**Scale-up of the Electrokinetic Fence technology for the removal of pesticides. Part I: Some notes about the transport of inorganic species**

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**Abstract**

This work describes the application electrokinetic fence technology to a soil polluted with herbicides in a large prototype containing 32 m³ of soil. It compares performance in this large facility with results previously obtained in a pilot-scale mockup (175 L) and with results obtained in a lab-scale soil column (1 L), all of them operated under the same driving force: an electric field of 1.0 V cm⁻¹. Within this wide context, this work focuses on the effect on inorganic species contained in soil and describes the main processes occurring in the prototype facility, as well as the differences observed respect to the lower scale plants. Thus, despite the same processes can be described in the three plants, important differences are observed in the evolution of the current intensity, moisture and conductivity. They can be related to the less important electroosmotic fluxes in the larger facilities and to the very different distances between electrodes, which lead to very
different distribution of species and even to a very different evolution of the resulting current intensity. 2-D maps of the main species at different relevant moments of the test are discussed and important information is drawn from them. Ions depletion from soil appears as a very important problem which should be prevented if the effect of natural bioremediation and/or phytoremediation on the removal or organics aims to be accounted.

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

Highlights
- In EK soil remediation technology, size of the experimental setup matters
- Same processes occurring, different observations made because of the dimensions
- Increase in the intensity over the experiment due to the conductivity and pH
- Depletion of ions from soil and concentration in the nearness of electrode wells
- Rapid dynamic response: almost no relevant changes after a 15-day treatment
1. Introduction

Nowadays, soil pollution is becoming one of the most important environmental problems for Humankind with important consequences in the availability and quality of water reservoirs for human supply. This issue should be faced from a multidisciplinary approach (civil, chemical and environmental engineers, biologist, geologist…), because of the complexity of the mechanisms involved in the reactivity and transport of pollutants, either those occurring naturally in the environment or those promoted by humans with the application of remediation technologies.

When electrochemical technologies are to be applied, this complexity becomes even worse, because of the interactions of those natural and anthropogenic processes with the processes promoted electrochemically. These electrochemically induced processes involve (Rodrigo et al., 2014):

- the important changes in the pH in the nearness of the electrodes (because of the electrolysis of water),
- transport processes of different species (pollutant or not) driven by the electric field applied (including electromigration, electrophoresis and electro-osmosis) and
- an increase in the temperature, caused by the ohmic resistance of soil.

All these processes interact among each other and with other chemical and physical processes (such as ion exchange, precipitation, volatilization, etc.) producing changes that, when properly engineered, contributes to the removal of pollutants from soil.

Many references can be found in the literature about all these processes (Ribeiro et al., 2005; Reddy et al., 2009; Alcantara et al., 2010, 2012; Gomez et al., 2010; Pazos
et al., 2010; Reddy et al., 2011; Ribeiro et al., 2011; Gomes et al., 2012; Cameselle and Reddy, 2013; Vieira dos Santos et al., 2016). Most of them are carried out at the lab-scale because this is the level in which the process can be better characterized, with a higher accuracy in details, allowing even a good mathematical description of the system with lots of experimental results that allow researchers formulating the models and fitting their parameters. Then, processes need to be scaled-up, and here a problem arises. Financial support for doing large-scale studies is not easy to be obtained without the participations of companies, and in this case, they are interested in keeping the information to get a benefit and NDAs prevents a good diffusion of results. In addition, information taken from the full-scale restoration of polluted soil is very important, but it lacks the accuracy of the data obtained in research programs.

At this point, it is worth to say that scale-up in disciplines such as chemical or environmental engineering does not only mean “make things with a bigger size”. Unfortunately, this is a very common mistake, typically associated to researchers or professionals not directly related to these technological disciplines. In contrast, this concept also involves a deeper understanding of the processes, which have been previously characterized at lower scale with smaller devices (for which operation conditions can be more easily controlled and details about processes can be more easily elucidated) (López-Vizcaíno et al., 2016). Thus, the key in scale-up is the definition and understanding of the “controlling mechanisms” in full-scale, rather than the study of the fundamentals of a process, which for sure, in a lower scale and with more controlled conditions can be obtained with a higher accuracy giving very valuable data. However, rather often, these data cannot explain the real behavior of the system and here is where this important concept arises. In the case of soil remediation, there is a coexistence of three electricity-driven processes (electrokinetic, electrochemical and electric heating
processes), which also coexists with other chemical processes (such as ion exchange reactions such as precipitations, etc.) and physical processes (hydraulic fluxes, evaporation, etc.). The prevalence of any of these mechanisms over the others can lead to a very different performance of the technology (Alshawabkeh et al., 1999; Yuan et al., 2006; Karagunduz et al., 2007; Yuan et al., 2007; Buchireddy et al., 2009; Li et al., 2016) and it is worth to evaluate how the size of the experimental setup influences on these mechanisms if results carried out at small scale aims to be extrapolated for full-scale applications.

This work reports important information about the scale-up of electrokinetic fence (EKF) technology for the remediation of soil polluted with herbicides, by comparing results obtained in a prototype of 32 m³ with those obtained in a mockup of 175 L. These lower-scale results were obtained in different works previously published in the literature (Risco et al., 2015, 2016e), within a wider-scope research program in which different electrodes placement were compared for the efficient removal of pesticides from soil (Risco et al., 2016a, 2016b, 2016c, 2016d). At this point, a preliminary work about scale-up informs about the many inputs that should be accounted for proper scale-up study (López-Vizcaíno et al., 2016). Within this general scope, Part I is focused on the description of the processes that affect to inorganic species contained or produced in soil during the application of the remediation technology.

2. Materials and Methods

2.1. Materials

The soil used in this work is provided from a region of Castilla la Mancha (Spain), with important agrarian activities. This soil has been used in others works carried out to our research group (Risco et al., 2015, 2016a, 2016b, 2016d, 2016e; López-Vizcaíno et
al.). It is classified as low plasticity soil, according with ASTM D2487 (International, 2006) and ASTM D4318 (International, 2010a) and as silty loam within the textural classification of USDA (Staff, 1993) (clay=4.9%, silt=68.2% and sand=26.9%). The mineralogical composition is described in detail elsewhere (López-Vizcaíno et al., 2016).

Two different commercial pesticides have been used to simulate an accidental spill: ESTERON 60 supplied by Dow AgroSciences, and FLUOXIL 24 purchased from CHEMINOVA AGRO. The active component of ESTERON 60 is the 2,4-dichlorophenoxyacetic acid (2,4-D) with a composition of 60% (v/v), in an emulsified solution with calcium dodecylbenzenesulfonate. FLUOXIL 24 is composed by 24% (v/v) of Oxyfluorfen, non-polar and hydrophobic herbicide, dissolved in aqueous solution by the emulsifier action of xylene (59%), cyclohexanone (13%) and calcium dodecylbenzenesulfonate (4%).

2.2. Soil remediation prototype

The EK remediation test was carried out in an especial facility built in the Institute of Chemical and Environmental Technologies (ITQUIMA) of the UCLM (Ciudad Real, Spain), which consists of two electrokinetic soil remediation prototypes, with soil-treatment capacities of 16 and 32 m³, respectively, of which only the second reactor has been used in this work. Dimensions of this later prototype are 2 m of height and a square plant of 16 m² (4 m × 4 m). Specific parameters construction of reactor were described in literature previously (López-Vizcaíno et al., 2016). Fig. SM-1 shows a scheme of the plant and section of the cell.

The electrode configuration selected to be studied in this prototype corresponds to an electrokinetic fence (EKF), using a sequence of six alternating electrodes (three cathodes and three anodes) positioned in semipermeable electrolyte wells and separated
167.8 cm (Fig. SM-2). The electrodes used were cylinders of graphite (15 cm in diameter and 100 cm in length). The wells used were PVC cylinders with lateral perforations (31.5 cm in diameter and 140 cm in depth) to facilitate the flow and transport of electrolytes.

To monitor the different parameters during the test, thermocouples, tensiometers water and pressure sensors (or "divers") were located at different positions into the soil. Moreover, a complete distribution of twenty micro-boreholes were disposed into the soil for sampling and to monitor the pH, electrical conductivity, pressure and temperature of the pore (Fig. SM-2).

Additionally, a system designed to extract the volatilized pesticide composed of extractor hoods and a blower was connected to the prototype. This setup drives the gases produced in the electrolyte wells to an absorber tank, which contains with 10 g L⁻¹ of SDS (Fig. SM-3) to retain the pesticides volatilized.

To obtain a soil with hydro-mechanical properties similar to those of a real soil in the environment, the following procedure was applied:

- Installation of a first layer of gravel (height 0.2 m) and a second layer of river sand (height 0.1 m) separated with a geotextile to avoid mix of the particles with different size. These layers act as a drain support.

- Installation the soil into the reactor by compaction of six layers of controlled height (layers 1 to 4, 0.2 m; layer 5, 0.15 m and layer 6, 0.11 m). The compaction were carried out with an INCOINSA 21215 vibrating plate with a compaction surface of 0.2 m². To check the compaction process, after of dispose each layer, several samples of soil were extracted to analysis its water content and dry density

- Installation a surficial layer of sand that acts as a capillary barrier to minimize evaporation losses.
Construction of the electrolyte wells and instrumentation of the plant.

These steps were extensively explained in a previous work focused on scale-up of electrokinetic remediation processes (López-Vizcaíno et al., 2016). After these stages, an accidental pesticide spill was simulated by the discharge of 10 L of two aqueous emulsions containing 50.8 g L\(^{-1}\) of 2,4D and 50.8 g L\(^{-1}\) Oxyfluorfen, respectively, for one day. This concentration corresponds to an initial target concentration of 20 mg kg\(^{-1}\)soil if the pesticides were homogeneously distributed throughout the soil. The test starts when the power supply (MAGNA POWER ELECTRONICS (7.5 Kw: 0-1000 V and 0-25 A)) was turned on with a constant voltage of 168 V (1.0 V cm\(^{-1}\)).

2.3. Lab-scale soil remediation column

For comparison purposes, a small lab-scale column was used (in addition to a pilot-scale mockup whose results were described in the literature and that it is not going to be described in this section). The lab-scale cell was made of transparent methacrylate and divided into five compartments. A scheme is shown in Fig. SM-4.

The width of the plant was 3 cm. The central compartment, where the soil is located, has a length of 15 cm and it was compacted manually and separated of the electrode compartments by a nylon mesh (0.5 mm). This compaction was carefully done to avoid the formation of heterogeneities zones in the soil, which can result in preferential paths for the fluid transport. Likewise, the compaction procedure was carried out with the target to obtain a similar water content and dry density than in the prototype. One of these compartments served as anode and other as cathode. Graphite bar electrodes (10 cm × 1 cm × 1 cm) were used as anode and cathode. Each electrode compartment was connected to an additional compartment to collect the liquid overflowing from the wells. The experiments were performed in a potentiostatic mode, setting a voltage at 1.0 V cm\(^{-1}\).
2.4. Analytical techniques

The water content \((w)\) and dry density \((\rho_d)\) of natural soil were determined based on standards ASTM D2216 \((\text{International}, 2010b)\) and ASTM D7263 \((\text{International}, 2009)\). Particle size distribution from a size smaller than silt was obtained using a laser diffraction particle size analyzer with an aqueous module. Temperature, suction and phreatic level were monitored with thermocouple PT-100, tensiometers T5X from UMS and divers sensors from Eijkelkamp. pH, conductivity and temperature of the liquid pore were measured with a multiparametric analyzer sensION+ MM150 DL from Hach.

3. Results and discussion

The electrokinetic fence (EKF) prototype evaluated in this study was operated for more than one month keeping an electric field of 1.0 V cm\(^{-1}\) between consecutive electrodes. Resulting current intensity informs about the development of electrochemical processes on the surface of the anode and cathode and, in its turn, these electrochemical processes drive the rest of the processes that are occurring into the soil.

Fig. 1 shows the changes observed in this parameter over the experimental period studied in this work. As it is observed, current intensity increases from an initial value below 10 to a value over 20 A. This value is reached for the first time in less than 2 d, and from that moment on is approximately maintained during the whole experimental period (average final value 20.43 A)
Figure 1. Time-course of the changes of the intensity during the EKF tests carried out in the prototype.

The dispersion in the data is caused by the daily shutdown of the powering system. This shutdown was carried out in order to take characterization samples in safe conditions and it only took about ten minutes a day, so it was not expected to affect significantly to the performance of the system.

Removal of the two pesticides was previously studied in mockups of 175 L plants in two different tests (one per each pesticide) (Risco et al., 2015, 2016e). In comparing the intensity monitored in those tests with those of lower scale systems, it can be noticed that in the lower scale systems, the intensity undergoes a decrease from the range 0.50-0.60 (in which the test starts) down to 0.2-0.30 A, for which current intensity stabilizes. In a simplistic view, taking into account the Ohm’s Law, this indicates that ohmic resistance of the soil changes in a different fashion in both devices. In the case of the prototype, it decreases at the beginning of the remediation process down to a value in
which it is then maintained until the end of the test, while the observation in the lower scale facilities indicates just the opposite trend: ohmic resistance increases during the test up to a constant value.

According to the values obtained, obviously, the intensity is not directly related to the amount of soil contained in the setup (or size), because the ratio between mass of soil in both setups is near to 182, while the increase in the resulting intensity from the mockups to the prototype is only 81 times. Likewise, there is not a direct relationship to the ratio between total electric fields applied, which is below 13 (which also match with the ratio between the distances of electrodes, because the same electric field was applied in the two studies). This means that simple extrapolation of this parameter for the pre-design of the scale up is not an easy task in this type of soil remediation technologies. Opposite, a much more complex study has to be carried out. Initially, two inputs should be considered to determine this value: the water content of the soil and the ionic conductivity.

In the case of the mockup, the current intensity evolution could not be explained in terms of the changes in the water content of the soil. This content increases from an initial value of 16 % up to a final value around 19%, and, hence, this parameter does not allow to explain an increase in the resistance by the increase in the volume of partially saturated zones. At this point, it is worth to take in mind that the increase in the water content obtained in the EKF mockups was explained in terms of the electroosmotic fluxes generated in the soil, because the water content decreases in same setup down to the nearness of 11% when no electric field was applied (due to evaporation).

For this reason, the decrease in the conductivity has to be explained in terms of the dragging of the ions contained in the groundwater from the soil to the electrodes wells by electromigration, which resulted in a depletion of ions in the soil. The concentration of these ions increased significantly in the wells and helped to compensate the productions
of hydroxyl ions in the cathode and protons in the anode. With respect to a reference experiment in which no electric field was applied, the removal of conductivity from water contained in soil was found to be of 23.4%, value that can explain the changes in the resulting current intensity observed in the mock-ups. It is worth to say that the same soil was used in both setups and that the same procedures were applied to prepare it (obviously adapted to the final size).

In the case of the 32 m³ - prototype, water content behaves in a different fashion that in the mock-up, although always in values that correspond to partially saturated soil. Water content of the soil was risen from 6.4% to saturation in 24.6% before the remediation test, which was the target value to start the experiment. During the electrochemical test, it decreases from this initial value of 24.6% down to 23.14%. This final value is over the 19% water content obtained in the mockups (overcomes it by 20%) and, obviously, this is positive to explain the lower resistance of the soil. Fig. SM-5 shows the maps corresponding to the average water content and to the distribution in the soil by height, dividing the soil into three horizontal layers in the plane xy.

It should be taken into account that the range of colors used in Fig. SM-5 goes only from 20 to 25%. Taking into account this narrow zone, it is easy to observe that there is not a large change of water content in soil but simply a zone near to one of the cathodes in which water content is a little bit lower than in the rest, in particular in the bottom layer of the soil in this zone. Small non-homogenies in the soil can help to explain these differences, because, according to the symmetry of the system, they were not expected and, hence, they do not have a clear explanation.

At this point, it is worth to describe that this type of prototype underwent previous tests to characterize evaporation and sealing. Both tests were described in a previous manuscript (Lopez-Vizcaíno et al., 2016) and clearly indicated that the system had no
leaking and water contained in the soil can be easily evaporated. Anyhow, although evaporation is also expected to occur during the remediation process carried out in the prototype scale, the water content of soil is much higher than in the mock-ups.

In order to explain the differences, one very important observation to explain moisture is related to the electroosmotic flowrates, as it was pointed out before. While in the two mockup systems it was obtained net electroosmotic fluxes of 1.8 and 0.8 cm d\(^{-1}\), they were negligible in the prototype system because no extra water was collected in the cathodes and /or needed to be added in the anodes during the complete one-month long test. The only way to explain these results is by assuming a compensation between the electroosmotic and the hydraulic fluxes in the prototype. At this point, it was considered interesting to perform one test in a very small lab-scale plant in which the same soil was placed. Results obtained are shown in Fig. SM-6 and they demonstrate the importance of the driving force in these systems (pressure for hydraulic and electric field for electroosmotic flowrates) and they also clearly indicate that electroosmotic fluxes increases in small devices for the same electric field applied. Thus, in the smallest scale plant, for 1.0 V cm\(^{-1}\), electroosmotic flux corresponds to 183.27 cm d\(^{-1}\) value that it is two log-units above the one obtained in the mockups. From the comparison of the plots shown in Fig. SM-6, it can be drawn that this electroosmotic flux can be compensated by the hydraulic flux, with simply a water column difference as low as 3 cm. This difference is a relevant value for the lab-column, but it is completely negligible in the case of the prototype and, of course, non-detectable under the operations conditions used. In the case of the pilot mockup, differences of this magnitude are also difficult to be monitored and, although in a lower extension, this balance of the two type of fluxes can stand for the lower value observed of the net electroosmotic flux as compared to the obtained in the lab-scale column.
Regarding conductivity of the groundwater, the other parameter that affects the ohmic resistance of the system, Fig. 2 shows the changes observed in the conductivity of the anode and cathode wells, as well as the 2-D map of the conductivity changes in soil during four representative moments of the test.

![Figure 2](image-url)

Figure 2. Changes in the conductivity of the (a) cathodic and (b) anodic wells. (c) 2-D maps of conductivity distribution in four representative times of the test.

As observed, there is a large increase in the conductivity of the fluids contained in the three anodic and three cathodic wells up to values around 40 mS cm\(^{-1}\). No great differences are observed between results obtained in each well, as compared to the results obtained in the other two wells with the same polarity of electrode. Meanwhile, the average value of conductivity in the soil changes from 1.79 (day 0) up to 10.73 mS cm\(^{-1}\) (day 30) (with values at days 2 and 15 of 2.76 and 7.82, respectively, that indicates a continuous increase over the duration of the test). In comparing these values with the values obtained in the mockups, a very different trend is observed, because in that case the conductivity of soil decreases during the tests by 23.4%. Obviously, to explain the
increase in conductivity of the soils not only the transport of ions from soil to electrodes of different charge should be considered, but also the variations of pH has to be taken into account. Otherwise, increases in the conductivity in soil and electrode wells are hard to be explained.

Regarding the pH, it is worth to remember that it produces one of the most important changes expected. Oxidation and reduction of water (which develops in the anode and cathode of the prototype, respectively), producing oxygen, hydrogen, protons and hydroxyl ions according to Eq (1) and (2).

\[ \text{H}_2\text{O} - 2\text{e}^- \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ \]  
\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \]

Amount of gases produced is negligible as compared to the magnitude of the prototype and both hydrogen and oxygen are dissipated in the atmosphere without being necessary any further safety evaluation because of the small quantity produced and the gas extraction system connected to each one of the electrolyte well. However, protons and hydroxyl ions remains for a longer time in the place where they are produced, because they are more slowly transported, having a great importance in many other processes occurring in the soil.

As it can be seen in Fig. 3a and 3b, pH in the three anode wells decreases down to extreme values (lower than 1) while pH in the three cathodes increases up to values around 12, not finding further differences between any of the anolyte or catholyte wells respect to the others of the same polarity. Transport of protons from the anode to the cathode (acidic front) and from the cathode to the anode (basic front) is then established and, in less than two days of operation, clear profiles of pH are formed around the electrodes wells as the 2-D maps shows (obtained at four representative times of the test).
Obviously, the acidic and basic fronts neutralize to each other at a given distance of the electrodes and as it can be observed in Fig. 3c (green color), the amount of soil with a non-extreme pH is almost maintained from the second day of the EKF test. Hence, only two-three days period is enough not only to stability the intensity but also the pH profiles thorough the soil and in the wells.

Figure 3. Changes in the pH of the (a) cathodic and (b) anodic wells. (c) 2-D maps of pH distribution in four representative times of the test.

Thus, the amount of soil in which pH is kept within the range 6 to 8 is close to 70%, value much higher than those obtained with the same technology in the mockup scale, which were 45% (EKF test with oxyfluorfen) and 10% (EKF test with 2,4-D). Differences can be easily explained by the very different distances between electrodes and the different transport rates associated, which obviously should have an influence on the final map. At this point, it has to be taken into account that protons and hydroxyl ions are not only transported by migration but also by many other processes (dragged with
electroosmotic and hydraulic fluxes, diffusion, etc.) and, hence, size of the experimental
facility is a factor of the major significance.

In order to confirm that the scale of the setup (in which it is carried out the
assessment of the EKF) has a definitive influence on results, Fig. 4 shows the results
obtained during electrokinetic tests carried out to evaluate the transport of 2,4-D and
oxyfluorfen in a typical lab-scale column (the same that was used in the evaluation of the
hydraulic and electroosmotic fluxes). More results about these tests will be discussed
afterwards because those tests were not carried out for evaluating the pH fronts but with
the aim of evaluating the mobility of pesticides in setups of different sizes.

Figure 4. a) Changes in the pH of the electrolyte wells and in the pH distribution during
the electrokinetic treatment of pesticides in a lab-scale plant. (Full points: oxyfluorfen;
Empty points: 2-4-D). Final pH distribution : b) 2,4-D, c) Oxyfluorfen.
The 2-D map of pH in the soil shows a soil that it is kept within the neutral pH range in more than 80% and in which only the zone closer to the cathode well shows an alkaline pH. It is important to take in mind that in this case not the xy plane but the xz plane is represented, which is more representative for this setup taking into account the geometry of electrodes. Regarding the evolution of the pH in the wells, cathode wells meet almost the same value of that obtained in the prototype (and also in the mockups), while in the anode wells, the pH only decreases down to 2.7. This means that in this short distances, neutralization of the pH fronts is more intense and in fact, the basic front is avoiding any negative effect of the acidic front, helping to attain than a very high ratio of the soil is kept at close neutral pHs (between 6 and 8). Another important observation is that pH in the electrodes wells reach a constant value in less than one day, and hence, stabilization in this parameter is confirmed to be rapidly meet in electrokinetic soil remediation systems.

Hence, the increase in the intensity during the EKF test can be explained by the increase in the conductivity, which in turns, it is explained by the very important effect of the pH changes produced on the electrodes.

Electromigration is the main process to explain the transport of protons and hydroxyl anions and it is also the key the explain the mobility of ions because electroneutrality should be maintained over time in every point of the soil. Fig. 5 shows how the 2-D map of the changes in the concentration of three different anions during four representative moments of the test. These three anions (chloride, sulfate and nitrate) are typically contained in most soils and they have a great relevance in life associated to soil as they act as nutrients for microorganisms and plants and their exhaustion may have a very negative impact on the soil characteristics. In addition, in the case of nitrate (and also for sulfate, although in a lower extension) it is known its use by many types of
microorganism (about 60% of aerobic microorganisms) as substitute of oxygen for the oxidation of organic matter. Hence, its depletion from soil may minimize the contribution of natural bioremediation processes in the remediation of organic pollution from soil.

Figure 5. Changes in four representative moments of the 2-D maps of anions monitored during the EKF tests.

As expected anions monitored are dragged from soil and transported to the anodes wells. This is clearly observed for chloride, nitrate and sulfate and as it can be seen very similar profiles are obtained in the three cases. This is a very important observation because, as it has been pointed out, the dragging of ions from soil is not positive but a very negative consequence of this technology that should be accounted for the evaluation of combined processes like the electrobioremediation technology (Mena et al., 2016) and that also influences on natural bioremediation or phytoremediation processes. Anyhow, it is true that an electrode configuration like the EKF is not as bad as other (like rows of electrodes), for which dragging is promoted by geometry. However, this depletion of ions
should be considered and tried to be minimized, by using technique such as the periodic polarity reversal. Opposite to changes observed in the pH or in the resulting current intensity, stabilization of the concentrations according to the 2-D maps takes more than two days. For the case of the sulfate and chloride it seems to be reached before the 15th day of operation. The slower response of nitrates may be related to their much more complex chemistry, which involves their very easy cathodic reduction to ammonium and the electrochemical production of nitrogen oxides, as well as their expected significant ion exchange with soil, which is expected to be promoted in the vicinity of electrodes because of great changes in the concentration of proton and hydroxyl ions.

The same general conclusions can be drawn from the 2-D maps of the two cations monitored, that are shown in Fig. 6.

Figure 6. Changes in four representative moments of the 2-D maps of cations monitored during the EKF tests.

In this case, the cations are concentrated in the nearness of the cathodes and as it can be seen in the plots corresponding to sodium, not great differences are obtained between the 15th and the 30th day of operation, indicating that transport of ions in
electrokinetic soil remediation processes is very rapid and it does not need longer times
to be completed. A very interesting observation is what it seems a “disappearance” of
calcium, which it is not real but just the expected result according to the strongly basic
pH in the nearness of the cathode: calcium is immobilized in the soil matrix and hence it
is not present as a free species in the water taken during the monitoring. Obviously, this
fixation of calcium is also negative from the viewpoint of natural biological processes
that may occur in soil, and it must have a negative impact on natural bioremediation and
phytoremediation of organic pollutants because fixed calcium is not available as nutrient.
This negative impact may be easily prevented by adding acids to the catholyte, although
this strategy should be very carefully assessed because this addition may produce other
negative consequences on soil.

A last common observation that it is worth to point out from all 2-D maps shown
in this work (pH, conductivity, anions and cations) is the boundary effects produced by
the walls of the prototype, which explains the accumulation of conductivity and ions
(including protons and hydroxyl ions produced electrodically) just in the rear part of the
wells (that part outside the electrokinetic zone). This accumulation is clearly a
consequence of the walls, and almost surely the main difference which can be found with
respect to a full-scale application. Obviously, it will not be found in a full-scale
application, for which the physical constraints produced by the walls do not exits.

4. Conclusions

From this work, the following conclusions can be drawn:

- Size of the experimental setup used to study soil remediation processes is key
to understand their performance. Despite the same processes are occurring at
a similar rate, dimensions of the facilities modify completely the final
distribution of parameters, and hence no relevant conclusions should be extrapolated from small size. This is clearly observed in the case of the pH, for which 2-D maps show important differences despite the same processes are occurring.

- For the same electric field, in EKF, electroosmotic fluxes become less important in the larger scales. This phenomenon has an influence on the moisture distribution of the soil and in the dragging of pollutants.

- The increase in the intensity during the EKF test observed in the prototype is explained by the increase in the conductivity, which in turns, it is explained by the very important effect of the pH changes produced on the electrodes.

- There is a depletion of ions in the soil and a concentration in the electrode wells. This transport should be controlled in full scale applications, in particular when combination with other treatment technologies is looked for.

- In electrokinetic soil remediation, processes affecting inorganic species are very rapid and for most of the processes happening it can be considered that the operation parameters stabilize in less than two weeks. For the case of pH and intensity, this period seems to be shortened to two days.

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References


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Supplementary materials

Figure SM-1. Scheme of (A) Plan view and (B) section of EKR reactor.
Figure SM-2. Positioning of electrode wells and of the main instrumentation used and picture of the setup

Figure SM-3. Gas extraction system coupled to the soil remediation prototype
Figure SM-4. Scheme of the lab-scale soil remediation cell

Figure SM-5. Water content distribution after the EKF test
Figure SM-6. Effect of the height (full points) and electric field (empty points) on the flowrates produced in the lab-column setup.