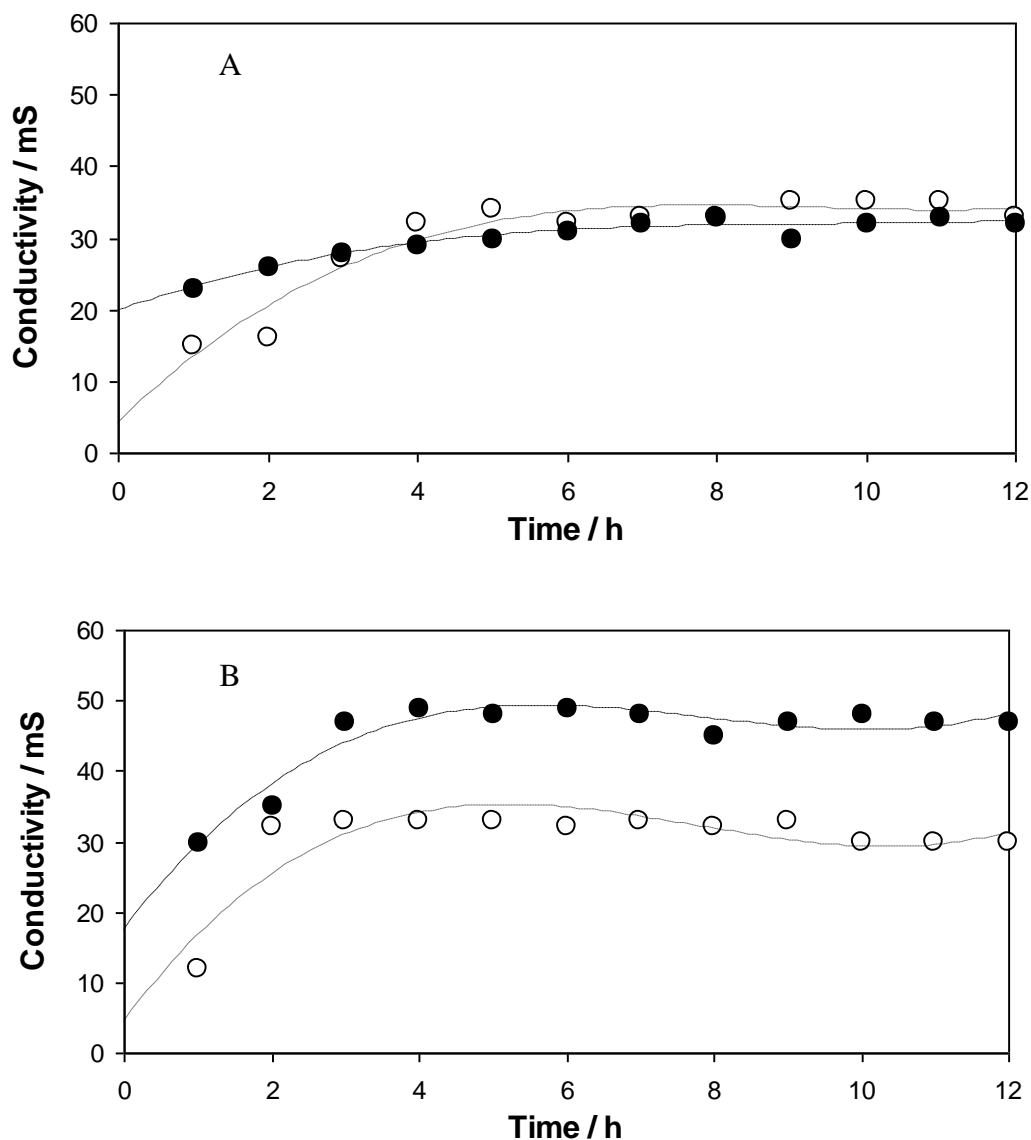
Figure 1. Conductivity of the different samples obtained during the electro-remediation of Vertisol (A) and Gleysol (B) soil using the different combinations of electrodes (anode / cathode): Ti / Ti (open circles) and Ti | Ti / IrO_2 - Ta_2O_5 (black circles).

These results indicate that pollutant removal with this type of treatment is practically the same, and that the elimination of pollutants in the different kinds of soils in the presence of $FeSO_4$ in acidic conditions does not change the efficiency of removal. In this sense, the ferrate ion was an efficient oxidant species, where the Fe^{2+} of ferrous sulfate could generate the ferrate ion as FeO^{2-}_4, which was transformed to Fe^{3+} in this acidic condition [11].

The last result was verified with chromatographic analysis of each extract, where it can be seen that the Vertisol soil had a higher quantity of different compounds (Table 3) than Gleysol soil (Table 4). This effect was probably supported by the fact that the polluted Vertisol soil had some aliphatic contaminants, whereas the polluted Gleysol soil had a major content of aromatic compounds.
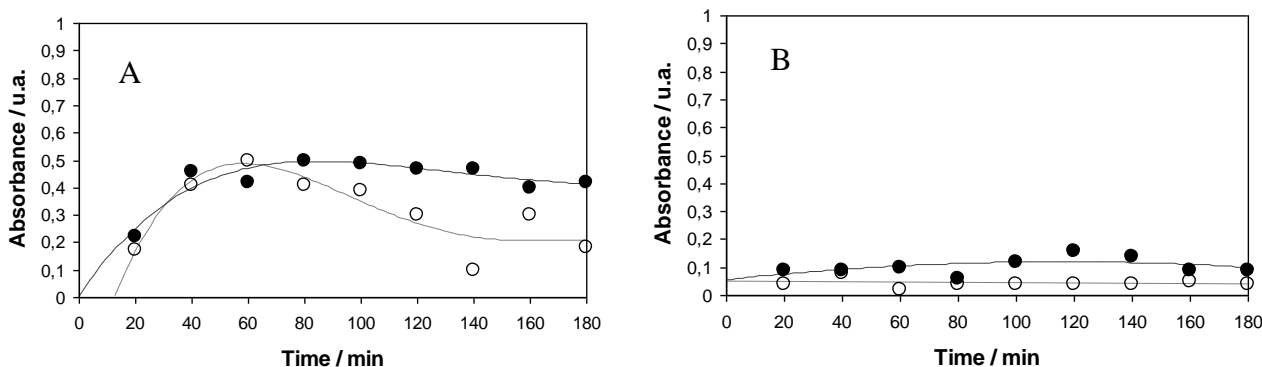
Figure 2. Absorbance at 300 nm of the different samples obtained during the electro-remediation of pollutants in Vertisol (A) and Gleysol (B) soil using the different combination of electrodes (anode / cathode): Ti / Ti (open circles) and Ti│Ti / IrO$_2$ - Ta$_2$O$_5$ (black circles).

Table 3. Retention time and area of each product in the chromatogram obtained after electro-remediation of Vertisol soil.

System	Compound	Retention Time (min)	Area (%)
Polluted Soil	1,2-benzenedicarboxilic acid.	31.67	47.3
	Dotriacontane.	2.27	2.27
	Hexatriacontane.	3.07	3.07
	Hexacosane.	6.23	6.23
Electro-remediation of polluted soil using Ti | Ti	Napthalene.	0.17	16.65
	1,4,6-Trimethylnapthalene.	0.19	17.55
	2,3,5-Trimethylnapthalene.	0.44	17.77
	Fluorene.	0.52	18.51
	Heptadecane.	1.38	20.01
	Pentadecane.	1.08	20.66
	Octadecane.	2.12	21.28
	Tetradecane.	1.11	21.38
	Methyldibenzothiophene.	2.7	22.08
	Nonadecane.	1.97	22.49
	Anthracene.	1.3	22.65
	Phenanthrene.	1.37	22.87
	2-Butanone.	0.57	23
	2,8-Dimethyldibenzothiophene.	1.42	23.28
	3,4-Dimethyldibenzothiophene.	1.11	23.45
	Eicosane.	2.08	23.64
	Henicosane.	1.98	24.73
	Pentadecane.	1.41	25.12
	Tricosane.	0.98	26.77
	Tetracosane.	0.63	27.74

Table 3. Retention time and peak area obtained for each product after electro-remediation of Vertisol soil (Continued....)

System	Compound	Retention Time (min)	Area (%)
Electro-remediation of polluted soil using Ti | Ti / IrO$_2$ - Ta$_2$O$_5$	Naphthalene.	0.1	16.41
	Undecane.	0.06	16.69
	Pentadecane.	0.4	17.24
	Tridecane.	0.17	18.14
	Hexadecane.	1.44	18.65
	Tetradecane.	0.59	19.5
	Heptadecane.	1.41	20
	Pentadecane.	1.47	21.76
	3,4-Dimethyldibenzothiophene.	1.04	23.43
	2,8-Dimethyldibenzothiophene.	1.24	23.51
	Eicosane.	2.19	23.62
	Phenanthrene.	1.88	23.95
	Heneicosane.	1.99	24.71
	Octadecane.	0.39	26.49
	Docosane.	0.31	27.47
	Tetracosane.	0.62	27.73
	Tricosane.	0.12	34.59

Table 4. Retention time and peak area obtained for each product after electro-remediation of Gleysol soil.

System	Compound	Retention Time (min)	Area (%)
Polluted Soil	Phenanthrene.	4.11	22.08
	Anthracene.	4.11	22.08
	Flouranthene.	3.85	26
	Di-(2-ethylhexyl)phthalate.	3.72	29.96
	1,2-Benzendicarboxylic acid.	14.62	31.67
	Benzopyrene.	3.8	32.9
Electro-remediation of polluted soil using Ti | Ti	Naphthalene.	4.72	16.11
	Dodecane.	3.17	18.64
	2,3,5-Trimethylnaphthalene.	4.21	17.99
	1,2-Benzendicarboxylic acid.	42.63	30.89
Electro-remediation of polluted soil using Ti | Ti / IrO$_2$ - Ta$_2$O$_5$	Phenanthrene.	2.23	21.9
	Anthracene.	0.78	22.03
	Flouranthene.	3.43	25.25
	Pyrene.	3.13	25.85
	1,2-benzendicarboxylic acid.	1.88	29.92

4. CONCLUSIONS

Electro-remediation of soil using $FeSO_4$ in acidic conditions applying 20 V for 4 h had the same efficiency in removing grease and fats by Soxhlet extraction in Vertisol pelic soil and Gleysol soil at 84% efficiency, in contrast with that obtained in water (33% for Vertisol and 62% in Gleysol soil).

This behavior is a consequence of the ferrate ion, which was an efficient oxidant species, where the Fe^{2+} of ferrous sulfate could generate the ferrate ion as FeO_4^{2-}, which was transformed to Fe^{3+} in acidic conditions during the electro-remediation of polluted soil.

These results demonstrate a new alternative to treat high permeability soils with organic compound pollutants, in which application of the electro-remediation process is sometimes difficult.

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