**Electrochemically assisted fences for the electroremediation of soils polluted with
2,4-D: a case study in a pilot plant**

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Abstract

Soils polluted with 2,4-D (model of ionic herbicide) can be remediated using a fence of alternating anodes and cathodes surrounding the main contamination point. This work reports results obtained in case study consisting of a 175 dm³ pilot plant, in which a soil polluted with an average concentration of 20 mg Kg⁻¹ of 2,4-D (spread by simulating an accidental spill) undergoes electroremediation for two months with an electric field of 1.0 VDC cm⁻¹ (between consecutive electrodes). Intensity, temperature, pH, moisture and pollutant concentration in electrolyte wells were daily monitored, and at the end of the experiments, an in-depth post-mortem analysis was carried out. In less than two months, the remediation technology attains a transport of more than 22% of the 2,4-D contained in the soil to the flushing fluids. However, the main mechanism for the removal of 2,4-D was found to be volatilization (which totalizes up to 57% of removal of 2,4-D). The

significance of this mechanism was confirmed with the comparison of the results obtained in the remediation test with the results obtained in a reference test consisting of the monitoring of the dispersion of the 2,4-D pollutant in a soil which does not undergo electroremediation treatment. These results are of a great importance for future scaling-up of the technology.

Keywords: 2,4-D, herbicide, electroremediation, natural soil, fence, pilot plant

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Highlights

- Fence electrokinetic can be used to remediate soils polluted with ionic herbicides
- A fence of electrodes surrounding the spilling point helps to transfer pesticide to flushing fluids
- Volatilization has a great importance to explain remediation results and should be accounted in large processes
- In less than two months, the remediation technology attains a transport of more than 22% of the 2,4-D contained in the soil to the flushing fluids

1. Introduction

Nowadays, the application of pesticides is very common in most agricultural regions of the World in order to improve crop production. However, the excessive use of these compounds may risk the quality of soil and water [1]. Moreover, occasional heavy rainfall, combined with a low capacity adsorption of soils to retain these organic compounds, may lead to fast diffusion of pesticides, producing the contamination of surface and groundwater reservoirs, affecting even to the quality of the potential supplies of drinking water. This fact has been associated with important risks for human health.

There are a great number of pesticides currently in use, with a wide range of physicochemical and biological properties [2]. For decades, herbicide 2,4-dichlorophenoxy acetic acid (2,4-D) has been one of the most used herbicides [3] and, as a consequence of its widespread use, in agriculture it has become a serious problem of soil and groundwater contamination [1, 4-12].

In literature, most of the research published regarding this pollutant is focused on the herbicide degradation in liquid phase, evaluating the treatment of surface or groundwater polluted with 2,4-D with different technologies [9, 13-26]. However, few studies presents an in situ treatment of the soil [23], which could avoid the loss of the herbicide by filtration, dragging of superficial water, evaporation, etc. To meet this objective, the technology employed needs to be capable to control the diffusion of the herbicide into the soil [27-30]. A technology of soil remediation that offers these requirements is Electrokinetic Remediation [31]. This remediation is carried out by the combination of processes (electromigration, electrophoresis, electro-osmosis, electrolysis and electrical heating) that occur in the soil when a low - level direct current (DC) is applied through a group of electrodes sited in the soil. These electrokinetic processes produce an

improvement in the transport of contaminants toward one of the electrode compartments, from where they can be removed.

Several authors have critically reviewed its state of knowledge [32-36]. At this point, it is important to remark that the position of the electrodes placed in the soil is a key parameter in the efficiency of the remediation, because this will determine the direction and magnitude of the electrokinetic processes, and consequently, the significance of the transport of herbicide. For this reason, different research works focused on the evaluation of the electrode configuration have been carried out in the last years [37-45]. The results obtained in this research indicate that the most effective electrode configuration from a viewpoint of the transport of pollutants consists of a group of anodes surrounding a central cathode or vice versa, depending on the transport properties of the pollutant. The number of the electrodes and the electrode spacing used has to be directly related to the mass of treated soil. Up to now, most of these works have been focused on the removal of metal ions and almost no experience can be found regarding the removal of herbicides.

According to the literature one of the most promising electrokinetic processes for the treatment of polluted soils is the electrokinetic fence (Figure 1). It consists of a sequence of alternate electrodes facing the groundwater plume with the aim to capture pollutants contained in the soil and avoid their dispersion by diffusion or advection. This work reports a case study in a pilot plant of 175 liters in which this technology was applied to remediate a soil spiked with herbicide 2,4-D by using a ring arrangement of alternating polarity electrodes surrounding the spill point. Results obtained are going to be compared to those obtained in a reference test consisting of monitoring the pollutant dispersion in a soil not undergoing any type of treatment.

Figure 1. Layout of the fence technology with a circular arrangement of electrodes

2. Materials and methods

2.1. Materials.

Soil from a quarry located in 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) were listed elsewhere (López-Vizcaíno et al., 2014). Herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) (Sigma-Aldrich) was analytical grade

2.2. Preparation of the polluted soil

The process of the preparation of the soil is important because of the complexity of natural soil. The process was divided into different stages: 1) positioning of three layers of gravel with different granularity for mechanical and drain support; 2) moistening the soil to 20% (a value fixed by the Proctor compaction study); 3) compaction of the soil in the electrokinetic reactor by compacting layers of a fixed height (5 cm) until achieving a density typical for natural soil (approximately 1.4 g cm^{-3}); 4) drilling of the electrolyte wells and instrumentation of the plant.

2.3. 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 dm³ (LWH: 70x50x50 cm³). The electrodes used for both the anodes and the cathodes were graphite rods with dimensions 1x1x10 cm³, positioned in semipermeable electrolyte wells, using a sequence of alternate electrodes surrounding the point in which the spill of herbicide was simulated. The cathodic wells are connected to 100 cm³ 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 rhizons were inserted into the soil. Figure 2 shows a scheme of the well configuration (part a) and of the instrumentation of the plant (part b). At the top of the soil a capillary barrier consisting of a c.a. 1 cm width layer of sand was placed in order to minimize the evaporation of water and the volatilization of herbicide.

P2, P4 and P6 Cathodic wells

P1, P3 and P5 Anodic wells

TT1-TT5 Thermocouples

T1-T8 Tensiometers

R1-R6 Rhizons

● Pour point

Figure 2. a) Scheme of well configuration in balnk and fence electrorremediation plants. b) Diagram of the instrumentation used in the electrokinetic remediation plant

2.4. Experimental procedure.

Once the plant was completely instrumented, the procedure began with the pollution of the soil (simulating accidental spill). To do this, in the central point of the electrokinetic reactor it was simulated the accidental leak of 6.0 dm^3 of an aqueous solution of $500 \text{ mg 2,4-D dm}^{-3}$ during 11 days (leaking rate of $0.0227 \text{ dm}^3 \text{ h}^{-1}$). After that, the filling of the electrolyte wells (water, pH 7.64 and 0.391 mS cm^{-1} of conductivity) was carried out. The level of the electrolyte wells were controlled by a level control system connected to the feed tank to adjust the volume of added water to the soil. The test started when the power source, a 400 SM-8-AR ELEKTRONIKA DELTA BV, was turned on, applying a constant voltage gradient of 1.0 VDC cm^{-1} between opposite faced electrodes (30 V).

During the experiments, the pH, the conductivity, and the 2,4-D 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 daily sampled (5 cm^3) and drained at the end of the process through an outlet situated at the bottom of the reactor. Electrical current, temperature, pH, moisture and 2,4-D concentration in electrolyte wells were daily monitored, and at the end of the experiments an in-depth sectioned analysis of the complete soil section was done. Several sampling points were distributed in the soil with the assistance of rhizons.

2.5. Analyses.

To quantify the amount of 2,4-D in the soil, it is used an L-S extraction process. It is carried out in Eppendorf tubes (15 cm^3) and using water as solvent (ratio polluted soil/solvent = 0.2 w/w). Both phases was vigorously stirred in a VV3 VWR multi-tube and subsequent phase separation was accelerated by the use of a centrifuge rotor angular

CENCOM II P-elite. The 2,4-D concentration in aqueous phase was determined by UV-visible spectrometry (Shimadzu UV-1603) at 283 nm of wavelength.

3. Results and Discussion

Figure 3 shows the changes in the current intensity during the electroremediation test in which a fence of six electrodes (with alternating polarity) is applied to a soil, after 260 hours of being polluted in the central point with a great amount of 2,4-D (simulation of an accidental spill).

As it can be observed, during the first days, the intensity produced by the electric field of 1.0 V/cm (measured between faced electrodes) was within the range 0.4-0.6 A with just small fluctuations. Then, a decrease down to the range 0.2-0.4 A is observed. This decrease indicates changes in the soil during the treatment, which increase their resistance and hence, decrease the resulting intensity for the same applied electric field. The average intensity applied during the 61 days long test was 0.23A.

Figure 3. Time course of the current intensity during the remediation test

The intensity monitored is related to the rate of the main electrochemical processes occurring on the electrodes: the oxidation and reduction of water. The products obtained in these well-known reactions are oxygen and protons in the oxidation, and hydrogen and hydroxyl ions in the reduction of water (eqs 1 and 2, respectively).

Both gases, oxygen and hydrogen, are stripped in the wells and they are not expected to have any relevance on the soil treatment. However, the effect of the protons and hydroxyl ions is much more important. Figure 4 shows the changes in the pH of the electrolyte contained in the wells. As expected, the pH in the catholyte wells increases up to extremely alkaline values (range 13-14) while the values in the anolyte wells decrease down to very acidic values (range 1-2). No significant differences are observed in comparing the anode and cathode wells among them but just small fluctuations.

Figure 4. Changes in the pH of the electrolyte wells during the electroremediation of soil with electrochemically assisted fences. Cathodic wells: P2 (♦), P4 (■) and P6 (▲). Anodic wells: P1 (◇), P3 (□) and P5 (Δ).

In most electroremediation processes, the extreme changes of pH produced in the wells reflect on changes in the pH of the soil, with the formation of the well-known acidic and basic fronts. These fronts are clearly observed when the electrode configuration consists of rows of electrodes of different charge facing each other, as we discussed in previous works [46-48]. For this reason, it is interesting to see what happen with the electrode arrangement tested in this work (the electrochemical fence system). These results are shown in Figure 5. To obtain these data, several rhizons were strategically placed in the soil. As it can be observed, pH is kept in its original value in the external zone to the fence, while in the internal zone of the fence, the values depends on the particular sampling point monitored and, although as an average, they are approximately kept in neutral values, there are position in which the neutralization of the fronts failed and pH becomes strongly alkaline (rhizon 6) or acidic (rhizon 4)

Figure 5. pH changes in different positions of the soil during the electroremediation test.
a) External zone: R1 (♦), R2 (■), R7 (▲) and R8 (x). b) Electrokinetic zone: R3 (♦), R4 (■), R5 (▲) and R6 (x). Continuous line: average pH value.

Another interesting fact to be pointed out in this discussion of the phenomena taking place in the soil, is the electrical heating of the soil. Soil heating is one of the most interesting processes taking place during the application of electric fields to soil and it can modify importantly the removal of pollutants, in particular when they behave as volatile or semivolatile species, that is, when they can be easily transferred to the atmosphere. Figure 6 shows the changes monitored during the test, in the thermometers placed in strategic

positions of the soil, in order to map the temperatures profiles. As it can be observed, the temperature inside the limits of the fence is a little bit higher than outside this borders but the general trend recorded in each position is the approximately same, with fluctuations which may be related to the changes in the temperature of room in which the test were carried out. In addition, it can be observed a higher value of temperature just in the period for which resulting intensity was lower, which suggests that soil resistance increased significantly in this period.

Figure 6. Changes in the temperature in selected positions of the soil during the electroremediation with electrochemically assisted fences. a) External zone: TT2 (dark

grey points), TT 4 (black points) and TT5 (light grey points). b) Electrokinetic zone:
Continuous line: average value.

Once considered electrolytic and soil heating processes, the third important set of processes that have to be considered in this evaluation of the technology are associated to water fluxes. Figure 7 shows the flowrates associated to the three electro-osmotic fluxes collected in the cathode wells. It is interesting to observe that although electric field was applied from the time marked in the Figure, there is a large period in which no volume is collected in the cathodes. After that initial moment, the flow received increases up to a constant value from which these steady state values are maintained till the end of the experiment. Although the system is symmetrical from a geometrical point of view, the flowrate collected in each well is different, being significantly higher in the well named as P4. Heterogeneities of the soil (in spite of the very careful method of preparation) can help to explain this observation.

Figure 7. Changes in the electro-osmotic flowrate in different cathodic wells: P2 (♦), P4 (■) and P6 (▲). Continuous line: average flowrate; discontinuous line: total flowrate.

The effect of the different flows induced by the electric field reflects on the moisture of the soil. After the treatment tests, post-mortem analysis were carried out to the different soils tested and 3-D maps of different parameters were obtained. Figure 8 shows the moisture map of a herbicide-dispersion reference-experiment (so-called in this work as Reference Test and carried out to evaluate the diffusion of the pollutant in a soil not undergoing any treatment) and in the fence-electroremediation test. First important conclusion is that water is more homogeneously distributed in the soil plant that undergoes the fence treatment and also that moisture is significantly higher in this case. Another important observation is that moisture decreases with time in the Reference Test and this is an indicative of the water evaporation that it is taking place in the system. In 70 days, moisture of the soil decrease from 16.2 down to 10.6 %. This is an important point because electroremediation technologies require high moisture to be applied in successful conditions and opposite to the Reference Tests, results obtained in the electroremediation test demonstrate that the fence technology successes in this point. To confirm this importance of water evaporation in this type of treatment, soil evaporation was measured in separated tests carried out at two different temperatures. It was found that the evaporation rate was constant (linear decrease in the amount of water contained in the tanks) and the calculated values of the evaporation rate were $0.0066 \text{ cm}^3/\text{cm}^2/\text{h}$ at 22.6°C and $0.0136 \text{ cm}^3/\text{cm}^2/\text{h}$ at 28.2°C , which are consistent with the observations made in the Reference Test.

Figure 8. 3-D maps of moisture in the soil after the tests.

Figure 9 shows the amount of 2,4-D removed from the system associated to flushing flows produced in the soil during the treatment test. As it can be observed, 2,4-D associated to the hydraulic flux (gravity) is almost negligible during the performance of the experiment as compared to the herbicide removed in the anolyte and catholyte, because no flow was continuously extracted from the system, but just accumulated. However, the amount obtained the last day (when the free volume was extracted from the plant) was similar to that obtained in the two types of wells. It is important to take in mind the main mechanisms expected for the transport of the herbicide in a soil undergoing an electric field. Herbicide 2,4-D is transported to the anode by electromigration because, in fact, the herbicide consists of an anion. However, in this case the amount of herbicide drained by the electro-osmotic flux is higher and this drainage is a little bit higher and it may be considered as the main removal mechanism associated to electrokinetic transport with this technology, according to results.

Figure 9. 2,4 -D removed with the different fluxes produced by the electric field applied in the soil. Cathodic wells (♦), Anodic wells (▲), gravity flux (■). Discontinuous line: total mg of 2,4-D collected.

The 2,4-D removed in the anolyte, catholyte and gravity fluxes should reflect on a decrease in the concentration of pollutant in the soil. Figure 10 shows the mapping of 2,4-D carried out with the post-mortem analysis and compared to the 3-D map obtained in the reference 2,4-D dispersion test (in this case, data shown were obtained at two different experimental moments: 26 and 70 days). It is important to remind the way in which the accident is simulated and that the target concentration of 2,4-D in the soil if the pollutant added were homogeneously distributed was expected to be 20 mg kg^{-1} , which was taken as the reference value to make removal calculations. The way of adding the 2,4-D promotes that an important fraction of the 2,4-D could be volatilized during this initial period and this could have a great importance in the study of real spill accidents. As it can be observed, after 26 days around 49.7 % of the 2,4-D added is removed and the 42

additional days does not reflect on a much higher removal but just in a redistribution of
 the 2,4-D with a total removal 54.06%. This is a clear indication that removal by
 volatilization is not very important once the pollutant is distributed in the soil at the
 operation temperature but it should be very important in the initial moments. By mass
 balance calculations, it can be obtained an average value of $8.74 \cdot 10^{-4} \text{ mg cm}^2 \text{ d}^{-1}$ in soils
 with a uniform distribution of 2,4-D and concentrations around 10 mg kg^{-1} (calculated
 from the second period of the reference test). To confirm this point, several lab-scale tests
 were carried out using a solution of 500 mg dm^{-3} of 2,4-D to measure the volatilization
 rate. From these lab-scale tests, it was found an approximate volatilization value of 0.0017
 $\text{mg/cm}^2/\text{h}$ at room temperature for such highly concentrated solutions. Obviously a linear
 decrease in this rate is expected as the concentration decreases, explaining the lower
 evaporation rate found once the simulated spill of 2,4-D is completed.

Figure 10. 3-D maps of 2,4-D after the test carried out

In comparing the values in the Reference Test with those obtained in the fence electroremediation test, it can be drawn that the removal attained by the fence is very important and it is not only limited to the zone inside the fence but also it is important outside of the fence. Thus, after the 61 day-long treatment average concentration of 2,4-D in the soil is 4.1 mg kg^{-1} .

In addition to the electrokinetic processes, the transport of 2,4-D to the atmosphere by volatilization should also be considered, in order to fully understand the complete treatment. In this work, the amount of 2,4-D volatilized can be calculated by adjusting the mass balances taking into account that 2,4 D drained with the different liquid streams is fully characterized, as well as the 2,4-D remaining in the soil mockup after the treatment (worked out by the post-mortem analysis). Resulting value is 1727.1 mg (57.6%), that it is comparable to the value obtained in the simulation of the incidental discharge of herbicide and indicates that this volatilization mechanism is the most important in the removal of herbicide from soil. This means that in the design of full-scale processes, technology to properly control this flow of gases is one of the key points to be considered. Otherwise, a diffuse atmospheric pollution could be produced.

Table 1 shows a summary of the main results obtained with this technology. As it can be observed 21,87 % of the 2,4-D initially contained in the soil is transferred to the flushing fluid fluxes and a much higher amount of 2,4-D (as compared to the pollutant dispersion reference experiment) is volatilized, meaning that the main challenge for this technology is to prevent this uncontrolled way of pollution dispersion. After 61 days of treatment pollution of the soil is decrease in more than 80% that is an important value as compared to the 50% of herbicide naturally spread in the soil not undergoing any treatment technology. These results are of a great importance for future scaling-up of the technology, in particular if it is taken into account that this arrangement of electrodes can

be a good alternative for the remediation of soils polluted with herbicides at full scale as it has been demonstrated for the removal of metal ions in previous studied.

Table 1. Summary of the main results obtained during the reference and the fence electroremediation tests

Tests/ parameters	reference	reference	fence
Time (days)	26	70	61
Average temperatura (°C)	20.3	20.3	20.21
Average intensity (A)	-	-	0.23
2,4-D remaining in the soil after the treatment (%)	50.27	45.94	20.57
2,4-D removed in anode wells (%)	-	-	6.69
2,4-D removed in the cathode wells (%)	-	-	8.33
2,4-D collected with hydraulic fluxes (%)	-	-	6.84
2,4-D transferred to atmosphere (%)	49.73	54.06	57.57

4. Conclusions

The removal of 2,4-D from spiked soils using a fence of alternating anodes and cathodes is a promising technology which may reduce the pollution from the soil in almost 80% with treatment periods below two months. However, volatilization of the pollutant is an issue of the major importance that should be accounted in the design of full scale processes, as it has been drawn from the data obtained in the reference and in the fence tests. The herbicide removal is comparable inside and outside the zone delimited by the

fence of electrodes and in the experimental case studied in this work the concentration value decrease from the expected initial value of 20 mg/Kg down to 4.1 mg/kg.

Acknowledgements

The authors acknowledge funding support from the EU and Spanish Government through the MINECO Project CTM2013-45612-R and INNOCAMPUS.

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