Removal of oxyfluorfen from spiked soils using electrokinetic soil flushing with linear rows of electrodes

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Abstract

This study focuses on the evaluation of the Electrokinetic Soil Flushing (EKSF) strategy to remediate soil following a simulated spill of the herbicide oxyfluorfen. EKSF is attained by placing (in the soil mockup) two rows of electrodes of different polarity facing each other. The results are compared with those obtained in a reference experiment in which the same spill was simulated and no remediation actions were taken. In addition to the daily monitoring of the most important parameters in the flows, after the remediation test, a post-mortem analysis was performed to obtain a 3-D map of the pollutant distribution. Those results demonstrate that despite the hydrophobic character of oxyfluorfen, it can be efficiently transported by EKSF. Hence, after 34 days of treatment, a 26.8% improvement in the removal of oxyfluorfen was achieved (explained in terms of the effect of the electric field on the pollutant) compared with the reference experiment

1 in which only volatilization can explain the removal of the herbicide. Comparison of the
2 removal of oxyfluorfen by EKSF with that of 2,4-D (studied in a previous study)
3 demonstrates that comparable dragging to the cathode and volatilization are obtained.
4 However, the lower efficiency of the transport of oxyfluorfen by gravity fluxes and
5 electromigration (explained because it is contained as micelles) yielded worse
6 performance of EKSF for this water-insoluble pesticide and hence less efficient
7 remediation. This contradictory result reveals the importance of tests at large-scale
8 facilities such as that used in this work to predict the performance of real systems in future
9 full-scale applications.

11 **Keywords**

12 Oxyfluorfen, herbicide, electroremediation, natural soil, electrokinetic soil flushing, pilot
13 plant

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1 **Introduction**

2
3 Pollution of soils is currently an environmental issue of major significance. Therefore,
4 the improvement of soil remediation processes is at the cutting edge of environmental
5 technology. In the development of such processes, a positive impact on the environment
6 is sought [1, 2], associated with both

7 (1) avoiding the rapid diffusion of pollution after an accidental discharge event, and

8 (2) removing pollutants from soils with an in situ technology that does not require
9 excavation and hence a substantial modification in geotechnical soil properties.

10 To meet this objective, a great variety of processes have been developed to remediate
11 soils, including physical (e.g., heating and evaporation), chemical (e.g., oxidation) or
12 biological (e.g., bio-oxidation) processes. One of the most interesting technologies is
13 based on the effect of electric fields induced in the soil using electrodes placed in different
14 positions. These electric fields transport water, pollutants and other species through the
15 soil, increase the temperature (by resistance heating) and cause chemical changes,
16 including precipitation and ion exchange (associated with the acidic and basic fronts
17 produced, respectively, on the surfaces of the anodes and cathodes). The transport
18 processes are typically known as electrokinetic processes. The arrangement of electrodes
19 in the soil and the operation conditions applied allows multi-decadal, full-scale promotion
20 of different types of electrochemically assisted soil remediation processes [3-8], in
21 particular, for the removal of metal ions [9, 10].

22 Electrokinetic soil flushing (EKSF) is one of the most promising technologies [3, 11-14],
23 consisting of adding a flushing fluid near the anodes placed in the soil and collecting near
24 the cathodes. The flushing fluid removes pollution without significantly affecting the
25 physical properties of the soil; the fluid may consist of water, when a highly soluble

species is to be removed, or a surfactant solution, for low water-solubility species. This technology is for use in soils with low hydraulic-conductivity, and its efficiency has been demonstrated with inorganic species, soluble organics and non-soluble organics [15-19]. Recently, EKSF has been studied for the removal of metals [9, 18, 20-26], pesticides [1, 27-29], polycyclic aromatic hydrocarbons [5, 30-39], and PCBs [15, 40-42]. The transport of hydrophobic organic compounds (HOC) through the soil should be evaluated because these pollutants cannot be mobilized by electro-osmosis (low water solubility) or electromigration (non-polar molecules), and thus the use of special flushing-fluids is necessary [38, 43]. These flushing-fluids usually consist of surfactant solutions that are able to improve the mass transfer of HOCs from the soil into the aqueous phase by breaking up HOCs into the hydrophobic cores of surfactant micelles [40, 44-60].

The use of herbicides in agriculture has many economic advantages but also serious environmental drawbacks. Currently, great effort is being exerted in the development of more environmentally friendly pesticides, but the development of processes that can rapidly remove them from soils when accidental discharges occur remains necessary, and because of its characteristics, EKSF could be quite useful for this purpose. Several of the most commonly applied herbicides have low solubility, and the development of technology to remove them from soils is a topic of major interest. Among these herbicides, oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene] is a good model of a non-soluble herbicide commonly used in agriculture to control broadleaf and grassy weeds. The compound 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 K_{oc} ($\log K_{oc} = 3.46-4.13$) and high K_{ow} ($\log K_{ow} = 4.86$). This herbicide is not a good candidate for phytoremediation or bioremediation, and even its transport in clay soils is not favored [61-63].

The objective of this study is to evaluate the use of EKSF to remediate soil in which an accidental discharge of commercial oxyfluorfen reagent (FLUOXIL 24 EC) was simulated. It contains oxyfluorfen and a surfactant cleansing agent (calcium dodecylbenzenesulfonate) that allow the breaking up of oxyfluorfen into surfactant micelles. The tests were performed at a pilot plant to evaluate the interactions between the different processes at the proper scale; this scale is one of the primary innovations of this study. The electrode arrangement was a linear row of anodes facing a linear row of cathodes. This is the most typical configuration for EKSF processes. The results are compared with those obtained in a reference experiment in which the diffusion of the herbicide following an accidental discharge is not controlled but simply monitored. In addition, the results are also compared to those obtained in a previous study [27] in which the same technology was used for a different model of herbicide, 2,4-D, with greater solubility in water. Due to the very different properties of both pollutants, comparison will give very valuable conclusions about EKSF technology.

Materials and Methods

Preparation of the polluted soil. 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 parameters used to classify this soil by the Unified Soil Classification System (USCS) are provided elsewhere [27, 37]. In addition, particle size distribution of the soil was determined using a laser diffraction particle size analyser (model LS 13320, Beckman Coulter) with an aqueous module. The results of this analysis show that the soil are composed on these fractions: 4.9% clay, 68.2% silt and 26.9% sand, and it can be classified as a silty loam according with the texture classification of the United States Department of Agriculture (USDA). Oxyfluorfen 24%

(with calcium dodecylbenzenesulfonate as the surfactant cleansing agent) was used as a model of a non-polar, hydrophobic herbicide. The commercial herbicide used was “Fluoxil 24 EC” (CHEMINOVA AGRO, S.A., Madrid, Spain). The soil preparation process is important because of the complexity of natural soil. The process was divided into four different stages: 1) installation of three layers of gravel with different particle sizes for mechanical and drain support; 2) moistening the soil to 11% (natural water content); 3) compacting layers of the soil of a fixed thickness (5 cm) in the electrokinetic reactor until the natural density of the soil (approximately 1.4 g cm^{-3}) was achieved; 4) drilling the electrolyte wells and the instrumentation of the plant.

Experimental setup. The electrokinetic experiments were conducted in an electrokinetic remediation plant consisting of an electrokinetic reactor, a power source and tanks of electrolyte. The reactor was a methacrylate prism with a soil capacity of $175 \times 10^3 \text{ cm}^3$ (LWH: $70 \times 50 \times 50 \text{ cm}^3$). The electrodes used as both the anodes and the cathodes were $1 \times 1 \times 10 \text{ cm}^3$ graphite rods, positioned in semipermeable electrolyte wells, with an electrode configuration of rows facing the electrolyte wells, as described elsewhere [64, 65]. The cathodic wells are connected to 100 cm^3 sewers to accumulate the fluid transported through the soil and to facilitate sampling. The reactor is designed to separate and collect the fluids through an outlet on the side wall of the reactor. To monitor the flux of water and the evolution of temperature during the experiment, tensiometers, thermocouples and rhizon samplers (or simply, “rhizons”) were inserted into the soil. Figure 1 shows a diagram of the electrokinetic remediation plant and of the instrumentation of the plant with the notation that will be used in the discussion of results.

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2

3 **Figure 1.** Diagram of the electrokinetic remediation plant and the configuration of the
 4 instrumentation. R_i: rhizon no. i; TT_i: thermocouple no. i; T_i: tensiometer no. i; P_i: well
 5 no. i

6 **Experimental procedure.** Following the instrumentation of the plant, the experimental
 7 procedure began with the pollution of the soil (simulating accidental spill). To do this, the
 8 accidental leak of 6.0 dm³ of an aqueous solution of FLUOXIL (containing 500 mg dm⁻³
 9 oxyfluorfen) was simulated in the center of the electrokinetic reactor. Then, the
 10 electrolyte wells were filled with water selected as flushing fluid (pH 7.64 and 0.391 mS
 11 cm⁻¹ of electric conductivity). The level control system of the electrolyte wells was
 12 connected to the feed tank to adjust the volume of added water to the soil. The test began
 13 when the power source, a 400 SM-8-AR ELEKTRONIKA DELTA BV, was turned on,
 14 applying a constant voltage gradient of 1.0 VDC cm⁻¹.

15

Anolyte sampling was conducted manually, and catholyte sampling was conducted by pumping the water accumulated in the cathodic containers. Gravity fluid was sampled daily (10 cm³) and drained at the end of the process through an outlet situated at the bottom of the reactor. Electrical current, temperature, pH, soil water content and oxyfluorfen concentration in the electrolyte wells were monitored daily, and at the end of the experiments, an in-depth sectioned analysis of the complete soil section was performed.

Analyses. The oxyfluorfen concentration was determined by High Performance Liquid Chromatography (HPLC) using an Agilent 1100 (Agilent Technologies, Palo Alto, California, EEUU) with a UV detector (220 nm) and a 150x3.0 mm Gemini 5 μ C18 110^a column (Phenomenex, Ref. 00F-4435-YYO), with a flow rate of 0.25 cm³ min⁻¹ of Acetonitrile (70%)/Water (30%). To quantify the amount of oxyfluorfen in the liquid samples, an L-L extraction process was performed in Eppendorf tubes (15 cm³), using ethyl acetate as a solvent (ratio polluted soil/solvent = 0.7 w/w). Both phases were vigorously stirred in a vortex mixer (VV3 VWR multi-tube) for 2 minutes, and then the organic phase was separated from the water. The organic phase was then placed into tubes to be stripped with N₂ gas. A volume of 1.5 cm³ of acetonitrile was then added and stirred for 3 minutes, before injection into the HPLC. To quantify the amount of oxyfluorfen in the soil, an L-S extraction process was performed in Eppendorf tubes (15 cm³) using ethyl acetate as a solvent (ratio polluted soil/solvent = 0.4 w/w). Both phases were vigorously stirred in a vortex mixer (VV3 VWR multi-tube), and subsequent phase separation was accelerated using a centrifuge rotor angular (CENCOM II P-elite) for 20 minutes at 4000 rpm. Then, the liquid was stripped with N₂ gas, and acetonitrile was added before injection into the HPLC. Measurements of pH and electric conductivity were completed

using an InoLab WTW pH-meter and a GLP 31 Crison conductivity meter, respectively. The electric current was measured with a KEITHLEY 2000 Digital Multimeter. The temperature measurements were performed with PT-100 thermocouples.

Energy consumption.

The energy supplied is calculated using equation 1, where I is the electric current, E is the applied electric potential and V_{soil} is the volume of the treated soil.

$$\text{Energy}_{\text{consumption}} = \int \frac{I \cdot E}{V_{\text{soil}}} \cdot dt \quad (1)$$

Results and Discussion

The simulated accidental spill of oxyfluorfen in this study lasted 6 hours (in which 6.0 dm⁻³ waste were added to the center of the mockup containing ca. 150 kg of soil), and the EKSF began 2 days after this spill. Figure 2 shows the changes observed in the electric current intensity and temperature in response to the 1.0 V cm⁻¹ electric field applied between the two facing rows of electrodes (the separation between the center of the two facing rows of electrodes is 38 cm, and thus the applied cell voltage was 38 V).

Figure 2. Time course of the electric current (a) and temperature (b) during the EKSF test.

Thermocouples: TT1, TT2, TT3, TT4 and TT5.

As illustrated, the electric current intensity increases rapidly up to 0.6 A, when it begins to decrease at a constant rate. This intensity is near that reported in a previous work in which the treatment of 2,4-D with the same technology was studied, which helps demonstrate the reproducibility of the results [27] obtained in the experimental mockup used to evaluate soil remediation technologies because, for the same soil and operation conditions, the same globalized rate of transport and oxidation reactions (which is the real meaning of the current intensity in electrochemical processes) was obtained. The initial soil conditions in both tests are the same, and the only difference is the herbicide that polluted the soil.

The electric current intensity is a direct measurement of the electrochemical reactions occurring on the surfaces of the electrodes, and it is also related to the transport of charges (both ionic and colloids) and to the ohmic heating of the soil. The higher the intensity applied, the higher the expected change in all of these parameters. However, (as can also be observed in Figure 2) the temperature does not increase significantly. Hence, although

thermocouples placed adjacent to the electrodes register greater increases in temperature, these increases do not significantly exceed the environment temperature, indicating that cooling due to the evaporation of water from the soil also plays an important role in the energy balance of the soil remediation mockup.

Figure 3 shows pH changes in the electrolyte wells and rhizons placed in the soil at different positions. The values are as expected based on previous studies of the same EKSF technology with facing rows of electrodes [27, 38, 43, 64]. The pH values in the wells are extreme: approximately 13.0 at the cathodes and 1.0 at the anodes. However, the pH value in the rhizons clearly diverges with time depending on the proximity to the anodes and cathodes, demonstrating the effects of the acidic and basic fronts. As soon as the front reached the rhizon, the pH began to increase or decrease towards extreme values.

Figure 3 also shows the 2-D plot of pH (average value of samples in the same xy position at different z coordinate), as measured in the postmortem analysis following the test. In this figure, the acidic and basic fronts are clearly observed, and this strategy of electrode placement has a clear drawback compared with other strategies (such as the fence or the surrounding electrodes technologies): the greatly reduced control of pH without the assistance of buffer solutions or other strategies, such as alternation in the polarity of the electrodes [66].

Figure 3. Changes in pH during the EKSF process. (a) 2-D map of pH after the EKSF tests. (b) Time course of pH over the experiment ($\blacklozenge$ P1; $\blacksquare$ P2; $\blacktriangle$ P3; $\diamond$ P4; $\square$ P5; $\bullet$ P6; $+$ R1; $-$ R2; $-$ R3; $\blacklozenge$ R4; $\blacksquare$ R5; $\blacktriangle$ R6; $\times$ R7; $*$ R8; and $\bullet$ R9).

One very important parameter in EKSF processes is the electro-osmotic flux (EOF) because it may transport the pollution from the soil and help collect it in the cathode wells. Figure 4 shows that the EOF referred not to the volume of flushing fluid added in the anode wells but to the volume of flushing fluid collected from the cathode wells. As shown, the amount of electrolyte collected in two of the wells is comparable, but the other well received no volume. The system was set up very carefully to avoid heterogeneities, but this result is indicative of the significance of the heterogeneities in this type of process, which will certainly be of major significance in full-scale processes.

Figure 4. Changes in the electro-osmotic flow during the EKSF test (♦ C₁, ■ C₂, ▲ C₃).

The changes observed in the EOF can be related to the changes in the soil water content and the soil electric conductivity during the treatment. Comparison of the average value of both parameters obtained in the post-mortem analysis reveals two opposing influences on the EOF. The water content of the reference test (soil not undergoing electrokinetic treatment) decreases from the initial value of 11% to 9.9%, whereas the water content in the soil that underwent EKSF increases to 21.9%. This increase indicates the accumulation of water in the soil and is expected to produce a positive effect on the EOF (because of the expected lower electric resistances associated with water saturation and hence with the saturation of the soil voids). In contrast, the electric conductivity in the reference test (measured in the post-mortem analysis) remains 0.197 mS cm^{-1} , whereas it decreases to 0.158 mS cm^{-1} in the EKSF test. This decrease can be explained by the dragging effect of electromigration on the ions contained in the soil, which has a negative influence on the electro-osmotic flow. The combination of both influences can help explain the strange variation observed during the test.

Another important parameter to be considered in this study is the amount of oxyfluorfen transported by the different mechanisms because it aids in understanding the performance

of the system and in obtaining useful knowledge for full-scale applications. To calculate this parameter, the herbicide collected in the anodes, cathodes and by gravity must be quantified; this information is provided in Figure 5.

Figure 5. Amounts of the herbicide transported and removed from the soil during the EKSF test, a) (■ anodes; ♦ cathodes; ▲ gravity flows; ● rhizons). Inset: detail of the amount of oxyfluorfen collected at the different rhizons (+ R1; - R2; ♦R3; ■ R4; ▲R5; ×R6; *R7; ●R8; - R9)

As can be observed, and in contrast with the results with 2,4-D [27], the oxyfluorfen is collected primarily in the cathode wells, indicating that the primary mechanism is the transport of the oxyfluorfen colloids by the electro-osmotic flow. The transport of 2,4-D to the cathodic wells (16.36%) is slightly less than that observed for oxyfluorfen (19.25%), despite the higher EOF obtained. The amount collected at the anode (0.4%) is much less than in the test with 2,4-D (18.7%), indicating that electrophoresis of the micelles is not favored. This is a major difference between the results for oxyfluorfen and those for 2,4-D. Figure 5 also shows the total amount of oxyfluorfen collected in the different rhizons in the soil, with the accumulation rate decreasing over time (because of

1 the lower resulting concentration in soil). Lower amounts of the herbicides were observed
 2 in the rhizons adjacent to the cathodes, although a clear relationship cannot be established,
 3 perhaps because of the opposing directions of the different flows, which do not permit
 4 observation of well-defined patterns.
 5 Figure 6 shows a 3-D plot of the oxyfluorfen remaining in the system after 34 days of
 6 treatment in comparison with a 3-D plot of the reference test, in which the soil did not
 7 undergo any treatment following the application and dispersion of the same simulated
 8 accidental spill of oxyfluorfen, in which 6 L of pesticide dispersion were added for 6.0
 9 hours in a central position of the mockup (recall that the remediation test began 2 days
 10 after the simulated spill event).

Figure 6. 3-D plots of the final distribution of oxyfluorfen for the reference (a) and EKSF tests (b).

A perfect distribution of the simulated accidental discharge would yield 20 mg kg^{-1} . As observed, in the reference experiment, these values were reduced to approximately 19 mg kg^{-1} . The difference can be easily explained by the volatilization of the herbicide. The distribution is not homogenous as expected from a theoretical perspective, considering that the discharge was applied at the center of the soil (hence, a concentric dispersion was expected). These results were also observed in the tests performed in the complete experimental program in which this work is included (focused on the evaluation of strategies to remediate pesticides from soils [27, 67]), and they may be explained by the very effective diffusion of the pesticide in the soil matrix. In addition, similar results were also observed for other types of organic pollutants, such as phenanthrene [38, 43].

The average concentration after passing a specific energy of 65 kWhm^{-3} to the soil during the EKSF treatment was 13.84 mg kg^{-1} , and the difference between the 18.93 mg kg^{-1} obtained in the reference experiment and this value (26.88%) may be explained by electrochemically induced transport mechanisms. No significant differences exist between the distributions of the herbicide in the three layers, with the exception of a greater concentration in the top layer, which can be associated with the slower distribution of the pesticide along the z-axis following the spill. Therefore, the mobility of the pesticide is favored in the xy direction, where the current distribution lines are more intense and deteriorate in the z direction, suggesting that without the gravitational assisted gradient, the mobility of the oxyfluorfen micelles is not favored.

Finally, Figure 7 compares the results for the removal of the herbicide oxyfluorfen in this work with those of a previous work focused on 2,4-D, using the same technology and experimental device [27]. Such a comparison can assist in drawing relevant conclusions regarding the influence of the nature of the pesticide on the performance of the EKSF treatment because of the very different transport characteristics of the two herbicides, as noted above. In both case, it was tested the adsorption of pesticide in the soil is nil.

Figure 7. Comparison of (a) the herbicides oxyfluorfen (grey) and 2,4-D (black) and (b) the water balances following the EKSF remediation test.

In the case of oxyfluorfen, the removal by electromigration (which is the main mechanism in the removal of 2,4-D with this EKSF technology) is not favored. In contrast, removal by dragging is the primary mechanism, even though the volume of water transported towards the cathodes is much less than in the 2,4-D removal. The higher EOF in the removal of 2,4-D is associated with the different electric conductivity of the groundwater contained in the soil. Thus, in the case of the oxyfluorfen EKSF remediation, the average final electric conductivity was 0.174 mS cm^{-1} , whereas for 2,4-D, this value was 0.232 mS cm^{-1} . The removal by volatilization is comparable in both tests, as is the evaporation

of water, both of which can be easily explained by the vapor-liquid features of both pesticides and the comparable temperature at which both tests were executed. Thus, the vapor pressure of oxyfluorfen (0.026 mPa at 25°C) is very similar to that of 2,4-D (0.02 mPa at 25°C) at the conditions applied. In comparing the gravity fluxes of the herbicides and water, essentially no difference was observed in water transport. However, very important differences were observed between the herbicides due to the lower mobility of the micelles of oxyfluorfen than that of the soluble 2,4-D. Thus, the mobility of the oxyfluorfen is electrochemically assisted in the zones in which the current lines are more intense. As is well known, the current distribution between two rows of electrodes of different polarities is normal to these electrodes, and hence the transport of micelles perpendicular to the direction of the current lines is not favored.

Conclusions

From this work, the following conclusions can be drawn:

- EKSF with a linear row of electrodes of the same polarity facing a row of electrodes of different polarity is an efficient technology for the removal of oxyfluorfen from soils and can attain a 26.88% improvement in the removal of oxyfluorfen (vs. natural volatilization) after 34 days of treatment (65 kWh m⁻³ of specific energy applied).
- The effect of pH fronts is clearly observed under the application of this technology (EKSF with a linear row of electrodes of the same polarity facing a row of electrodes of different polarity), and a gradient of pH in the direction anode-cathode is obtained. This gradient might affect the mobility of pollutants in the soil.

- Temperatures do not vary very significantly in soil undergoing EKSF, although slight increases are observed near the electrodes, indicating that ohmic losses are not the primary processes in soil remediation with this technology.
- Vertical water fluxes (evaporation and gravity fluxes) do not depend on the pollutant contained in the soil but only on the characteristics of the soil. Essentially the same flux values are obtained in the remediation of soil polluted with oxyfluorfen or 2,4-D
- Removal of 2,4-D and oxyfluorfen by volatilization is comparable, which is in agreement with the similar vapor pressure of both herbicides
- Gravity flux efficiently drags 2,4-D but not oxyfluorfen. Therefore, oxyfluorfen micelles can be easily transported in the anode-cathode direction following the current distribution lines (electrophoresis), but this transport is not as easy in the vertical direction.

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