Removal of chlorsulfuron and 2,4-D from spiked soil using Reversible Electrokinetic Adsorption Barriers

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Abstract

This work focuses on the application of REKAB (Reversible Electrokinetic Adsorption Barriers) technology to remediate two soil matrixes spiked with 2,4 dichlorophenoxyacetic acid (2,4-D) and chlorsulfuron (CLSF), two herbicides that exhibit a high water-solubility and very different volatility and adsorption properties (2,4-D is more volatile). Results obtained after 15-day treatment tests are compared with those obtained using single electrokinetic soil flushing technology (EKSF) and very important differences were pointed out. Both technologies are efficient in the removal of herbicides from soils. However, while in the EKSF, transport of pesticides to electrode wells is very important and evaporation is favored, in particular for the removal of 2,4-D, in the case of REKAB, retention by the carbon bed is the primary mechanisms (40 % and 60 % of 2,4-D and CLSF respectively) and both, evaporation and transport to electrode wells, although significant, are less important than in the EKSF. After the 15 day-treatment only

28% of 2,4-D and 12 % of CLSF remained in the soil as pollutants and evaporation losses are less than half than those obtained in the EKSF technology.

Keywords

Electrokinetic; soil remediation; adsorption barriers; 2,4-D; chlorsulfuron

Highlights

- REKAB technology allows removing more than 70% of pesticide within 15 days
- Adsorption onto the carbon bed is the primary mechanisms in REKAB remediation
- Adsorption totalizes 40% of the removal of 2,4-D and 60% of the removal of CLSF
- Volatilization of herbicides is prevented in the REKAB technology
- Less efficient transport of herbicides to the electrode wells in REKAB

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Introduction

Environmental electrochemical engineering is becoming hot topic nowadays because of the very promising applications that currently are being developed[1]. In addition to the very promising application in the treatment of industrial wastewater [2-5], soil electro-remediation technologies are focusing the interest of many research groups and applications to the removal of organics from polluted soils seems to be a worthy topic of study [6-9]. One of the types of pollutants with a greater interest are herbicides because they can be a source for diffuse pollution, either associated to bad dosages or to accidental discharges [10]. For this reason, the application of electrochemical technology for their removal has been studied during the recent years[11].

There are many types of technologies that can be applied to the removal of pesticides from soil[6, 12-22], and our group has focused during the recent years not only in the development of soil washing treatments[23, 24] (off-site technology) but also in two on-site technologies, the electrokinetic soil flushing (EKSF)[25-27] and electrokinetic fences (EKF)[28]. However, in the recent years a new technological approach has been proposed for the removal of organics: the permeable reactive barriers (PRB), demonstrating great advantages as compared to the EKSF of the EKF technologies. In addition to their application for the removal of inorganic species, use of biological barriers[29], ion exchange resin[30] or activated carbon[31] barriers has been studied with great detail for the remediation of soil polluted with organic pollutants, pushing up research in the search for new applications[32-37].

One of the most interesting approaches, because of the expected high efficiency in the removal of organics, are the permeable barriers consisting of adsorption beds [31, 35]. A first experience in the application of the combination of EKSF with adsorption barriers was proposed for the removal of trichlorophenol from spiked soils[31], where it was

demonstrated its high efficiency and easy performance. This technology is based on the mobilization of pollutants contained in the soil by the application of an electric field through an adsorbent bed. Transport of pollutants can be associated to electromigration (ionic pollutants), electrophoresis (colloids and microdrops of emulsified pollutants) and dragging with the electro-osmotic flux. The higher the contact of the pollutant with the adsorption bed, the higher is the efficiency of the process. For this reason, advantages of reversible changes in the polarity were also pointed out in the literature[38]. A comprehensive example was shown with the removal of diesel pollution from soils[39, 40], in which the periodic reversion in the polarity did not only improve the efficiency but it also helped to regulate the pH (preventing extreme pH even near to the electrode wells) and to avoid the depletion of ionic species in the soil.

In this work, the removal by REKAB (Reversible Electrokinetic Adsorption Barriers) technology [41, 42] of two very well-known herbicides (2,4 dichlorophenoxyacetic acid (2,4-D) and chlorsulfuron (CLSF)) is going to be studied. Both herbicides have a great solubility in water (900 and 31800 mg dm⁻³ for 2,4-D and chlorsulfuron, respectively) and they have a very different volatility (0.02 mPa and 3×10⁻⁶ mPa for 2,4-D and CLSF, respectively, at 25°C). This is important, because in previous studies[26, 43], pollutant evaporation was found to be a very important process during the application of EKSF technology and, consequently, it was advised the use of combined EKSF- gas capture processes as a conclusion of the work. As in that work, in the present study, a lab-scale plant is used in which soil is spiked with a concentration of 30 mg kg⁻¹ of herbicide and the electric field applied between electrodes is 1.0 V cm⁻¹. Each day the polarity of electrodes was reverted. This arbitrary period was chosen taking into account previous experience of our group in the REKAB technology [44, 45]. In this work, not only results of the REKAB technology but also a comparison with EKSF is going to be carried out.

Material and Methods

Chemicals. Kaolinite, provided by Manuel Riesgo Chemical Products (Madrid, Spain), was used as a model of clay soil. Properties of this synthetic clay soil were provided by the commercial supplier, and are detailed elsewhere[46]. This synthetic soil was used in order to avoid side processes caused by the presence of organics in natural soil and then, to clearly evaluate the performance of the technology studied. All chemicals, including anhydrous sodium sulfate, sodium phosphate (Fluka, Spain), 2,4-D, CLSF (Sigma-Aldrich) were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 °C) was used to prepare all solutions. Sodium Dodecyl Sulfate (Fluka, Spain) used as solubilizing agent while hexane and ethyl acetate (Sigma-Aldrich, Spain) were used as solvent for extraction of liquid and solid samples.

Electrokinetic cell. Bench setup used in this work is shown in Figure 1a [31]. It was made of transparent methacrylate and divided into five compartments. The central compartment with length of 20 cm was loaded with herbicide-polluted soil, which was compacted manually and separated of the electrode compartments by a 0.5 mm nylon mesh. Graphite plates (10.0 cm × 10.0 cm × 1.0 cm) provided by Carbosystem (Madrid, Spain) were used as electrodic material. Each electrode compartment was connected to an additional compartment to collect the liquid overflowing from the wells that is transported by the electrokinetic processes. The experiments were performed in a potentiostatic mode, i.e., setting a voltage at 1.0 V cm⁻¹. The duration of the experiment was two weeks.

Figure 1. Experimental setup used in this work. Part a). Picture and schematic layout.

Part b). Division of soil for the postmortem characterization

Preparation of the soil. The soil was spiked with 960 cm^3 of herbicide aqueous solutions (100 mg dm^{-3}) until attaining an initial pollutant concentration of 30 mg per kg of soil. The initial target moisture level of the soil was 30%. Polluted soil was compacted manually in the central compartment of the cell. 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. In all cases, tap water was used as flushing fluid. The level of the anode wells were maintained by means of a level regulation loop. On contrary, from cathode well water was daily pumped.

Experimental procedure. During the experiments, the electrical current, the temperature on different portions of the soil, the electroosmotic volume removed from the cathodic well, pH, conductivity, pesticide and TOC concentration of the electroosmotic fluid were monitored. At the end of the experiment, a *post mortem* analysis was carried out to evaluate the final state of the treated soil (post-study characterization): pH, conductivity, humidity, herbicide and TOC concentrations were measured. For this analysis, the soil compartment was divided into sixteen portions and the PBR into four (Figure 1b).

Sampling procedure of each soil-portion consists of taking it out carefully from the set up and manually homogenizing it. After that, representative samples were taken for carrying out each analysis.

Analysis procedures. Measurement of the moisture was carried out by drying the soil samples in an oven for 24 h at 105 °C. Moisture was estimated taking into account the weight difference in the samples before and after drying. For the determination of the pH and conductivity in the soil samples, the standard method (E.P.A.-9045C, 1995) of the saturated paste was used. This method consists of the mixture of 10 g of dry soil with 25 cm³ of distilled water, which was magnetically agitated for 20 min. After sedimentation, the aqueous supernatant phase was prepared to analysis. All the samples (*pre and post mortem*) were filtered with 0.45 µm nylon filters from Whatman before their analysis.

The decay of herbicides was monitored by reversed-phase chromatography and total organic carbon (TOC). The chromatography system was an Agilent 1100 series coupled a UV detector. The analytical column Phenomenex Gemini 5 µm C18 was used. For the four compounds, the temperature oven was maintained at 25 °C and volume injection of 20 µL. 2,4 D was identified using mobile phase consisted of 60 % acetonitrile and 40 % water to 2 % acetic acid with a flow rate of 0.4 cm³ min⁻¹ and detection wavelength of 280 nm. The mobile phase for CLSF analysis consisted of 40 % acetonitrile and 60 % water (0.1 % H₃PO₄) with a flow rate of 0.4 cm³ min⁻¹. The detection wavelength used was 225 nm. Total Organic Carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Measurements of pH were carried out with an InoLab WTW pH-meter. Conductivity was measured using a Conductimeter GLP 31 (Crisol Instruments, Spain). The soil temperature was monitored using a Digital Soil thermometer.

Results and Discussion

In this work, in order to evaluate the performance of the REKAB process (Reversible ElectroKinetic Adsorption Barrier) two spiked soil columns undergo 15-day long remediation tests. Main changes during the test, as well as a detailed post-mortem analysis, are going to be discussed in this section and results are going to be compared with those obtained using EKSF and described in a previous work[46].

Figure 2 shows the changes in the pH and conductivity in the two soil columns tested. Polarity of the electric field applied between the electrodes was reversed once a day (value selected arbitrarily) and this periodic change helps to explain the zig-zag changes observed over the experiment in the pH value of the electrolytes contained in the wells.

Figure 2. Changes in the main operation parameters during the remediation of the soil polluted with 2,4-D by electroremediation powered by power supply at 1.0 V cm^{-1} . (a)

2,4 -D and (b) CLSF. **Part 1.** Values of pH and conductivity in the electrolyte wells: pH in the anode (■) and cathode (●); conductivity in anode (◇) and cathode (Δ). **Part 2.** pH (full points) and conductivity (empty points) map of the soil after the remediation test. Upper right position (●, ○), upper left position (■, □), bottom right position (◆, ◇) and bottom left position (▲, Δ) of the soil after the remediation test.

Opposite to what it is typically obtained in non-reversible ESKF processes, pH in the anodic and cathodic wells does not tend to extreme values but to more neutral values, despite the well-known and widely explained production of protons (during water oxidation) and hydroxyl anions (during water reduction) in the anode and cathode wells, respectively, shown in eqs. 1 and 2. This observation means that reversion in the polarity contribute to the better performance of the electrokinetic remediation by preventing the occurrence of extreme pHs in the soil.

For a better understanding of the results of this work, Table 1 compares results obtained in the REKAB technology with those obtained in a previous work in which similar conditions were applied by EKSF[46]. Comparison of the pH in the steady state values obtained in the REKAB and in the EKSF indicates important differences between both electrokinetic configurations, with more extreme values of the pH in the case of the EKSF technology, for which no neutralization is obtained by polarity reversion. However, these extreme values of pH in the wells do not reflect on the soil values, which only shows a slight increase in the pH for the REKAB process.

Table 1. Comparison of steady state pH, conductivity and moisture obtained after applying 15-day long remediation test (EKSF or REKAB) to soil spiked with 2,4-D and CLSF.

Technology (herbicide)	J A m ⁻²	Moisture %	pH _{an} / pH _{ca}	Cond _{An} /Cond _{ca} μS cm ⁻¹	pH _{soil}	Cond _{soil} μS cm ⁻¹	Flushing fluid added cm ³ h ⁻¹	Flushing fluid collected cm ³ h ⁻¹
EKSF (2,4-D)	3.52	32.82	2.19/ 14.51	3032.3/ 6133.4	7.82	178.9	5.3	3.2
EKSF (CLSF)	3.26	30.19	2.32/ 14.55	2734.3/ 10215.5	8.09	256.9	3.1	2.6
REKAB (2,4-D)	3.42	30.62	7.50/ 10.91	743.5/ 779.5	8.33	587.9	4.3	1.7
REKAB (CLSF)	3.35	31.31	6.54/ 11.39	726.5/ 1062.8	8.19	563.7	4.0	0.3

Regarding conductivity, during the REKAB process no significant changes can be observed in the electrolyte contained in the wells. This behavior contrasts to the fluctuations observed in the soil, with higher axial dispersions in the nearness of the electrode wells, which can be clearly related to the transport of the ionic species and the fluctuations in the value of pH. In comparing the value obtained in the REKAB with those obtained in the EKSF, it can be pointed out a much higher value of conductivity in the processes studied in this work. This higher value can be explained because opposite to EKSF, the periodic reversion of the polarity prevents the washing up of ions contained in the soil. This is also observed by comparing the conductivity of the electrolytes contained in the wells, which is much higher in the case of the EKSF, although in this case not only the transport of ions but also the more extreme changes in the pH should be taken into account to explain the high values.

Figure 3 shows the time course of the current density and flowrate of fluid added to the anodic well in the two tests carried out. Current density determines the kinetic of the transport and reactive processes, because it is related to the oxidation and reduction of water on the electrode surfaces (main expected reactions) and hence to the transport of cations to the cathode and anions to the anode.

Figure 3. Part a. Time-course of the current density (■, □) and flow rate of fluid added to the anodic well (●, ○) monitored during the remediation process for 2,4-D (full points) and CLSF (empty points). **Part b.** Moisture map 2,4 D (full points) and CLSF (empty points) of the soil after the remediation test. Upper right position (●, ○), upper left position (■, □), bottom right position (◆, ◇) and bottom left position (▲, Δ) of the soil after the remediation test.

As it can be seen, current density is kept almost constant over the tests in values near to 3.4 mA cm⁻², while the flowrate increased in the same period from almost 1 cm³ h⁻¹ up to values slightly over 4.0 cm³ h⁻¹. In comparing the two tests, great similarity in the evolution of both parameters can be pointed out, which can be considered as an indirect indication of the reproducibility of the tests carried out in this work, despite the large

number of parameters involved. Initially, this reproducibility could be expected because the only change in between the two tests is the herbicide spiked in the soil matrix.

Regarding moisture of the soil, there are no significant differences between both test and final average value is slightly higher than the initial 30% contained in the initial soil matrix. In comparing results obtained applying the REKAB process with those obtained using EKSF (Table 1), no important differences are observed between the two processes, despite the large changes in the values of the flowrates, for which the differences (associated to evaporation) are higher in the case of the REKAB process.

Figure 4 focuses on the concentration of herbicides measured in both electrodes wells during the tests and it also shows the cumulative amount of herbicides removed from them. It is important to state that the electrode polarity reversed daily, so they act both as anode or as cathode depending on the day. The final values of 2,4-D and CLSF collected in the electrode wells are very low and this means that reversion in the polarity is not a very good choice for the efficient EK transport. This observation was also pointed out with the conductivity in the discussion of Figure 1. Anyhow, transport of herbicides to the wells was not the main removal mechanism looked for with the REKAB, but the adsorption of the pollutant in the activated carbon bed placed in the soil column.

Figure 4. Changes in the concentration of herbicide that arrive at the electrodic wells during the remediation test. Part a) time course. Part b) data accumulated. 2,4-D concentration in the anodic chamber (■) and cathodic chamber (●), CLSF concentration in the anodic chamber (□) and cathodic chamber (○).

Changes in the concentration in the electrode wells should reflect on the concentration of both pollutants in soil and they are shown in Figure 5. In comparing the two tests, it is very important to observe that CLSF is removed more efficiently than 2,4-D after the 15-days long treatment, despite the similar concentration collected at the wells. This fact points out a very different behavior of both pesticides from the view point of adsorption onto the carbon bed.

Figure 5. (a) 2,4-D and (b) CLSF concentration map of the soil after the remediation test. Upper right position (●), upper left position (■), bottom right position (◆) and bottom left position (▲) of the soil after the remediation test. (*) initial concentration.

This different adsorption capability of activated carbon towards 2,4-D and CLSF can be easily understood by checking the adsorption isotherms which were calculated for the

range of concentrations of interest by mixing solutions containing 100 mg dm^{-3} of herbicide and different amounts of activated carbon and they are shown in Figure 6. As it is observed, for the concentration range tested, the adsorption capacity of the activated carbon is not saturated, being this capacity of adsorption of CLSF much higher than that of 2,4-D, in agreement with the results obtained in the REKAB process.

Figure 6. Adsorption isotherms of CLSF (◆) and 2,4-D (■) onto the activated carbon used at 25°C

Differences between the behaviors of both pesticides were also observed during the application of the EKSF process and it is very interesting to compare the profiles of pesticides in soil after the application of the two remediation technologies, because it may help to understand the transport mechanism and hence it could be used to optimize the removal in real cases. Thus, Figure 7 compares the average profile of concentration in the

soil after 15 days of treatment in the removal of the two herbicides by REKAB and EKSF. CLSF is not efficiently removed by EKSF and opposite to REKAB, after 15 days of treatment the concentration in soil is much higher than that of 2,4-D. At this point, it is worth to remember that large differences in the case of the EKSF between the 2,4-D and the CLSF were explained in terms of the very different volatility of both herbicides (0.02 mPa vs 3×10^{-6} mPa at 25 °C for 2,4-D and CLSF, respectively). This higher volatility results in higher concentrations of 2,4-D in the vapor phase in equilibrium with the liquid, in comparison with the transfer of CLSF. These large differences explain that transfer of 2,4-D to atmosphere is very important. Thus, evaporation was found to be a key process during EKSF, because of the long duration of the test and the not very efficient EK transport of pollutants. This helps to advice combined EKSF gas stripping processes for real applications. In the case of the REKAB process, profiles of herbicide concentration after the tests are more similar and they indicate a clear better removal of CLSF, which contrasts with the better removal of 2,4-D observed in the case of EKSF technology and can be explained by the more efficient adsorption pointed out by the adsorption isotherms.

Figure 7. 2,4-D (■,□) and CLSF (◆,◇) average concentration map of the soil after the remediation tests.. Empty symbols: Reversible Electrokinetic adsorption barrier (REKAB). Full symbols: electrokinetic soil flushing (EKSF).

As a summary, the mechanisms for the removal of pesticides in both technologies are very different. Percentages of herbicides removed by the different mechanisms, as well as herbicide remaining in soil after 15 days of treatment are shown in Figure 8.

Figure 8. Herbicides distribution in the EKSF and REKAB tests after the 15-day long treatment.

Despite being similar herbicides, this figure points out the importance of bench-scale studies in order to understand the performance of electrokinetic soil remediation technologies. Even for two pesticides with a very high water-solubility, the mass balances indicate that removal depends importantly on the adsorption and volatility properties. Obviously, the disposition of activated carbon beds into the soil during the EKSF (in fact, it is the REKAB process) contributes to the removal of herbicide importantly, more in the case of the CLSF because of the promoted equilibrium. It also minimizes the amount of herbicide evaporated and this is important because, for the design of full-scale treatments, results indicate that gas extraction and treatment should not be forgotten. Regarding EK transport processes, reversion in the polarity shows a negative impact in the collection of herbicide into the electrode wells which is in agreement not only because of the changing direction of the flows but also because of the action of the carbon bed.

Conclusions

From this work the following conclusions can be drawn:

- REKAB is an efficient technology for the removal of soluble pesticide from soils and after 15-day long test more than 70% of the pollution can be removed.
- REKAB involves adsorption, electrokinetic transport and evaporation as the main mechanisms that explain the removal of 2,4-D and CLSF.
- Important differences between REKAB and EKSF. Adsorption of pesticide is the primary removal mechanism and it helps to minimize the effect of evaporation
- Removal of pesticide in electrolyte wells is less important in REKAB because of the reversion of the polarity. This reversion has a positive effect on the pH regulation and on the prevention of the washing up of the salts contained in the soil

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