Assessment of IrO_2-Ta_2O_5|Ti electrodes for the electrokinetic treatment of hydrocarbon-contaminated soil using 1D and 2D electrode arrays

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ABSTRACT

In recent years, physicochemical processes such as the electrokinetic treatment (EKT) have gained acceptance as suitable alternatives to restore hydrocarbon (HC)-contaminated sites. EKT entails relatively short times, moderate operation costs and high removal efficiencies, being usually applied in heterogeneous soils with low permeability. In this work, 1D and 2D configurations, which require one sole pair of electrodes (facing each other) or six anodes around a central cathode (radial array), respectively, have been tested by employing Ti cathodes and anodes, as well as purpose-made IrO_2-Ta_2O_5|Ti as dimensionally-stable anodes (DSA®). The electrodes were partially introduced into a real Vertisol soil contaminated with heavy and intermediate fractions of HC. The distance between the cathode and each anode was of 6 cm at laboratory scale employing a 276 cm^3 container with 2.2 kg of polluted soil and a 115 cm^3 container with 87.8 g of polluted soil for the 2D and 1D arrays, respectively. From GC-MS analysis of fat and oil content, it has been found that the radial 2D array with one central Ti cathode and six IrO_2-Ta_2O_5|Ti anodes performed better, reaching 58% HC removal near the anode applying 30 V and an electric field of 2.4 A cm^{-1}. The effect of the treatment on the morphology of the anodes has been analyzed by SEM-EDX.

Keywords: Electrokinetic treatment, soil remediation, hydrocarbons, DSA® electrode.

1. INTRODUCTION

In recent years, the fragile equilibrium of our ecosystems is being jeopardized by the massive use of water, air and soil resources in multiple activities, from agriculture to industrial manufacture and urban growth. Both, abuse and misuse of hazardous materials and wastes have caused a vast number of environmental disasters and, as a result, life on Earth will become seriously threatened unless more restrictive legislation and highly effective decontamination technologies are established worldwide.

Soil and groundwater pollution is well known, but the problem has been only recently addressed from public and private stakeholders, who aim at analyzing the kind of contamination and its impact in terms of concentration. Nowadays, some novel soil remediation technologies are defined as essential tools to recover the affected soil and ensure its viability for all living beings [1]. Generally speaking, contaminated soil treatments include physical, chemical, thermal and biological techniques, which are versatile enough to offer solutions to most pollution issues.

In order to assure the most adequate management of traditional and innovative technologies for soil treatment, it is important to gain knowledge on as many factors as possible, as for example the type of pollutant and soil characteristics, the role of underlying groundwater and the time available for carrying out the decontamination of the affected area [2]. Physicochemical technologies, which represent the most diverse group of remediation technologies, include soil vapor extraction, solidification/stabilization, oxidation, soil flushing, and electrokinetic separation [2-3]. On the other hand, there exist some contaminants that are difficult to remove due to their high inherent persistence coupled with the low solubility and strong adsorption to soil surfaces and organic matter in clay soils of low permeability [3]. The physicochemical processes such as the electrokinetic treatment (EKT) can be a good alternative to restore sites contaminated by hydrocarbons (HC) and, according to the literature [2-3], this is a promising and innovative technology for achieving the remediation within a minimum amount of time, at moderate operating costs, and it allows obtaining higher efficiencies

compared to other technologies mentioned above. The EKT involves the application of low current or potential gradient between at least a pair of electrodes, namely anode and cathode, which are partially inserted into the soil [2], in the presence of a supporting electrolyte (0.1 M NaOH) that enhances different transport phenomena and acts as hydraulic and ionic conductor. The EKT is most usually applied in heterogeneous soils with low permeability, being possible to employ it *in situ* or *ex situ* [4].

Regarding the experimental setup of EKT, different configurations can be used. The electrodes can be arranged horizontally or vertically on the x-y spatial plane. Most laboratory or pilot EKT studies are carried out in two dimensions configurations (2D, Figure 1A), where the central electrode is the cathode and the anode corresponds to radial zone composed of six identical electrodes, as well as in one dimension arrays (1D, Figure 1B), where the plate-shaped electrodes correspond to the cathode (-) and the anode (+) facing each other at a certain distance [3,5]. During the EKT trials, the simultaneous occurrence of water electrolysis gives rise to the appearance of an acid front from anode to cathode and an alkaline front from cathode to anode [2-3], and three fundamental mass transport phenomena govern the removal of pollutants from the soil matrix, namely electromigration, electroosmosis and electrophoresis, being the first two the most relevant for the removal of HC present in soil [6].

Although the EKT seems to be quite simple, there are several physicochemical factors influencing the transport of pollutants and, consequently, the effectiveness of the remediation. Among the main factors, the occurrence of oxidation and reduction reactions as a result of the application of electrical current is prevailing, and this depends on the nature of the electrodes used. Sometimes, cheap materials such as iron, steel or graphite are preferred [6]. But, in order to avoid introducing contaminants into the system, inert substrate materials such as titanium having an electrocatalytic coating composed of metal oxides, so-called dimensionally-stable anodes (DSA®), are generally chosen [3,7-8] The structure of the electrodes must be porous to ensure good contact with the electrolyte and

favor the release of the gases produced from water electrolysis [6], whereas their size, shape and interelectrode distance affect the removal rates [9]. DSA® electrodes enhance the kinetics, favor the thermodynamic control at interfacial level, therefore improving their performance and selectivity, and provide corrosion protection, among other benefits. DSA® has been widely used for chlorine production, electroplating, organic synthesizers and wastewater treatment [10-13]. Apart from Ti, Zr, and Ta can also be used as substrates to deposit different oxides like IrO_2, RuO_2 and SnO_2 [14,15]. In particular, IrO_2-Ta_2O_5-coated Ti anodes were rapidly developed in the past decades owing to their high stability and great durability under aggressive operation conditions, especially when large oxygen evolution is expected as occurs in anodic oxidation. The thermal decomposition method for fabricating IrO_2-Ta_2O_5 coatings is well-accepted due to its low cost and simple application. Recent studies have shown that Ti substrate becomes oxidized during heating steps [16].

In the present investigation, IrO_2-Ta_2O_5|Ti anodes made by painting followed by thermal decomposition have been used in the electrokinetic treatment of real HC-contaminated Vertisol soil. Both, 1D (linear) and 2D (radial) configurations have been compared in terms of fats and oils removal at different regions of the reactor. Ti anodes have been used as well for comparison, and the effect of EKT on the morphology of both kinds of anodes has been assessed by scanning electron microscopy coupled to energy-dispersive X-ray spectroscopy (SEM-EDX).

2. MATERIALS AND METHODS

2.1. Construction and characterization of IrO_2-Ta_2O_5|Ti

2.1.1. Pretreatment of Ti substrates

Titanium (ASTM grade 2) was employed as substrate for preparing the DSA®. Planar (5.3 cm x 2.5 cm x 0.2 cm) and cylindrical (diameter of 1.0 cm and a length of 5.0 cm) Ti electrodes were sandblasted [13,15,17,18]. The substrates were etched with a 40% oxalic acid solution for 20 min [13,15,19,20], then rinsed with deionized water and finally dried. The main objective of the pretreatment was to increase the electrode surface area and promote a better anchorage of the modifier solution.

2.1.2. Construction of IrO_2-Ta_2O_5|Ti

For the electrode synthesis, the modifier solution was prepared by dissolving H_2IrCl_6 (Strem Chemicals, 99.9%) [15,17,18,20] in hydrochloric acid [11,13], and $TaCl_5$ (Strem Chemicals, 99.9%) in isopropanol [13,17,18]. Both solutions were mixed and the metal weight ratio (Ir:Ta) in the precursor solution was 20:80. Finally, the modifier solution was applied onto the pretreated titanium substrates using a brush [13,15], and metal oxides were obtained by thermal decomposition in two steps: the first one, at 523 K for 10 min, followed by a second one, at 723 K for 1 h [13,17,18].

2.1.3. Characterization of IrO_2-Ta_2O_5|Ti

IrO_2-Ta_2O_5|Ti was used as the anode and Ti as the cathode to carry out an exhaustive electrolysis for 1 h with a constant potential difference between them (E_{cell}), from 5 to 30 V in steps of five units, in the presence of clean Vertisol soil with the 1D electrochemical cell. During each electrolysis, the current density was measured in order to obtain the current density (j) vs. E_{cell} plot. The morphology of the DSA® electrodes was evaluated from micrographs obtained by SEM using a Jeol JSM 6500 microscope operating at 15 kV, whereas microanalysis was performed using its EDX Oxford Inca 300 analyzer.

2.2. Electrokinetic treatment of HC-polluted soil

2.2.1. Clean and HC-polluted soil

In this study, Vertisol soil from an industrial area in the central region of Mexico (20º 34" N and 101º 12" W, 630 mmHg, 1720 m) was used with and without HC content. It has been characterized on the basis of the NMX2-12/1-1987 regulation and the chapter 9 of SW82-EPA. The Vertisol soil had a pH = 6.64, with clay (< 0.002 mm), silt (0.05 – 0.002 mm) and sand (> 0.05 mm) content of 52.54%, 22.16% and 25.30%, respectively. It presented a clay texture and dark gray color, showing an apparent and real density of 1.7 and 2.5 g/cm^3, respectively, with a 32% of pores. This kind of soil has 2.68% of organic content, as well as 38.2 meq kg^{-1} soil of cation exchange capacity, and contains SiO_2, $Na_3(PO_4)$-$Al(PO_4)$, MgO-MnO and 5.500 mg of fat and oil per kg of dry soil [21].

2.2.2. Configurations employed

1D and 2D electrochemical systems were implemented for the electrokinetic treatment of clean and HC-contaminated soil. As shown in Figure 1A, the 2D system was devised as a radial array with six cylindrical bars as anodes surrounding a single cylindrical bar as central cathode. The interelectrode gap between the cathode and each anode was of 6 cm (Figure 1A). The anodic cylinders were made of Ti or IrO_2-Ta_2O_5|Ti, whereas the cathode cylinder was always made of Ti. In the 1D system (Figure 1B), one single anode (Ti or IrO_2-Ta_2O_5|Ti) and cathode (Ti) faced each other at a distance of 6 cm and, at 1 cm to the right and to the left of the anode and cathode, a filter paper was employed as physical barrier to contain the soil [5].

2.2.3. Electrokinetic conditions

A GP-4303DU DC power supply was used to apply a given current between the electrodes during the EKT trials. For the 1D configuration, an acrylic rectangular cell of dimensions 2.0 cm x 14.4 cm x 4.0 cm was used, containing 87.8 g of HC-polluted soil with face-to-face configuration. The samples were immediately wetted,

protecting the soil with a physical barrier as paper. This system was utilized to obtain the *j* vs. E_{cell} plot. On the other hand, the experiments with a 2D configuration were carried out in a 23.0 cm x 23.0 cm x 6.0 cm container, using 2.2 kg of clean or HC-contaminated Vertisol soil. In both configurations (1D and 2D), the soil samples were previously moistened in 0.1 M NaOH for 18 h.

2.2.4. Evaluation of soil remediation

The removal of HC was assessed through the determination of the content of fats and oils (F&O), which were measured by Soxhlet extraction according to the NMX-AA-005-SCFI-2000 protocol. The process was based on the dissolution of fats, oils and other soluble organic compounds in hexane in diatomaceous soil. They were extracted on a Soxhlet equipment using hexane as a solvent to develop the reflux for 4 h under a specific temperature until the criterion of 80 refluxes was achieved. The extracts were obtained from fats and oils and then were resolved using 98% dichloromethane analytical grade, and the obtained solution was analyzed semi-quantitatively by gas chromatography coupled to mass spectrometry (GC-MS, Hewlett Packard) according to EPA method 8270 D rev 4 (1998). On the other hand, the main physicochemical parameters of the soil, such as pH and electrical conductivity were measured with equipment from Hanna. Both of them were determined before and after the EKT trials by using the NOM-021-RECNAT-2000 protocol.

3. RESULTS AND DISCUSSION

3.1. Electrokinetic treatment of polluted soil using a 1D (linear) array

In Figure 2, the clear increase of current density when raising the cell voltage from 5 to 25 V is shown, whereas only a slight *j* increase can be observed from 25 to 30 V, as a result of the secondary reactions involving water electrolysis [5]. Based on this, the cell voltage chosen to carry out the EKT trials using the 1D configuration was 30 V, which generated an electric field of 2.4 A cm^{-1} with a consequent maximum removal of fats and oils of 640 mg kg^{-1} using IrO_2-Ta_2O_5 | Ti as the anode

and Ti as the cathode, with a distance of 6 cm in presence of 0.1 M NaOH. For the comparative evaluation of the anodes, the total quantification of HC was made through the determination of the F&O content in different regions of the container: close to anode, in the center and close to the cathode. The initial F&O content was 3087.00 mg kg^{-1}. As shown in Figure 3, the final F&O content was 1694.93, 2058.31 and 2228.78 mg kg^{-1} in each region, respectively, using the Ti anode. This accounts for 45%, 33% and 27% of HC removal in the anodic, central and cathodic region, respectively. Therefore, the lowest decontamination occurred in the center and close to cathode. Very worth noting, when the IrO_2-Ta_2O_5|Ti was used as the anode, the removal efficiency was not enhanced in those two regions. In fact, even somewhat worse results were obtained, with 23% and 19% of decontamination. However, the F&O content was reduced up to 1303.98 mg kg^{-1} in the anodic region, accounting for 58% of HC removal. This can be explained by the greater electrocatalytic ability of this anode compared to the Ti one. In fact, DSA® electrodes are able to produce hydroxyl radicals (•OH), which very oxidizing species that can progressively degrade the organic matter to less toxic compounds.

3.2. Comparative electrokinetic treatment of polluted soil using 1D (linear) and 2D (radial) arrays with Ti and IrO_2-Ta_2O_5|Ti anodes

The removal efficiencies reached by using modified electrodes with a 2D (radial) configuration (58%) were more than twice the values achieved when employing the 1D (linear) array (21%) with the IrO_2-Ta_2O_5|Ti anode and the Ti cathode, because with Ti as anode and cathode, the removal efficiency was minor (45%). In all cases, the treatment was prolonged for 24 h.

In the 2D configuration with the IrO_2-Ta_2O_5|Ti and Ti as the anode and cathode, respectively, which yielded the highest removal efficiency, some chemical compounds disappeared during the treatment, as analyzed at the end of the trials. Therefore, octadecane and pentadecane were transported and became accumulated close to the anode and in the center, respectively. Other chemical compounds, such as cyclotriacontane and hexacosane, appeared close to anode

and in the center, respectively. Interestingly, heptacosane, octacosane and hexadecane disappeared from the polluted Vertisol soil upon the EKT.

The pH value was also determined after the EKT trials for the contaminated soil (C.S.) with the 1D and 2D configurations. According to the results depicted in Figure 4, an acidic front (pH near 3.0) appeared close to the anode in both electrode arrays, whereas it was near-neutral in the center and alkaline (about 10.0) close to the cathode, which can be associated to the anodic oxidation and cathodic reduction reactions of water to yield O_2 and H_2, respectively, in agreement with trends reported in the literature for EKT [6].

Regarding the electrical conductivity variation shown in Figure 5, there was a more significant increase in the area close to cathode in both electrode configurations, whereas the modification was less relevant in the anodic and central regions. This behavior agrees with the correct migration and mass transport of the HC in the presence of ionic species in the electroremediated soil, as a consequence of the electrical field applied under the experimental conditions for these tests into the three treatment areas in EKT. It can also be noticed that the largest modification of the electrical conductivity occurred in the 2D system, with values in the range 8 - 14 mS cm^{-1} instead of 5 - 7 mS cm^{-1} found in the 1D configuration. In fact, in the cathodic region, the electrical conductivity with the 1D array was half the value of that obtained in the 2D array, which agrees with the accumulation of HC in that region at the end of the experiments. This finding demonstrates that HC was removed from the polluted soil during EKT by electro-migration, electro-osmosis and electrophoresis, as also reported in the literature for several configurations [6-7].

The presence of the modified IrO_2-Ta_2O_5|Ti anode enhances this phenomenon due to its mesoporous morphology [10-12,17-20], as it was confirmed by SEM (Figure 6A vs Figure 6B). Furthermore, the existence of the IrO_2 electrocatalyst was verified by EDX analysis (Figure 7A vs Figure 7B) [17-23]. As shown in the SEM image of the cross section of a IrO_2-Ta_2O_5|Ti anode in Figure 8, the thickness of

the IrO_2-Ta_2O_5 coating was between 200 and 310 μm, which agrees with values reported in the literature for electrodes obtained by thermal decomposition [22,23].

4. CONCLUSIONS

The comparative evaluation of linear and radial electrode arrays has demonstrated the superiority of the latter configuration for the EKT of HC-contaminated Vertisol soils, which was confirmed upon examination of the decay of fat and oil content. Using IrO_2-Ta_2O_5│Ti as the anode material, 58% HC removal was reached after 24 h of treatment applying 30 V and an electric field of 2.4 A cm^{-1}. These experiments showed an acid pH close to anode, neutral in the center and alkaline close to cathode at the end of the experiments, with an electrical conductivity from 8 to 14 mS cm^{-1}. The SEM-EDX analysis of the IrO_2-Ta_2O_5│Ti anodes revealed their different composition when compared to Ti ones, which contributed to obtain the much greater removal compared to the arrays with Ti anodes.

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FIGURES AND TABLE CAPTIONS

Figure 1. Experimental setups: (A) Radial 2D array with one central cathode and six surrounding anodes with cylindrical shape (diameter of 1.0 cm and a length of 5.0 cm); (B) Linear 1D array with one cathode and one anode facing each other with planar shape (5.3 cm x 2.5 cm x 0.2 cm). Electrode materials: Ti as cathode (-) and Ti or IrO_2-Ta_2O_5 | Ti (DSA®) as anode (+), with a separation of 6 cm between anodes and cathode.

Figure 2. Current density vs. potential difference between anode and cathode (E_{cell}) using the IrO_2-Ta_2O_5 | Ti anode and Ti cathode as planar (5.3 cm x 2.5 cm x 0.2 cm) electrodes with an interelectrode distance of 6 cm. Independent electrolyses were carried out at 5, 10, 15, 20, 25 and 30 V for 1 h in 0.1 M NaOH.

Figure 3. Removal of fats and oils in three different regions: close to the anode, center and close to the cathode. Results obtained in a previous EKT trial as Reference data are compared with those achieved upon EKT using a 1D configuration with the IrO_2-Ta_2O_5|Ti or Ti anode. Conditions: 30 V applied in the presence of 0.1 M NaOH, using Ti as the cathode.

Figure 4. Value of pH in three different regions: close to anode, center and close to cathode. Results obtained in a previous EKT trial as Reference data are compared with those achieved upon EKT using the 1D and 2D configurations, both with IrO_2-Ta_2O_5|Ti as the anode, to treat contaminated soil (C.S.). Conditions: 30 V applied in the presence of 0.1 M NaOH, using Ti as the cathode.

Figure 5. Value of electrical conductivity (E.C.) in three different regions: close to anode, center and close to cathode. See Fig. 4 for further details.

Figure 6. SEM images of the (A) IrO_2-Ta_2O_5|Ti and (B) Ti electrodes, which were used as the anode and cathode, respectively, at a magnification of 2000x.

Figure 7. EDX analysis of the electrodes shown in Fig. 6.

Figure 8. SEM image of the IrO_2-Ta_2O_5|Ti anode at a magnification of 40x to measure the thickness of the oxide layer.

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