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# Removal of oxyfluorfen from spiked soils using electrokinetic soil flushing with the surrounding arrangements of electrodes

C. Risco [a], H. Rubí-Juárez [b], S. Rodrigo [c], R. López-Vizcaíno [c], C. Saez [a], P. Cañizares [a], C. Barrera-Díaz [b], V. Navarro [d], M.A. Rodrigo [a],*

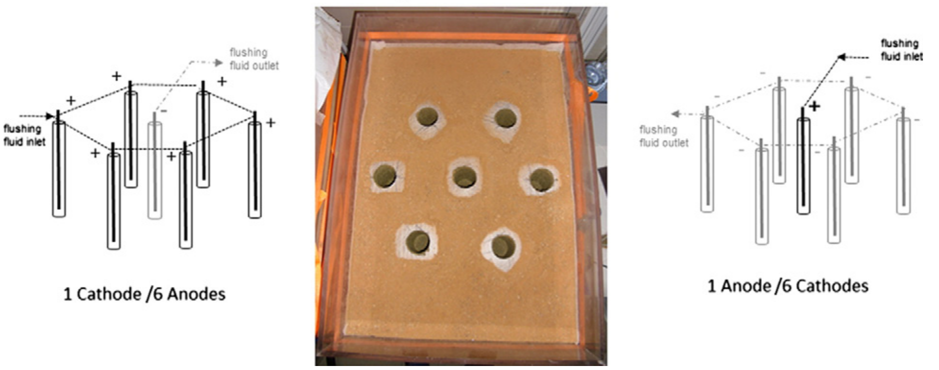
[a] Department of Chemical Engineering, Instituto de Tecnologías Química y Medioambiental, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain
[b] Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón intersección Paseo Tollocan S/N, C.P., 50120, Toluca, Estado de México, Mexico
[c] Department of Chemical Engineering, Facultad de Ciencias y Tecnologías Químicas, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain
[d] Geoenvironmental Group, Civil Engineering School, University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

## HIGHLIGHTS

- The electrode arrangement has a crucial influence on the results attained by EKSF.
- The 1C6A configuration is more efficient and overcomes 1A6C by 53%.
- Dragging of herbicide by EOF and volatilization are efficient mechanisms in EKSF.
- The pH in soil is well controlled by both the 1C6A and the 1A6C configurations.
- A large number of parameters are involved in the results of EKSF.

## GRAPHICAL ABSTRACT

EKSF with surrounding arrangements of electrodes



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## ABSTRACT

This work reports the results of a study in which the remediation of soil that undergoes an accidental discharge of oxyfluorfen is carried out by using electrokinetic soil flushing (EKSF). Two different electrode configurations were tested, consisting of several electrodes surrounding an electrode of different polarity (so-called 1A6C, one anode surrounded by six cathodes, and 1C6A, one cathode surrounded by six cathodes). A pilot plant scale was used (with a soil volume of 175 dm$^3$) to perform the studies. During the tests, different parameters were measured daily (flowrates, pH, electrical conductivity and herbicide concentration in different sampling positions). Furthermore, at the end of the test, a complete post-mortem analysis was carried out to obtain a 3-D map of the pollution, pH and electrical conductivity in the soil. The results demonstrate that electrode arrangement is a key factor for effective pollutant removal. In fact, the 1A6C configuration improves the removal rate by 41.3% versus the 27.0% obtained by the 1C6A configuration after a period of 35 days. Finally, a bench mark comparison of this study of soil remediation polluted with 2,4-D allows for significant conclusions about the scale-up and full-scale application of this technology.

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* Corresponding author.
*E-mail address:* manuel.rodrigo@uclm.es (M.A. Rodrigo).

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## 1. Introduction

Electrokinetic soil remediation is a very efficient technology for the removal of hazardous ions from soil. However, at the moment, there are few studies that focus on organic soil removal (Alcantara et al., 2010, 2012; Alshawabkeh et al., 1999a; Cameselle and Reddy, 2013; Hahladakis et al., 2013, 2014; Lima et al., 2011; Lu and Yuang, 2009; Pazos et al., 2010; Reddy et al., 2011, 2009; Ribeiro et al., 2011, 2005; Weng, 2009).

For an optimal performance, the electrokinetic soil flushing (EKSF) process relies on a satisfactory electrode arrangement (Jeon et al., 2015; Kim et al., 2012, 2015; Rodrigo et al., 2014a). Until now, the most widely studied arrangement is facing two linear rows of electrodes with different polarities (Risco et al., 2016a). The advantages of this configuration are related to the expected better electric current distribution lines, which are also expected to produce a well-distributed pattern of electrokinetic flows within the soil and, hence, a very efficient drainage of pollution.

However, this is not the only possibility of placing electrodes in soil (Almeira et al., 2009; Alshawabkeh et al., 1999a, 1999b; Peng et al., 2013), and configurations in which various electrodes surround a central electrode of the opposite polarity have also been tested, showing very interesting performances. At this point, it is important to remark that the recent literature indicates that the position of the electrodes sited in the soil is a key parameter in the remediation efficiency because it determines the direction and magnitude of the electrokinetic processes, and consequently, it influences the transport of pollutants. For this reason, different research works during the last few years have focused on the evaluation of the electrode configuration (Adams et al., 1997; Almeira et al., 2009; Jeon et al., 2015; Kim et al., 2012). The results obtained in these studies indicate that the most effective electrode configuration (from a pollutant transport viewpoint) is a hexagonal configuration, that is, a ring of anodes with a central cathode, or vice versa, depending on the polarity of the pollutant. The number of electrodes and the electrode spacing used are directly related with the mass of the treated soil.

In a previous report of this group (Risco et al., 2016c), two of these configurations were applied in a soil that underwent a simulated discharge of herbicide 2,4-D. The study was conducted in a mock-up with a suitable size to fully understand the effect on the remediation of the different flows induced by the electric field. The results indicate that the pollutant was removed by electromigration, electroosmostic fluxes and volatilization. In this work, we aim to expand our technology knowledge using a very different model of pesticide, the oxyfluorfen. This herbicide belongs to the diphenyl ether chemical group and has low water solubility (0.116 mg/L at 20 °C), low vapor pressure (0.026 mPa at 25 °C), high Koc (log Koc = 3.46–4.13), and high Kow (log Kow = 4.86). As oxyfluorfen is not metabolized in plants and is subjected to very little translocation, photo-transformation is suggested as the only possible abiotic degradation process. Microbial degradation is not a major factor to be accounted for in this herbicide. The half-life in soil approximately ranges from 30 to 56 days, and the organic matter content of the soil seems to influence the oxyfluorfen persistence and activity (Sondhia, 2010; Sondhia and Dixit, 2010). Finally, regarding its transport properties, it has been observed (Mantzos et al., 2014) that oxyfluorfen hardly moves into silty clay soil and exhibits low run-off potential.

In this work, the effect of the electrode arrangements in EKSF is studied in a soil mock-up, and then, the remediation technology is applied for more than a month. The results are compared with a reference experiment in which the discharge is simulated but no treatment is applied. The results are also discussed with respect to the results obtained in our previous works, which focused on the removal of 2,4-D (Risco et al., 2016a, 2016c, 2015), a pollutant with an expected higher water solubility and volatility and, hence, with very different expected results in terms of the efficiency of the EKSF treatment. For this reason, the comparison carried out in this work will provide relevant conclusions on EKSF technology.

## 2. Materials and methods

### 2.1. Soil properties and flushing solutions

Field soil from Toledo (Spain) was used in this study. This soil is characterized by its inertness, low hydraulic conductivity and lack of organic content. The mineralogical composition and the parameters used to classify this soil by the Unified Soil Classification System (USCS) are listed elsewhere (Lopez-Vizcaino et al., 2014a, 2014b), (Risco et al., 2016b). In addition, particle size distribution of the soil was measured by a laser diffraction particle size analyzer (model LS 13320, Beckman Coulter) with an aqueous module. This analysis indicates that the soil is composed on these fractions: 4.9% clay, 68.2% silt and 26.9% sand, therefore it can be classified as a silty loam according with the texture classification of the United States Department of Agriculture (USDA).

Oxyfluorfen was used as the model of non-polar and hydrophobic herbicide. The commercial herbicide used was Fluoxil 24 EC (CHEMINOVA AGRO, S.A., Madrid, Spain) composed on 24% ($v/v$) Oxyfluorfen dissolved in aqueous solution by the emulsifier action of Calcium Dodecylbenzenesulfonate (surfactant included in a commercial solution).

### 2.2. Experimental setup

The electrokinetic experiments were conducted in two electrokinetic remediation plants, each of them consisting of an electrokinetic reactor, a power source and tanks of electrolyte. A layout of the two setups used is shown in Fig. 1. The reactors were methacrylate prisms with a soil capacity of $175 \times 10^3$ cm$^3$ (LWH: $70 \times 50 \times 50$ cm$^3$). The electrodes (used for both the anodes and the cathodes) were graphite rods with dimensions $1 \times 1 \times 10$ cm$^3$, positioned in semipermeable electrolyte wells, using the electrode configuration shown in Fig. 1, in which six electrodes surround a central electrode of different polarity (configuration 1A6C: anode surrounded by 6 cathodes; configuration 1C6A: cathode surrounded by 6 anodes). The cathodic wells are connected to 100 cm$^3$ sewers to accumulate the fluid transported through the soil and facilitate sampling. The reactor is designed to separate and collect the fluids through an outlet situated on the side wall of the reactor. To monitor the flux of water and the temperature evolution during the experiment, tensiometers, thermocouples and rhizon samplers (or "rhizons") were inserted into the soil. Fig. 1 shows the instrumentation of the plant.

### 2.3. Experimental procedure

The process of the preparation of the soil is important because of the complexity of natural soil. The process was divided into four different stages:

- installation of three layers of gravel with different particle sizes for mechanical and drain support;
- moistening the soil to 11% (natural water content condition);
- compaction of the soil in the electrokinetic reactor by compacting layers of a fixed thickness (5 cm) until achieving the natural density of the soil (approximately 1.4 g cm$^{-3}$);
- drilling of the electrolyte wells and instrumentation of the plant.

Once the plant was fully instrumented, the experimental procedure began with the pollution of the soil (simulating accidental spill). To do this, in the central point of the electrokinetic reactor, an accidental leak of 6 dm$^{-3}$ of an aqueous solution of 500 mg dm$^{-3}$ of Fluoxil 24 EC (oxyfluorfen 24%) was simulated. After that, the electrolyte wells