Removal of oxyfluorfen from spiked soils using electrokinetic fences

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Abstract

In this work, an accidental spill of Fluoxyl (commercial herbicide containing oxyfluorfen) is simulated in a pilot plant with a soil volume of 70x50x50 cm³. The transport of Fluoxyl obtained by the free diffusion of pollution and under the application of the electrokinetic fences (EKF) technology are compared in a 34-day treatment. In addition, the temperature, conductivity, and pH are monitored daily. At the end of the experiment, a post-mortem analysis is carried out in order to obtain a 3-D distribution map of the pollutant. The results show that EKF is a good technology to remove oxyfluorfen from the soil without excavation because it is able to attain a fast transfer of oxyfluorfen to the flushing fluid used. After 34 days, the decrease in the concentration of oxyfluorfen in the

1 simulated case without any treatment is only 5.5 %, whereas when EKF is applied, the
2 removal yield is approximately 63 % (60.7 % of improvement vs. natural volatilization).
3 Detailed analyses of the experimental data, the 3-D map, and recent literature suggest that
4 the main mechanism involved for the removal is the rapid transfer of oxyfluorfen to the
5 flushing fluid used. The results are also discussed in the context of a previous work in
6 which the same technology has been applied for the removal of the ionic herbicide 2,4-
7 D. A comparison allows sound conclusions to be made for future scale-up studies.

8 **Keywords**

9 Oxyfluorfen, herbicide, electroremediation, natural soil, electrokinetic fence, pilot plant

10 **Highlights**

- 11 - EKF is efficient for the treatment of soils that undergo discharges of oxyfluorfen
- 12 - Electrode arrangement applied in EKF minimizes the effects of the pH fronts
- 13 - A slight increase in temperature in the zone surrounded by the electrodes is
14 observed
- 15 - A slight temperature increase around the electrodes is observed.
- 16 - The current intensity and flow vary during the tests, despite the use of a constant
17 electric field
- 18 - Dragging of the oxyfluorfen micelles by EOF is the primary removal mechanism

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Introduction

Over the last decades, there has been increasing concern about the pollution of soils and that the uncontrolled spreading of pollution may affect water supplies. In particular, the pollution of hazardous wastes is interesting and has been the focus of recent relevant research, both in the characterization of the environmental problem and in the development of promising technologies to avoid the negative consequences of these serious environmental problems.

Among the pollutants that may cause soil pollution, organic pesticides and particularly herbicides are a group of great interest [1]. These products are quite relevant for the economic feasibility of crops, but their influence on the environment is very negative, despite the many efforts made in recent years to produce biodegradable pesticides, whose negative effects disappear within a reasonable period of time.

The development of technology capable of confining the pollution to a constrained zone and avoiding uncontrolled dispersion is an interesting target for the present research on soil remediation [2-10]. However, the main aim is to develop a technology capable of removing the pollutant and allowing the recovery of the soil [2, 11-13]. Within the technologies capable of confining pollution, electrokinetic fences (EKF) is perhaps one of the most interesting, at least from a theoretical point of view [11, 14].

The EKF technology has been studied for the retention and removal of ionic species [15-19], including pesticides [20-25]. The results published have been promising but also indicate that there is still much work to do in order to completely understand the

1 technology and to be able to use it in an efficient way. As with many other electrokinetic
2 technologies, understanding electrokinetic fences does not only consist of knowing the
3 mechanisms involved (which are already well-known and studied at the lab-scale), but
4 the combination of mechanisms in this type of process needs to be understood [17]. This
5 combination can be complex, especially when studied in systems of large scales (larger
6 than the small soil columns typically shown in most of the papers published in the recent
7 literature) because of the very different time-constants of these processes [26].

8 One additional disadvantage of this technology is its partial effectiveness for pollutants
9 with a low water solubility [27-29]. These pollutants need to be transformed into
10 emulsions in order to eliminate them [26, 30, 31]. This has been shown for the case of
11 oxyfluorfen, i.e., [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene],
12 which is a diphenyl ether herbicide commonly used in agriculture to control broadleaf
13 and grassy weeds. This herbicide is known to have low water solubility (0.116 mg/L at
14 20 °C), low vapour pressure (0.026 mPa at 25 °C), high K_{oc} (log K_{oc} = 3.46–4.13), and
15 high K_{ow} (logK_{ow} = 4.86). This substance is not metabolized in plants and can be slowly
16 digested by microorganisms [32-34]. Hence, oxyfluorfen is an interesting model
17 pollutant, which can give relevant data on soil transport under electrokinetic treatment.

18 Thus, the goal of this work is to study the use of electrokinetic fences in a pilot plant for
19 soil treatment containing an oxyfluorfen dispersion (Fluoxil 24 EC). The results obtained
20 are compared with those from a blank experiment. Detailed analyses of the experimental
21 data, the 3-D map, and the recent literature suggest that the main mechanism involved for
22 the removal is the rapid transfer of oxyfluorfen to the flushing fluid used.

23 24 25 **Materials and Methods**

Preparation of the polluted soil. Field soil from Toledo (Spain) was used in this study. This soil was 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 [30]. As a model non-polar and hydrophobic herbicide, 24% Oxyfluorfen (with calcium dodecylbenzenesulfonate as the surfactant, i.e., cleansing agent) was used. The commercial herbicide used was Fluoxil 24 EC (CHEMINOVA AGRO, S.A., Madrid, Spain). The process of soil preparation 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 of the soil to 11% (natural water content condition); 3) 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}); 4) drilling of the electrolyte wells and 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 for both the anodes and the cathodes were graphite rods with dimensions of $1 \times 1 \times 10 \text{ cm}^3$, positioned in semipermeable electrolyte wells, using a sequence of alternating electrodes. The cathodic wells were connected to 100 cm^3 sewers to accumulate the fluid transported through the soil and to facilitate sampling. The reactor was 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

1 evolution during the experiment, tensiometers, thermocouples, and rhizon samplers
 2 (hereafter, simply “rhizons”) were inserted into the soil. Figure 1 shows a scheme of the
 3 well configuration and the instrumentation of the plant. At the top of the soil, a capillary
 4 barrier consisting of an approximately 3-cm-wide layer of sand was placed in order to
 5 reduce the evaporation of water and the volatilization of herbicide.

6
 7 **Figure 1.** Scheme of the well configuration and diagram of the instrumentation used in
 8 the electrokinetic remediation plant. R_i : Rhizon no. i ; TT_i : Thermocouples no. i ; T_i :
 9 Tensiometers no. i ; P_i : Well no. i .

10
 11 **Experimental procedure.** Once the plant was completely instrumented, the experimental
 12 procedure began with the pollution of the soil (simulating an accidental spill). To do this,
 13 an accidental leak of 6.0 dm^{-3} of an aqueous dispersion of 500 mg dm^{-3} of oxyfluorfen
 14 (Fluoxil 24 EC) in the central point of the electrokinetic reactor was simulated. Then, the
 15 electrolyte wells (water, pH of 7.64, and conductivity of 0.391 mS cm^{-1}) were filled. The
 16 levels of the electrolyte wells were controlled by a level control system connected to the
 17 feed tank to adjust the volume of added water to the soil. The test started when the power

source (400 SM-8-AR ELEKTRONIKA DELTA BV) was turned on, applying a constant voltage gradient of 1 VDC cm⁻¹.

Analyses. During the experiments, the pH, the conductivity, and the oxyfluorfen concentration of the hydraulic fluids were monitored. For the monitoring, 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. The electrical current, temperature, pH, 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 conducted (post-mortem analysis) by dividing the setup into 48 pieces in order to obtain 3-D maps of the different parameters. To quantify the amount of oxyfluorfen in the liquid samples, a L-L extraction process was carried out in Eppendorf tubes (15 cm³) using ethyl acetate as the solvent (ratio of 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 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 HPLC. To quantify the amount of oxyfluorfen in the soil, an L-S extraction process was used. This was carried out in Eppendorf tubes (15 cm³) using ethyl acetate as the solvent (ratio of 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 by the use of an angular centrifuge rotor (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 HPLC. The HPLC used was an Agilent 1100 (Agilent

Technologies, Palo Alto, California, EEUU) with an UV detector using acetonitrile (70%)/water (30%) as the carrying fluid at a flowrate of $0.25 \text{ cm}^3 \text{ min}^{-1}$. A 150x3.0 mm Gemini 5 μ C18 110^a column (Phenomenex, Ref. 00F-4435-YYO) and a wavelength of 220 nm were utilized. Measurements of the pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively. The electric current was measured with a KEITHLEY 2000 Digital Multimeter. The temperature measurements were carried out with PT-100 thermocouples.

Results and Discussion

The simulated accidental spill of oxyfluorfen studied in this work lasted 6 hours (in which 6.0 dm^{-3} of waste was added to the central position of the model containing approximately 150 kg of soil). After 2 days, the EKF was applied into the system.

Figure 2 shows the fluctuations in the resulting current intensity during the remediation of soil polluted with oxyfluorfen. This illustration also presents the resulting electro-osmotic fluxes (EOF), collected in the three cathodic wells. Clearly, the treatment can be clearly divided into two stages:

- Stage one, in which the average intensity was approximately 0.45 A and in which the electro-osmotic fluxes were low and
- Stage two, in which the current decreased to a value of approximately 0.22 A, and the electroosmotic flow started to increase rapidly, up to a maximum and then decreased.

The increase in the intensity was related to the increase in the water content of the soil at the beginning of the electrokinetic treatment, which may be associated with the application of an electric field. Thus, when comparing the water content of the soil after

the EKF remediation test with that of the reference experiment (no application of an electric field), there was a discrepancy of 80.6% because the water content in the reference test decreased from the initial 11% to 9.9% after 34 days, instead of increasing to 18.7%, i.e., the case in the EKF test. In a previous experiment with 2,4-D, this fence technology also resulted in the increase of the soil water content. In that study, the increase was from an initial 11 % up to 19.1 %, which was very comparable to the result obtained in this test [27].

Figure 2. (a) Electric current applied to the electrodes and (b) electroosmotic flow collected at the three cathodic wells ($\diamond$ C₂, $\blacksquare$ C₄, $\blacktriangle$ C₆) during the performance of the EKF test.

The decrease observed in the second stage can be related to a partial flushing of the ions contained in the groundwater. This can be seen in Figure 3, which compares 2-D maps (average value of samples in the same xy position at different z coordinates) of conductivity in the reference experiment (soil that does not undergo remediation) with that in the EKF remediation test. A decrease of 23.4 % in conductivity was observed when comparing both maps. In addition, a very uniform concentration was observed. As will

be discussed later, this uniformity in concentration is characteristic of most of the parameters monitored in this plant.

Figure 3. 2-D maps of the conductivity in the reference test (a) and in the EKF test (b) after 34 days of accidental discharge.

A last point regarding Figure 2 is that the resulting electro-osmotic fluxes were slightly different from those obtained in the remediation of soil polluted with 2,4-D, even though the average resulting current intensities were almost the same (0.23 A vs. 0.25 A). Thus, in the previously studied case, the average electro-osmotic flow was 1.8 cm/d, while in this test, it was only 0.8 cm/d, because of due to the first stage. Neglecting this first stage, the value increased up to a closer value of 1.2 cm/d. The lower decrease in the conductivity was due to the ionic character of 2,4-D, which explains the differences.

One of the effects of electrokinetic remediation is soil heating due to the application of an electrical current. In Figure 4, the temperatures monitored by different thermocouples placed in the electrokinetic zone (zone surrounded by the electrode wells) and the external zone are shown.

Figure 4. Temperature changes at different positions of the soil during the remediation test (thermometer positions are explained in Figure 1).

The electrokinetic zone (see Figure 1) showed a temperature of 20.8°C, which was almost 4 degrees higher than the external zone (17.3°C) due to the ohmic heating. However, this increase was not high enough to lead to significant changes in the volatilization properties. At this point, it is important to note the importance of the room temperature in explaining the profile of the temperatures observed in the soil. During the course of the experiment, the average room temperature was 19.7°C, while the average temperature in the soil was 18.2°C. The lower average value registered in the soil can be explained by evaporative cooling produced by water, which was the primary energy exchange mechanism in the zones where ohmic heating was negligible (far from the electrodes). These results were in complete agreement with those obtained in a previous work in which the EKF technology was applied to remove 2,4-D from soils [27]. In that work, the reproducibility of this electric heating was clearly indicated when using the EKF remediation technology.

A very important parameter for the performance of electrokinetic soil remediation is the pH. The use of the technology may not be suitable for extreme pH values because it may result in irreversible damages to the biota contained in the soil during the application of

the technology in full-scale remediation cases. Also, it may influence (positively or negatively) the transport of pollutants by precipitation/dissolution or ion exchange. Figure 5 shows the changes in the pH of the electrolyte wells and in different selected positions in which rhizons were placed. Figure 5b also shows a 2-D plot of the pH obtained after the treatment, measured during the post-mortem analysis of the system.

Figure 5. pH changes during the EKF process. (a) pH changes during the electrokinetic remediation test measured in the electrolyte wells and in the rhizons. (b) 2-D plot of the pH distribution at the end of the test obtained after the post-mortem analysis. ♦ R1, ■ R2, ▲ R3, x R4, ■ R5, ● R6, + R7, - P1, — P2, ♦ P3, ■ P4, ▲ P5, x P6.

A very important piece of information that can be obtained from Figure 5 is that, as expected, the pH changed very abruptly in the anode and cathode wells because of the oxidation and reduction of water, which developed at a very high rate according to the monitored intensity values. Thus, the pH in the anode wells was close to 1.2 from very early on, while the pH in the cathode wells increased up to more than 12.5. However, these extreme changes were rapidly neutralized in the soil. Both the values obtained from samples taken in the rhizons during the course of the experiment and the values obtained at the end of the treatment (and measured in the post-mortem analysis) were reasonable. This was a clear indication of the appropriateness of the technology to prevent acidification or basification of the soil, in contrast with other electrode arrangements,

which can lead to extreme changes in the pH, such as rows of faced electrodes typically used in EKSF (electrokinetic soil flushing) processes [29].

As explained in the previous experimental section, the soil was polluted simulating an incidental spill for which a homogenous distribution will produce a concentration of 20 mg kg⁻¹. As noted before, a reference experiment was used in the model with the same dimensions for comparison. Figure 6 compares the 2-D plots of the oxyfluorfen concentration obtained after 34 and 70 days of the simulated accidental discharge.

Figure 6. Amount of oxyfluorfen remaining in the soil in the reference test (soil not undergoing any remediation process) after 34 (a) and 70 (b) days of the simulated incidental spill.

It can be seen that the pesticide distribution after this long period was almost uniform with zones over and below the target for a uniform distribution. The average concentration was slightly below the concentration added and decreased very slowly with time, i.e., 18.93 mg kg⁻¹ after 34 days and 18.41 mg kg⁻¹ after 70 days (Figure 6). This decrease can be explained in terms of the volatilization of the pesticide. When comparing the reference experiment with a previous experiment by our group on 2,4-D [27], it can be noted that the losses of oxyfluorfen by volatilization were very low compared to those of 2,4-D. In that case, the concentrations of 2,4-D after 26 and 70 days of the spill were 11.6 and 10.6 mg kg⁻¹, respectively. The vapour pressure of oxyfluorfen (0.026 mPa at

25°C) was very similar to that of 2,4-D (0.02 mPa at 25°C). Thus, the important difference observed in the volatilization seemed to be related to the thicker capillary barrier placed on the top of the soil surface, i.e., 3 cm in the experiment shown in this work vs. 1 cm in the test with 2,4-D. The thicker the barrier, the lower the evaporation of water and the volatilization of the herbicide.

The key analysis in this work is the evaluation of the removal of the pesticide attained by the electrokinetic treatment after the 34-day long test. These results are shown in Figure 7. As a first conclusion, this type of electrode arrangement (EKF) was very effective because the total amount of oxyfluorfen in the soil was reduced from 20.00 to 7.42 mg kg⁻¹ after 34 days. This reduction was very important, especially when taking into account that the volatilization was very low, and hence, only transport mechanisms induced by the electrochemical processes can explain the obtained results. As in the case of the reference experiment, the pesticide distribution was uniform, and only a slightly lower value was observed inside the zone surrounded by the electrodes (electrokinetic zone, Figure 1). This suggested that despite the large size of the plant used to study the transport of the pesticide (very important compared to other works published in the literature), which aimed to study the process under more realistic conditions, it was still not large enough to completely examine the distribution of pesticide inside the soil. It was also important that there was no gradient in the vertical axis. Nevertheless, these results were very valuable because despite this uniformity, valuable information was obtained for the scale-up of the EKF technology.

1

2 Figure 7. Comparison between the distribution of oxyfluorfen contained in the soil after
 3 34 days of EKF treatment and the reference test. (a) Upper zone, (b) middle zone, and (c)
 4 bottom zone.

5

6 To fully understand the transport mechanisms that decreased the concentration of the
 7 herbicide, Figure 8 shows the amount of oxyfluorfen collected at the different electrolyte
 8 wells, as well as the amount of pesticide collected during sampling in the different
 9 rhizons.

Figure 8. Transport of oxyfluorfen during the test by different mechanisms (● 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).

As shown, the most significant removal mechanisms were the transport of pesticide to the cathode wells and extraction from them. The only mechanism that can explain this transport was the drag of oxyfluorfen by the electro-osmotic flux to these wells. Gravity fluxes and transport to the anodes were much less important, indicating in this latter case that electro-migration was not a very efficient mechanism compared with the previous results shown for 2,4-D[27], in which this process was the primary mechanism for explaining the performance of the system. Regarding the sampling carried out in the rhizons, the similar values found in the rhizons confirmed the homogeneity in the distribution of oxyfluorfen in the soil from very early on, suggesting that transport by diffusion was very efficient. As the experimental time increased, the slopes of the curves were decreased, indicating the decrease observed in the 3-D map shown in Figure 8.

Finally, Figure 9 shows the distribution of oxyfluorfen after the electrokinetic fence treatment, and the results obtained were compared with those in a similar test carried out with 2,4-D [27].

Figure 9. Comparison of the herbicides (a) oxyfluorfen (grey) and 2,4-D (black) and (b) water balances after the electrokinetic fence experiment.

It can be seen here that the primary mechanism for the removal of the herbicide was completely different. For the removal of 2,4-D, a very significant amount of herbicide was removed in the anodic wells; however, in the case of oxyfluorfen, most of the pesticide was removed in the cathode wells, indicating that dragging with the electro-osmotic flux was the main electrokinetic mechanism. Figure 9 also shows that other important removal mechanisms were related to the vertical fluxes. In this regard, it can be noted that the removal by gravity and volatilization were comparable for both pesticides when the EKF technology was applied for the soil. This was important because the comparison done with the reference experiments showed contradictory conclusions, i.e., results obtained were very different for both herbicides and were explained in terms of the thicker capillary barrier placed on the top of the model to prevent evaporation of oxyfluorfen. Thus, the volatilization rate of the reference experiment with oxyfluorfen was 13.57 mg d^{-1} , while in the fence experiment, this rate increased up to 22.14 mg d^{-1} . The volatilization of 2,4-D was 13.20 mg d^{-1} in the electrokinetic experiment, but it was

surprisingly high in the reference experiment (24.00 mg d⁻¹). This was difficult to explain with our present knowledge of the technology because

1. The average temperatures of the experiments were comparable (20 ±2°C).
2. The same electric heating in the electrokinetic zone was observed when the soil went through the EKF remediation treatment.
3. The expected volatilization of both herbicides should be comparable taking into account the similar vapour pressure.

At this point, it is worth mentioning that the spilled oxyfluorfen was a commercial emulsion with SDS, which was very stable in terms of the pH. Thus, the measured z-potential changed in the range of (-45,-30) within the pH range of (2, 12). This indicated that even extreme variations of pH registered in the electrolyte wells did not affect the speciation of oxyfluorfen. In contrast, 2,4-D is an organic acid with a pKa of 2.73. This means that the extreme pH values reached in the anode and cathode wells can affect the distribution of ionic/non-ionic species and hence the volatility. Another important difference between the EKF and the reference tests was the higher soil water content during the EKF tests, which can affect the performance of the capillary barrier because it had to be wet in order to be effective.

Regarding the water fluxes, there were no significant differences in the evaporation of water, which can be easily explained by the similar temperature; however, there were strong differences in the fluxes of water by gravity and electroosmosis. In the case of the experiment with 2,4-D, the electroosmotic flux was almost three times the value measured for oxyfluorfen. This fact can only be explained by the difference in which the pesticide composition affected the electro-osmotic flux. Thus, according to the Helmholtz-Smoluchowski model (Eq. 1), the electro-osmotic flow can be affected by the dielectric constant (D), vacuum permittivity (ϵ_o), zeta potential (ζ), fluid viscosity (η), and potential

gradient (E_x). The zeta potentials of the soils were completely different because of the very different pollutant characteristics.

$$v_{eo} = -\frac{D\varepsilon_o\zeta}{\eta}E_x \quad (\text{Eq. 1})$$

Regarding the differences in the gravity fluxes, they have to be associated with the increased electroosmotic flow registered in the model polluted with oxyfluorfen and with the different heterogeneity of the soil, despite the great effort made in the preparation of reproducible model. It is important to note the difficulties faced in working with large setups but were clearly worthy by the relevance of the results. The lower gravity flow in the case of the remediation test of soil polluted with 2,4-D can explain the higher final average soil water content (19.1%) compared to that measured in the soil polluted with oxyfluorfen (18.7%).

In comparing the EKF strategy to other different electrokinetic soil flushing (EKSF) technologies for the removal of oxyfluorfen [35, 36], it may be pointed out that this strategy yields better results. Thus, for the same experimental type of setup and operating conditions, EKF achieves a 60.7% improvement in the removal of oxyfluorfen in about one month of treatment (versus natural volatilization, reference test), whereas EKSF with row of electrodes, EKSF 1C6A (1 cathode surrounded by 6 anodes) and EKSF 1A6C (1 anode surrounded by 6 cathodes) tests obtained 26.8, 27.1 and 41.6%, respectively. The energy consumption in EKF process was 34 kWh m⁻³ soil, similar to those obtained for EKSF with 1C6A and 1A6C setups (26.2 and 32.7 kWh m⁻³ soil) and much lower than that obtained with a EKSF test (65 kWh m⁻³ soil). Taking into account this data, the estimated cost of the completed treatment by EKF is around 38€ m⁻³ soil, in the range of that calculated by Alshawabkeh et. al. (48 \$USD m⁻³ soil) [37] and Virkutyte et al. (50-

120 \$USD m⁻³ soil)[11], and lower than the data reported for other soil remediation techniques[38], such as encapsulation, vitrification and physical separation.

5 Conclusions

6 From this work the following conclusions were drawn:

- 7 - Electrokinetic fences is a very efficient technology for the removal of oxyfluorfen
8 from spiked soils. After only a 34-day treatment, the concentration decreased from
9 20.0 to 7.4 mg kg⁻¹. However, it was not efficient in containing the pollution
10 because after the simulated accidental spill, the spreading was very fast, and
11 setting up the EKF after only two days was not enough to retain the pollution in a
12 constrained zone.
- 13 - The arrangement of electrodes used for the electrokinetic fences tested in this
14 work (circular-shaped fence of electrodes surrounding the spilling point)
15 prevented the occurrence of zones with extreme pHs by neutralizing the acidic
16 and alkaline fronts produced on the anodes and cathodes, respectively. This
17 arrangement of electrodes may also favour a slightly higher temperature in the
18 surrounding zone, which may affect volatilization.
- 19 - The physico-chemical characteristics of the discharged waste had a very important
20 influence on the obtained results. The primary mechanisms in the removal of
21 oxyfluorfen was the dragging of micelles by the electro-osmotic flow, while in a
22 previous work focused on 2,4-D, the primary mechanism was found to be
23 electromigration. However, for both cases, these pollutant characteristics affected
24 gravity and volatilization flows.

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