Scale-up of the Electrokinetic Fence technology for the removal of pesticides. Part II: does size matter for removal of herbicides?

R. López-Vizcaíno¹, C. Risco², J. Isidro², S. Rodrigo², C. Saez¹, P. Cañizares¹, V. Navarro³, M.A. Rodrigo¹,*

¹Department of Chemical Engineering, Facultad de Ciencias y Tecnologías Químicas, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

²Department of Chemical Engineering, Instituto de Tecnologías Química y Medioambiental, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

³Geoenvironmental Group, Civil Engineering School, University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

Abstract

This work reports results of the application of electrokinetic fence technology in a 32 m³ prototype which contains soil polluted with 2,4-D and oxyfluorfen, focusing on the evaluation of the mechanisms that describe the removal of these two herbicides and comparing results to those obtained in smaller plants: a pilot-scale mockup (175 L) and a lab-scale soil column (1 L). Results show that electric heating of soil (coupled with the increase in the volatility) is the key to explain the removal of pollutants in the largest scale facility while electrokinetic transport processes are the primary mechanisms that explain the removal of herbicides in the lab-scale plant. 2-D and 3-D maps of the temperature and pollutant concentrations are used in the discussion of results trying to give light about the mechanisms and about how the size of the setup can lead to different conclusions, despite the same processes are occurring in the soil.
Keywords

Electrokinetic Fences; soil remediation; 2,4-D; oxyfluorfen; scale-up

Highlights

- Facility size matters in the mechanisms that explain removal of herbicides from soil
- Electric heating of soil is the key to explain the remediation in the prototype
- Electrokinetic transport processes becomes more important as the size of the setup decreases
- Volatilization is the main mechanisms that explain the removal of 2,4-D and oxyfluorfen
1. Introduction

The great impact of the environmental problems associated to soil pollution has pushed Society to look for efficient ways to avoid this type of pollution, typically by the application of strict prevention actions. When these actions fail (or simply they are not enough to prevent soil pollution), different technological approaches, that help to minimize its impact, need to be applied. This interest of Society is reflected on day-to-day stricter regulations that are arising in many developed countries, where the social conscience about these important problems is greater. In turn, Society is motivating scientist in the search for efficient technologies (with funded research topics in research calls), among which, electrochemically-assisted processes are one of the most promising nowadays, for the treatment of soils polluted with very different types of pollutants.

These electrochemically assisted technologies are the sum of many contributing processes, activated directly or indirectly by the application of an electric field between electrodes placed in the polluted soil. The large number of processes, and the strong interactions of parameters in those processes, makes every application a unique case from which a direct application to other case cannot be expected but from which important lessons can be learned and applied to many other cases (Ribeiro et al., 2005; Alcantara et al., 2010, 2012; Pazos et al., 2010; Ribeiro et al., 2011).

As pointed out in a previous review, pesticides occurrence is becoming an important issue nowadays (Rodrigo et al., 2014). This occurrence is sometimes associated to the application of these chemicals in agricultural activities, leading frequently to diffuse pollution events, very difficult to be solved with current technologies because of the huge extensions affected. Less frequent but more important is the problem associated with accidental discharges during manufacturing or handling of pesticides. In those cases, a very acute and localized problem arose, and here, it is where electrochemically-assisted
soil remediation technologies may get a good contribution to the environmental restoration (Gomes et al., 2012; Cao et al., 2013; Vieira dos Santos et al., 2016).

In recent works, we have studied the effect of using different electrodes configuration in the removal of two widely-used herbicides with mockups of 175 L: oxyfluorfen (Risco et al., 2016c, 2016d, 2016e) and 2,4-D (Risco et al., 2015, 2016a, 2016b). Most of these electrodes configurations were studied for different types of pollutants (most of them inorganic) by other groups (Alshawabkeh et al., 1999; Virkutyte et al., 2002; Yeung, 2006; Yuan et al., 2006, 2007; Buchireddy et al., 2009; Reddy et al., 2011; Yeung and Gu, 2011; Cameselle and Reddy, 2013; Li et al., 2016). The significance of our work was based not only in the application of the technology to pesticides (which are also a model of organic pollutant) but most importantly on the comparison of the technologies in terms of the type of pollutant and electrode configuration.

From those works, it was obtained that the electrokinetic fence (EKF) technology showed very good prospects for being used in this application. It was also pointed out that size of the facility seemed to have a relevant role on results. This later conclusion warns and advices us about the necessity of scaling up the processes in other to obtain applicable results in full-scale restoration of polluted sites. A previous work about scale-up (López-Vizcaíno et al., 2016) gave us relevant information about engineering inputs that should be accounted and in Part I of this work this information was complemented by a compared discussion of the results obtained in the prototype with those obtained in lower scale systems for the transport of inorganic species.

Now, in Part 2 of this work, our interest is focused on the removal of the two model pesticides and in the comparison of the obtained results in the prototype with those obtained in lower scales. Thus, results obtained in the prototype are going to be compared with those obtained in the mockups (in which our previous results were obtained) and
even with those of a lab-scale soil column with dimension closer to those of most of the works reported in the literature. It is aimed to give light on how size affects to results of the studied of soil remediation, in addition to draw conclusions about the application of EKF to the remediation of a soil pollutes with high concentrations of two pesticides.

2. Materials and Methods

In this work the same soil, chemicals, experimental devices and procedures shown in Part I were used. The characteristic part of the results shown in this work deals with the concentration of the two herbicides used. To determine their concentration in solid and liquid samples a HPLC Agilent 1100 with an UV detector, from Agilent Technologies, has been used, following the analytical procedures described in previous works of our group which can be found elsewhere (Risco et al., 2015, 2016a, 2016b, 2016d). Fig. SM-1 shows a picture of the simulated accidental discharge of the soil with pesticides to complement the information supplied in Part I of this manuscript work.

3. Results and Discussion

Temperature is a factor of the major significance in electrokinetic soil remediation technologies. Electric resistance of the soil causes soil heating and, in turn, the rise in temperature may activate many other processes. Fig. 1 shows the changes in the average temperature, both in wells and soil, during the EKF test performed at the prototype.
Figure 1. (a) Changes in the average temperature of soil and electrolyte wells during the EKF tests and (b) 2-D maps of temperature in soil for four representative times.

At it can be observed, temperature in the soil at the end of the EKF test multiplies by three the initial value while temperature in the wells multiplies it by four. Therefore, and as indicated in the 2-D maps, a clear profile of temperatures is produced in soil. This profile indicates the more active areas in the nearness of the electrodes, not finding any differences between anodes and cathodes, except for small zones of the soil in which the value of temperature is a little bit different of that expected according to a perfect symmetry. As this point, it is worth to state that electrodes wells were connected to gas extraction system and hence volatilization of pesticides arriving these wells is expected to be enhanced by the increase in temperature.

In comparing values to those obtained in previous studies about the EKF technology in smaller scales (Risco et al., 2015, 2016e), it can be drawn that average temperature during the prototype test is 29.4ºC which is more than 10ºC above the average
 temperature maintained in the mockups (18.2 and 19.3°C for the oxyfluorfen and the 2,4-
D tests, respectively). In those lower-scale cases-of-study, the increase of temperature
was much lower, which it can be easily explained because of the lower ohmic loses
associated to the closer position between electrodes. Another difference is worth to be
pointed out. In the mockup, the portion of soil surrounded by electrodes (so-called
electrokinetic zone) showed a temperature which was almost 4 degrees higher than the
external zone, although this increase was found to be not high enough to lead to
significant changes in the volatilization properties. This is just the opposite behaviour of
what it is observed in the prototype, in which the temperature in the zone surrounded by
the electrodes is lower. This fact points out that, although the same processes are
occurring (in this case, the electric heating, which is more intense in the nearness of
electrodes), and the same energy transport mechanisms are affecting to soil, the different
sizes of the evaluation facilities lead to a completely different temperatures distribution
map. Regarding the lab-scale plant (results not shown), no significant differences in the
temperature were observed over the tests. In this case, the very low resulting current
intensities (in the range from 10 to 20 mA) helps to explain that any small increase in
temperature could be compensated by the evaporative cooling and also by the exchange
of energy with the environment (because of the high relationship surface/volume of the
lab-column used).

Obviously, temperature is expected to influence on pesticide distribution,
specially taking into account the high volatility of both species tested. Thus, vapour
pressure of oxyfluorfen is 0.026 mPa (25°C) while that of the 2,4-D is 0.02 mPa (25 °C).

Fig. 2 shows the concentration of 2,4-D measured in the electrolyte wells and also
a 2-D map obtained at four representative times of the test carried out in the prototype.
As it can be observed, there is a higher concentration in cathodes than in anodes, opposite
to it could be expected. This indicates that, although we could not measure electroosmotic flux in the prototype, there is a transport of water that also drags the pollutant to wells. Anyway, the concentrations are far below the expected values and this can only be explained in terms of the efficient gas extraction carried out. At this point, taking into account that pKa is 2.76, under the acidic pH of the anolyte, the molecular 2,4-D is the primary species present in the electrolyte well, which is the species that more easily mobilizes from the liquid to the vapor phase. This also helps to understand the lower concentration found in the wells.

Figure 2. (a) 2,4-D transported to the electrode wells during the experiment and not volatilized. (b) 3-D map of 2,4-D distribution at the end of the test.
Regarding the 3-D map of pesticide distribution, it can be seen a very homogenous distribution of the 2,4-D in the soil. It is worth to say that there are no significant differences in the planes xz and yz because the three horizontal xy layers (in which the soil was divided for a better characterization) show very similar profiles. Just a lower concentration of pesticide in the top layer, explained by the more important volatilization as it is in direct contact to atmosphere and to the gas collection devices. Another important point that should be remarked is that in the sand well marked with P in the scheme (the placed used to pollute the soil by simulating an accidental discharge), a volume of aprox. 44 L of aqueous solutions containing 0.285 g L\(^{-1}\) in 2,4-D still remains. This concentration is much lower than the initial 50.8 g L\(^{-1}\) added and clearly indicates that pollutant has been effectively dispersed during the test. As this central well is not filled with soil but simply with sand it was non sense to plot this data in the 3-D maps (whose concentrations are given in mg kg\(^{-1}\) soil), although this datum has been used to check the mass balance of pesticide in the system.

Same comments apply for oxyfluorfen, whose profiles are shown in Fig. 3, although the concentrations of pesticide measured in the electrolyte wells are much lower in this later case. However, they indicated that oxyfluorfen is also transported to electrode wells, and as expected in higher concentration to the cathodes (dragging with the electroosmotic flux). They also indicate that it is volatilized, process that can be promoted by the high temperatures reached on the electrodes wells.
Figure 3. (a) Oxyfluorfen transported to the electrode wells during the experiment and not volatilized. (b) 3-D map of oxyfluorfen distribution at the end of the test.

Regarding the 2-D maps, there are not differences in the middle and bottom layers, but opposite in the surface layer there are two points showing a high concentration of oxyfluorfen and one zone in which the concentration is lower. In comparing this map with the maps of temperatures at the end of the experiment, it can be seen that both zones with a higher concentration corresponds to regions in which the temperature is lower than the average value. Opposite, there are zones in this top layer in which the concentration is very low and they correspond to zones with higher temperatures. Regarding the amount
of pesticide not dispersed and still present in the sand-well, marked with P in the scheme (the placed used to pollute the soil by simulating an accidental discharge), a volume of aprox. 44 L of aqueous solutions containing with a concentration of 0.176 g L$^{-1}$ in oxyfluorfen still remained at the end of the test. As for the 2,4-D, this concentration is much lower than the initial 50.8 g L$^{-1}$ added and clearly indicates that also the oxyfluorfen has been effectively dispersed during the test. Likewise, this data was not plotted in the 3-D maps (whose concentrations are given in mg kg$^{-1}$ soil), although it has been used to check the mass balance of pesticide in the system.

Taking into account, the different distribution mechanisms of the two pesticides and also that a significant part of the pesticides transported by EK mechanisms is finally volatilized, the distribution of the initial 508 g of 2,4-D and 508 g of oxyfluorfen added during the simulated accidental spill is as follows:

- 7.6 g of oxyfluorfen (1.50%) and 12.3 (2.43%) were not dispersed and in the end of the tests still remains in the distribution sand well
- 66.2 g of oxyfluorfen (13.03%) and 51.2 g of 2,4-D (10.09%) were not removed from soil after the one month test
- 1.4 g of oxyfluorfen (0.27%) and 1.6 g of 2,4-D (0.32%) were collected in the electrolyte wells and not volatilized
- 432.8 g of oxyfluorfen (85.20%) and 442.8 g of 2,4-D (87.26%) were volatilized.

At this point, any comparison with lower scale systems can help to understand if the size of the facility used to evaluate the remediation technology matters. For this reason, in addition to the experiments carried out in the 175 L –mockups (whose results are going to be compared afterwards), it was decided to run another experiments in a lab-scale column (part of the results regarding pH distribution was previously described in
part I of this work). In those lab-scale experiments, it was decided not to pollute the soil but the pesticide (23 mg in each experiment) was added in the catholyte well (2,4-D) or in the anolyte well (oxyfluorfen) according to the expected transport direction (electromigration towards the anode in the case of 2,4-D and dragging with electroosmotic flux in the case of oxyfluorfen). Some interesting results obtained in those tests are shown in Fig. SM-2, in particular the electroosmotic flux changes and the amount of pesticide collected from the reservoir tank associated to each electrode well.

As it can be observed, the stationary electroosmotic flux rate is one log unit over the value reported for the mockups (25 cm d\(^{-1}\) vs range 0.8-1.8 cm d\(^{-1}\)). As compared to the value obtained in the experiments of characterization of electroosmotic flux shown in Part I, the initial value is comparable but during the remediation tests, it can be observed a decrease, which may be related to the changes in the composition of soil and electrolyte wells.

Electroosmotic flux drags a high amount of both pesticides to the cathodic reservoir tank. There is also a transport of pesticides toward the anode, which is enhanced in the case of the 2,4-D because of its ionic character. In these experiments, total amount of pesticide was 23 mg. This means that more than 50% is transported efficiently to the electrodes by electrokinetic transport mechanisms. Soil did not undergo any relevant change in the temperature during the test. Duration of the tests was 2 days, which corresponds to a specific electric charge passed of 0.62 Ah kg\(^{-1}\) soil in the case of the oxyfluorfen (for which the average intensity was 11.6 mA) and 0.95 Ah kg\(^{-1}\) in the case of 2,4-D (for which the average current intensity was 17.6 mA). These values are close to those applied in the prototype test (0.70 Ah kg\(^{-1}\)) and half of the applied with the mockups, which were 1.50 and 2.48 Ah kg\(^{-1}\), for the cases of oxyfluorfen and 2,4-D, respectively. This means that a similar progress of the treatment could be expected in the
three scales evaluated. Because the experiment were run at constant electric field and intensity was not an input but an output, it was not possible to predesign test with exactly the same specific current charge.

Fig. 4 compares the profiles of oxyfluorfen in the soil in the end of the three tests of soil remediation at different scales. In order to see the final profiles of concentration in the soil, it is important to pay attention to the fact that that the 2-D maps corresponds to the plane xy in the case of the two bigger plants and to the plane xz in the case of the lab-column. As it can be observed, and opposite to what it could be observed in the case of the distribution of inorganics species in the prototype, there is not symmetry in any of the plots and there are zones in which the concentration of the pesticide is higher than average. In the case of the prototype these zones were explained in terms of the temperature distribution and in the case of the lab-scale plant in terms of a very effective dragging of the oxyfluorfen micelles. This dragging, together with volatilization was found to be the key to explain the decrease of oxyfluorfen in the case of the mockup, in which the different final distribution, taking into account the symmetry of the system could only be explained in terms of non-homogeneities in soil.
Figure 4. 2-D maps of the distribution of oxyfluorfen after the EK treatment at three different scales: (a) lab scale (1 L), (b) mockup (175 L) and (c) prototype (32 m$^3$). Comparison of the 2,4-D profiles in the three plants is shown in Fig. 5. In the three cases, there is a relevant decrease from the initial 20 mg kg$^{-1}$ down to less than 12 mg kg$^{-1}$. Profiles are more uniform than in the case of oxyfluorfen, fact that could be easily understood by taking into account the higher solubility of 2,4-D. In the two lower scale plants there are zones with a higher concentration, that in the smallest scale can be related to transport of pesticides while in the middle scale (mockup) should be related to non-homogeneities (despite the special care taken during preparation of the mockups) because of the symmetry of the system.
Figure 5. 2-D maps of the distribution of 2,4-D after the EK treatment at three different scales: (a) lab scale (1 L), (b) mockup (175 L) and (c) prototype (32 m³).

Finally, Fig. 6 summarizes and compares the relevance of the electrokinetic vs the volatilization mechanisms for the removal of 2,4-D and oxyfluorfen in the three plants evaluated.

Figure 6. Percentages of pesticide remaining in soil and removed by electrokinetic and volatilization after the tests carried out at three different scales.
The higher the scale, the lower is the magnitude of the EK processes and the higher is the relevance of the volatilization. Obviously, this result is related to the higher temperature reached in the larger scale facilities, which in turn is related to higher ohmic loses in energy. Although mechanisms for EK transport are the same in the three scales, the huge differences in the distances are a key point to understand that EK transport is the most important mechanisms at the lowest scale (the most frequently used in scientific studies) and it turns into the less effective mechanisms at higher scales. This is explained by its non-effective competition with the volatilization promoted by the rise in the temperature of the soil.

4. Conclusions

From this work, the following conclusions can be drawn:

- The removal of herbicides from soil are affected by the size of the plant used to study the remediation process and hence, conclusions from small scale tests should not be extrapolated for full-scale applications.

- The controlling mechanisms in the prototype was the electric heating of the soil, which in turns produces a higher volatilization of the organics contained in the soil. Relevance of these processes in the lab-scale plant is very low because the low current intensity does not produce any relevant change in the temperature profile.

- The controlling mechanisms in the lab-scale plant are the electrokinetic transport process, in particular the dragging of the pesticides toward the cathode and the electromigration towards the anode. The relevance of these processes in the prototype test is very low because the electroosmotic flux is very low.
Acknowledgements

This work was supported by the European Union through project Spanish Government through project CTM2013-45612-R and INNOCAMPUS and CYTEMA E2TP Programs of the University of Castilla La Mancha. Special thanks to engineer Oscar Merlo for his very valuable contribution in the preparation and monitoring of the prototype.

References


Scale-up of the Electrokinetic Fence technology for the removal of pesticides. Part II: does size matter for removal of herbicides?

R. López-Vizcaíno¹, C. Risco², J. Isidro², S. Rodrigo², C. Saez¹, P. Cañizares¹, V. Navarro³, M.A. Rodrigo¹,*

¹Department of Chemical Engineering, Facultad de Ciencias y Tecnologías Químicas, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

²Department of Chemical Engineering, Instituto de Tecnologías Químicas y Medioambiental, University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

³Geoenvironmental Group, Civil Engineering School, University of Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

Supplementary materials

Figure SM-1. Picture showing details of the simulated event of pesticide discharge.
Figure SM-2. Changes in the EOF and amount of pesticides collected in electrolyte wells over the tests carried out at the lab-scale plant. Full points: oxyfluorfen collected in the cathode reservoir Empty points: 2-4-D collected in the anode. Diamond: cathode. Square: anode.