

1 **Reversible electrokinetic adsorption barriers for the removal**
2 **of organochlorine herbicide from spiked soils**

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9
10 **Abstract**

11 This work aims to describe the removal of clopyralid from clay soils using
12 electrokinetically assisted soil flushing (EKSF) coupled with a permeable reactive barrier
13 (PRB), consisting of beds of Granulated Activated Carbon (GAC). To do this, two
14 strategies have been evaluated in a bench-scale electroremediation facility (175 dm³):
15 electrokinetic adsorption barrier (EKAB) and reversible electrokinetic adsorption barrier
16 (REKAB). Results show that during EKAB and REKAB tests, clopyralid is removed
17 from the soil by adsorption in PRB, electrokinetic transport and, very less **decisively**, by
18 evaporation. The application of polarity reversion attains a higher retention of clopyralid
19 in the activated carbon-PRB and a better regulation of pH because of the neutralization
20 of H⁺ and OH⁻ generated in the electrolyte wells. After 30 days of operation, the removal
21 of clopyralid by EKAB is 45% while it reaches 57% in the case of REKAB. Results
22 obtained in this work are compared to those obtained in previous works in which
23 Electrokinetic Soil Flushing technology (EKSF) was evaluated, in order to check the
24 advantages and drawbacks of using the combined EKSF-GAC PRBs technology for the
25 remediation of soils polluted with soluble organics.

27 **Keywords**

28 Electroremediation, soil remediation, clopyralid, granular activated carbon, permeable
29 reactive barrier, reversible electrokinetic adsorption barriers

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32

33 1. Introduction

34

35 In recent years, the increase of the agricultural activity have enlarged the occurrence of
36 pesticides in soils and groundwater. These products are extremely hazardous to human
37 health and, therefore, their diffusion in the environment should be controlled (Gavrilescu,
38 2005; Eason et al., 2013). Therefore, the search of treatments for the efficient degradation
39 of this type of compounds has become a worthy topic of study. One of the most important
40 families of pollutants **gathers** the chlorinated hydrocarbon pesticides. Nowadays,
41 scientific community has focused their interest on it, mainly because they may become
42 an important source for diffuse pollution (Lu and Yuang, 2009; Lei et al., 2018). **Among**
43 **them, clopyralid (3,6-dichloro-2-pyridinecarboxylic acid, C₆H₃Cl₂NO₂) is one of the most**
44 **commonly used pesticides and it is considered as model pollutant (Ozcan et al., 2010). It**
45 **is an organochlorinated compound with a very high solubility in water. Because of this**
46 **high solubility, it can be rapidly transported promoting the problem of diffuse pollution.**
47 Conventional technologies for the treatment of contaminated groundwater, such as the
48 well-known **pump & treat**, have shown important drawbacks due to their high cost, long
49 treatment periods and/or difficulties to reduce the concentration of pollutants **down to**
50 permitted levels (Ribeiro et al., 2005; Pazos et al., 2010; Ribeiro et al., 2011; Yeung and
51 Gu, 2011; Alcantara et al., 2012). **Thus, new *in-situ* technologies such as electrokinetic**
52 **flushing (EKSF) or permeable reactive barriers (PRB) and even the combination of EKSF**
53 **with PRB are being developed (Rodrigo et al., 2014) (Bebelis et al., 2013).** PRB is a type
54 of **semi-passive *in-situ*** treatment that uses a medium that promotes chemical, **or**
55 biochemical reactions or sorption processes to transform or immobilize contaminants
56 (Hayes and Marcus, 1997; Scherer et al., 2000; Palmer, 2001; Choi et al., 2007; Chung
57 and Lee, 2007; Henderson and Demond, 2007; Weng, 2009). Thus, PRB can consist,
58 among others, of biological barriers (Mena et al., 2015; Mena et al., 2016b), ion exchange

59 resins (Garcia et al., 2015), ZVI (Choi et al., 2008; Suzuki et al., 2012) or activated carbon
60 (Saeedi et al., 2009; Yang et al., 2010; Ruiz et al., 2014; Huang et al., 2015) barriers,
61 being this last barrier the most commonly proposed for the removal of organics. On the
62 other hand, EKSF is based on the application of an electric field between the electrodes
63 sited in the soil capable to mobilize the pollutants contained in the soil by electromigration
64 (ionic pollutants), electrophoresis (colloids and micro-drops of emulsified pollutants) or
65 by dragging with the electro-osmotic flux (Alshwabkeh et al., 1999; Virkutyte et al.,
66 2002; Trellu et al., 2016) (Kolosov et al., 2001; Hamdan et al., 2014). In a combined
67 process, this mobilization could be used to transport the pollutants through the PRB and
68 thus it may favor their retention and immobilization.

69 In previous works of our group, the use of electrokinetic adsorption barriers was proposed
70 for the removal of many types of chlorinated hydrocarbons (Ruiz et al., 2014; Vieira dos
71 Santos et al., 2016; Souza et al., 2017; Sun et al., 2017). Ruiz et al., evaluated the
72 combination of EKSF with adsorption barriers for the removal of trichlorophenol from
73 spiked soils, where its high efficiency and easy performance were demonstrated. Vieira
74 dos Santos et al. and Souza et al. demonstrated the application of reversible electrokinetic
75 adsorption barrier (REKAB) technology to soils spiked with low-solubility pollutants
76 (oxyfluorfen and atrazine) and with soluble pollutants (2,4-D and clorsulfuron),
77 respectively. These studies focused on evaluating the interaction between the EK system
78 and the GAC-PRB, attempting to obtain insights into the primary mechanisms involved
79 in each case (which include electrokinetic transport, adsorption and evaporation). Sun et
80 al., evaluated the combination of EKSF with zero valent iron / activated carbon permeable
81 barriers for the remediation of soil polluted with phenantrene and trichlorophenol,
82 concluding that Fe/C-PRB exhibited a good and relatively stable performance by
83 removing approximately 80% of PHE and 90% of TCP from the contaminant flux passing
84 the PRB. This is one of the first works in which a combined Fe/carbon permeable barrier

85 was evaluated. In general, results obtained showed that this combined technology is
86 efficient but it depends on the contact of the pollutant with the adsorption beds. Thus, the
87 periodic reversion in the polarity seems to be a good way to improve the efficiency and
88 to prevent extreme pH and the depletion of ionic species in the soil. It is important to
89 highlight that all these studies were carried out in small lab-scale plants containing less
90 than 5 kg of polluted soil. In this context, scale up of soil remediation processes has been
91 found to be very important in order to understand the fundamentals of the
92 electrochemically assisted technologies and their influence on the performance of the
93 treatment. In previous works (Lopez-Vizcaino et al., 2017a, b), we shed light on how size
94 affects the results of soil remediation. We demonstrated that the removal of herbicides
95 from soil were affected by the size of the plant used and that conclusions from small scale
96 tests should not be extrapolated for full-scale applications. In fact, we confirmed that the
97 controlling mechanisms in the small scale tests were the electrokinetic transport process
98 (electroosmosis or electromigration). However, the relevance of these processes in the
99 prototype scale test was very low and, conversely, volatilization of organics was very
100 important. For this reason, to obtain relevant data about the performance of GAC PRBs
101 it is, at least, necessary to carry out the evaluation of the remediation process in a bench
102 scale plant (>150 kg of soil). This assessment will help to reach conclusions that can be
103 later used in full scale applications.

104 With this background, in this work it is studied the removal of clopyralid (polar pollutant
105 with low vapour pressure) from spiked soil (30 mg kg⁻¹) by EKAB (Electrokinetic
106 Adsorption Barriers) and REKAB (Reversible Electrokinetic Adsorption Barriers)
107 technologies. In order to shed light on how size affects to GAC PRBs, bench-scale plants
108 (175 dm³) were operated under a constant electric field (1.0 V cm⁻¹) over 30 days. On
109 contrary of that observed in lab scale plants, in bench and prototype scales the preparation
110 of the soil is critical in order to reproduce the geomechanical characteristics of the soil

111 (the closest as possible to a real matrix). In fact, in this scale it can be stated that each
112 mockup is unique and the replication of each test in equal conditions is not realistic.
113 However, to solve this inopportuneness, a reference test consisting of monitoring the
114 pollutant dispersion in a soil not undergoing any type of treatment is also carried out.
115 Moreover, results obtained are compared to those obtained during the EKSF of other polar
116 (2,4-D) and non-polar (oxyfluorfen) compounds previously studied and that show higher
117 vapour pressure (between 0.020-0.030 mPa at 25°C). This can help to clarify the
118 contribution of the different mechanisms to remediation process.

119

120 2. Materials and Methods

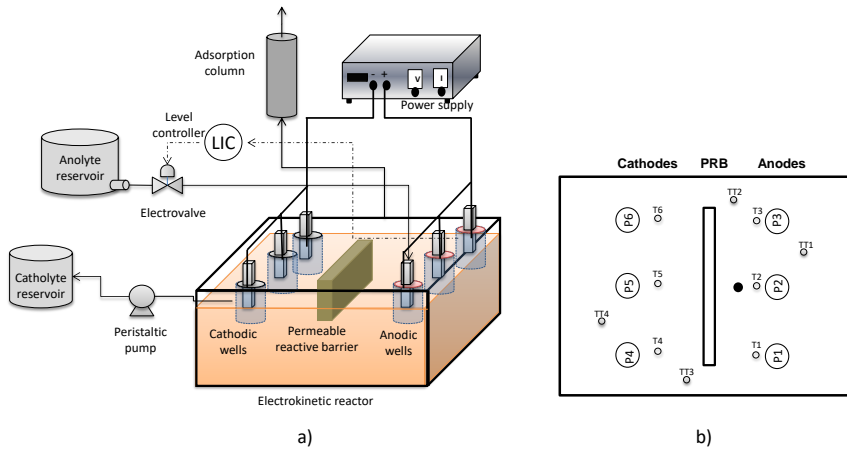
121 **2.1. Preparation of the soil.** The natural soil (from Toledo, Spain) used in this
122 work was characterized elsewhere (Lopez-Vizcaino et al., 2014a). It presents low
123 hydraulic conductivity and nil organic and microbiologic content. According to the its
124 particle size distribution (4.9% clay, 68.2% silt and 26.9% sand) and the texture
125 classification of the United States Department of Agriculture (USDA), it can be
126 categorized as a silty loam. As describe elsewhere, (Risco et al., 2016b; Risco et al.,
127 2016c; Risco et al., 2016d; Risco et al., 2016e; Risco et al., 2016g; Risco et al., 2016h),
128 the soil preparation process consists of: 1) installation of layers for mechanical and drain
129 support; 2) moistening the soil to 11% (natural water content); 3) compacting layers of
130 the soil (to attain 1.4 g cm^{-3} of natural soil density); 4) excavating the soil for positioning
131 activated carbon barrier, 5) drilling the electrolyte wells and the instrumentation of the
132 plant.

133

134 **2.2. Experimental setup.** The electrokinetic experiments were conducted in
135 an electrokinetic remediation plant consisting of an electrokinetic reactor, a power source
136 and tanks of electrolyte. The reactor was a methacrylate prism with a soil capacity of

137 $175 \times 10^3 \text{ cm}^3$ (LWH: $70 \times 50 \times 50 \text{ cm}^3$). The electrodes used as both the anodes and the
 138 cathodes were $1 \times 1 \times 10 \text{ cm}^3$ graphite rods, positioned in semipermeable electrolyte wells,
 139 with an electrode configuration of rows facing the electrolyte wells, as described
 140 elsewhere (Risco et al., 2016b; Risco et al., 2016c; Risco et al., 2016d; Risco et al., 2016e;
 141 Risco et al., 2016g; Risco et al., 2016h). The activated carbon barrier ($2 \times 38 \times 11 \text{ cm}$) was
 142 positioned between electrode rows. It consists of a mixture of 120 g of activated carbon
 143 and 450 mg of soil. The reactor has a cap to force the passage of air through an adsorption
 144 column of activated carbon, placed in order to retain the herbicide that can be volatilized
 145 during the treatment. Figure 1 shows a diagram of the electrokinetic remediation plant
 146 and of the instrumentation of the plant with the notation that will be used in the discussion
 147 of results.

148



149

150 **Figure 1.** a) Diagram of the electrokinetic remediation plant; b) configuration of the
 151 instrumentation. PRB: permeable reactive barrier; PP: pollution point; TT:
 152 thermocouple no. i; T_i: tensiometer no. i; P_i: well no. i. ● Spill point.

153

154 **Experimental procedure.** Following the instrumentation of the plant, the experimental
155 procedure began with the pollution of the soil (simulating accidental spill). To do this, the
156 accidental leak of 6.0 dm^{-3} of an aqueous solution of clopyralid (500 mg dm^{-3}) was
157 simulated between anodic wells and PRB and to a certain depth (10 cm from the surface).
158 Then, the electrolyte wells were filled with water selected as flushing fluid (pH 7.64 and
159 0.391 mS cm^{-1} of electric conductivity). The level control system of the electrolyte wells
160 was connected to the feed tank to adjust the volume of added water to the soil. After 48 h
161 of natural dispersion of the pollutant, the operation began and a constant electric field of
162 1.0 V cm^{-1} was applied between the two facing rows of electrodes with a 400 SM-8-AR
163 ELEKTRONIKA DELTA BV power source (Netherlands). In both EKAB and REKAB
164 tests the separation between the centers of the two facing rows of electrodes is 38 cm.
165 Thus, the applied cell voltage was 38 V. In REKAB test, the electrode polarity was
166 changed daily.

167
168 Anolyte sampling was conducted manually, and catholyte sampling was conducted by
169 pumping the water accumulated in the cathodic containers. Gravity fluid was sampled
170 daily (10 cm^3) and drained at the end of the process through an outlet situated at the
171 bottom of the reactor. Electrical current, temperature, pH, soil water content and
172 clopyralid concentration in the electrolyte wells were monitored daily, and at the end of
173 the experiments, an in-depth sectioned analysis of the complete soil section (20 soil
174 samples subdivided in three portions) and activated carbon barrier were performed.

175
176 **2.3. Analyses.** The clopyralid (analytical grade, Sigma-Aldrich, USA)
177 concentration was determined by High Performance Liquid Chromatography (HPLC)
178 using an Agilent 1100 (Agilent Technologies, Palo Alto, California, EEUU) with a UV
179 detector (220 nm) and a $150 \times 3.0 \text{ mm}$ Phenomenex Gemini $5 \mu \text{ C18 110}^{\text{a}}$ column (USA),

180 with a flow rate of $0.6 \text{ cm}^3 \text{ min}^{-1}$ of 30 % methanol (HPLC grade, VWR International,
181 USA) and 70 % formic acid solution at 1% (reagent grade, Sigma-Aldrich, USA). The
182 detection limit of the analytic technique was estimated at 0.01 ppm. To quantify the
183 amount of clopyralid in the soil and in the activated carbon, an L-S extraction process
184 was performed in Eppendorf tubes (15 cm^3 , VWR International, USA) using water or
185 methanol as a solvent (ratio polluted soil/solvent = 0.4 w/w), respectively. Both phases
186 were vigorously stirred in a vortex mixer (VV3 S040 multi-tube, VWR International,
187 USA), and subsequent phase separation was accelerated using a centrifuge rotor angular
188 (CENCOM II P-elite, J.P. Selecta, Barcelona) for 20 minutes at 4000 rpm. Measurements
189 of pH and electric conductivity were completed using an InoLab pH-meter (WTW,
190 Germany) and a GLP 31 Crison (Crison Instruments, Barcelona) conductivity meter,
191 respectively. The electric current was measured with a KEITHLEY 2000 Digital
192 Multimeter (Keithley Instruments, USA). The temperature measurements were
193 performed with PT-100 thermocouples (Metergroup, USA). The distribution of particle
194 size of the soil was determined using a laser diffraction particle size analyser (model LS
195 13320, Beckman Coulter, USA). The moisture content (%) is calculated from the sample
196 weight before and after oven-drying.

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199 3. Results and Discussion

200

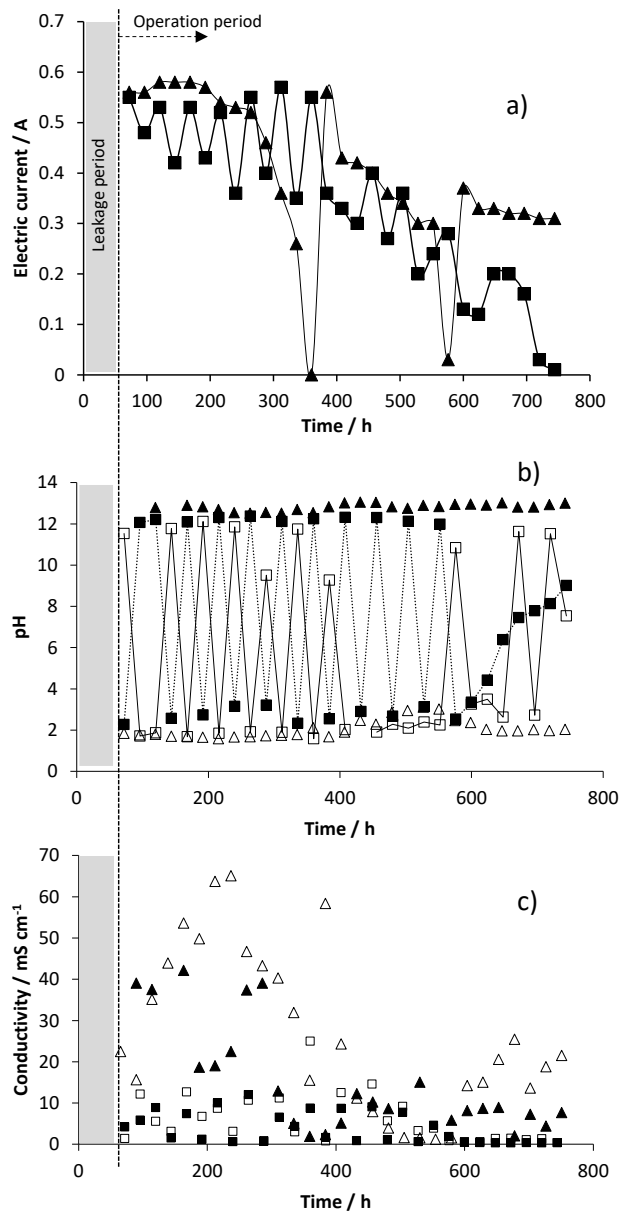
201 The changes observed in the electric current intensity and in the average pH and
202 conductivity of the anodic and cathodic wells during EKAB and REKAB tests are shown
203 in Figure 2. After the simulation of the accidental spill and before starting the remediation,
204 the electrokinetic reactor was not handled to promote the natural dispersion of the
205 pollutant (shaded area marked in the figure). After 48 h, the operation began and a

206 constant electric field of 1.0 V cm^{-1} was applied between the two facing rows of
207 electrodes. In the case of REKAB test, the electrode polarity was daily changed.

208

209 As it can be seen in Figure 2a, once the electric field is applied, the current increases to
210 approximately 0.6 A in both cases. As it is known, current intensity globalizes the
211 transport of charges along the soil sited between electrode rows and informs about the
212 rate of the electrodic and electrokinetic processes that occur in the electroremediation
213 cell. Thus, it mainly depends on both the reactions taking place on the electrode surface
214 (mainly, water oxidation and reduction) and on the ohmic resistance of the soil, which is
215 related to the soil conductivity. One of the parameters that could influence on the
216 conductivity of the soil matrix is soil moisture and, in this case, the location of permeable
217 barriers with different composition and physico-chemical properties. According to the
218 registered data, in spite of the location of the PRB of 2 cm of thickness, the initial intensity
219 registered in both tests is similar to that reported in previous works in which the
220 electrokinetic soil flushing (EKSF) with rows of electrodes was evaluated for the
221 remediation of spiked soils with 2,4-D (Risco et al., 2015; Risco et al., 2016b; Risco et
222 al., 2016f) and/or oxyfluorfen (Risco et al., 2016c; Risco et al., 2016g; Risco et al.,
223 2016h).

224



225

226 Figure 2. Time course of the electric current (a) and of the average pH (b) and

227 conductivity (c) of anodic (empty symbols) and cathodic (full symbols) wells during the

228 REKAB (■, □) and EKAB (▲, Δ) tests.

229

230 During EKAB, electric current remains constant for approximately 300 hours of
231 experimentation, and after that it decreases until stabilizing around 0.3 A. In addition,
232 due to the consumption of graphite rows used as anode there are two moments in which
233 the electric circuit was opened (current intensity goes to 0 A) and new electrodes had to
234 be inserted. This informs about the necessity of the periodical replacement of these
235 electrodes during EKAB process. On contrary, it is not observed during REKAB test
236 although current intensity shows a continuous decrease during the 800 h of operation.
237 This decreased trend is marked by the changes in the resistance in the medium which are
238 related to the changes in the ionic conductivity by the appearance of OH^- and H^+ , and
239 with changes in soil moisture (Lopez-Vizcaino et al., 2011a; Lopez-Vizcaino et al.,
240 2011b; Lopez-Vizcaino et al., 2014b), as it will be detailed below. In addition, the daily
241 fluctuations observed in this test are related with the changes in electrode polarity.

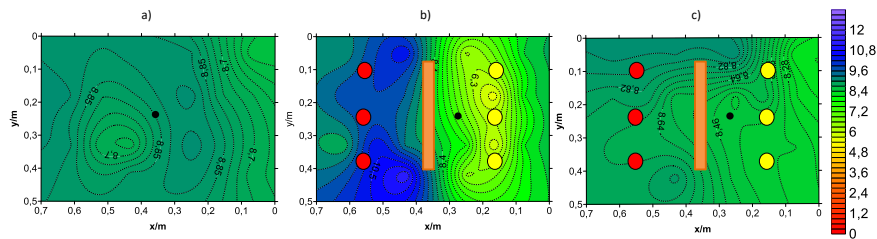
242

243 The average pH-changes in the electrolyte wells are shown in Figure 2b. In the EKAB
244 test, the values are as expected taking into account previous studies of the EKSF
245 technology with facing rows of electrodes (Risco et al., 2016f): a rapid increase until pH
246 13 in the cathodic wells and a rapid decrease until pH 1 in the anodic wells. On contrary,
247 in the REKAB test, the pH of the electrolyte wells fluctuates depending on the polarity
248 of the electrode rows (changed daily). As can be observed, it rapidly changes to acidic or
249 alkaline pHs, but these fluctuations becomes slighter from 400 h of operation in one of
250 the rows of electrolyte wells. This trend was not related to the electrokinetic process but
251 to an punctual operation problem associated with the regulation of the level of liquid in
252 these wells. Anyhow, global results are in agreement with the slight changes monitored
253 in the electrolyte conductivity during REKAB test (Figure 2c). This is related to the partial
254 neutralization of the H^+ and OH^- , alternatively generated in the electrolyte wells, which

255 avoid the **progress** of the acid and basic fronts. On **basis** of this, it is expected that after
256 REKAB process, the pH of the soil was around neutral value and that the changes in the
257 conductivity of the soil **were slighter**.

258

259 To verify the changes shaped in the soil, an in-depth analysis of the complete soil section
260 was performed after 800 h of testing. Figure 3 presents the 2-D maps of pH as measured
261 in the **final** analysis. For comparison purposes, 2-D plot of the final pH of the soil obtained
262 in the control test, in which electrokinetic process was not carried out, is also shown.



263

264 Figure 3. 2-D plots of the final pH of the soil after the reference (a), EKAB (b) and
265 REKAB (c) tests. ● Pollution point, ● Cathodic wells, ● Anodic wells, ■ PRB.

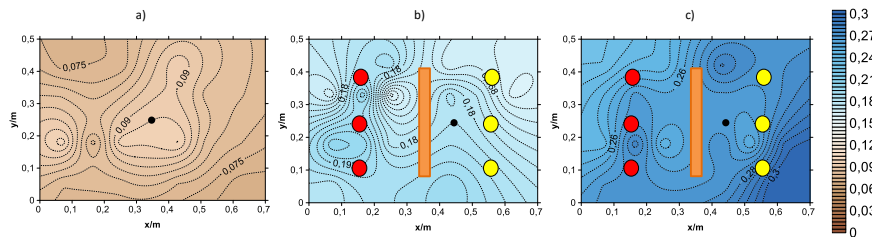
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267 As expected, it should be noted that the pH in both the reference and REKAB tests
268 remains close to neutrality (pH 7-8). On contrary, in the EKAB process the pH in the zone
269 close to cathodic wells trends to be basic (pH over 10); whereas in the anodic zone the
270 pH of the water contained in the soil becomes more acidic (pH around 5), even though
271 the profile observed in this zone is less marked than that obtained in the cathodic zone.
272 These results indicate that alternation in the polarity of the rows of electrodes seems to be
273 a good strategy for controlling the pH of the soil in EKSF processes without the assistance
274 of buffer solutions, as it was previously proposed in previous works carried out for smaller
275 scale plants (Mena Ramirez et al., 2015; Mena et al., 2016a; Mena et al., 2016c).

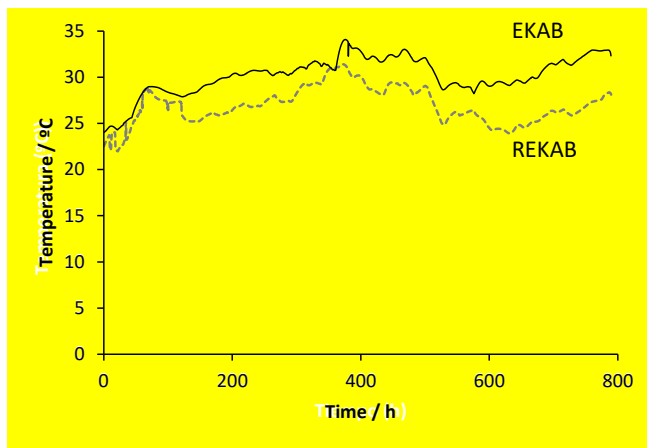
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277 Another very important parameter in EKSF processes is the soil-moisture. As it is known,
278 during EKSF processes, the addition of fluid in anodic wells is required to maintain a
279 constant level in the wells due to the transport of water to cathodic wells by means of
280 electroosmotic flux. Figure 4 shows the 2-D plots of the final moisture of the soil of the
281 three tests. In the reference test, after the simulated accidental spill of clopyralid solution,
282 the soil did not undergo electrokinetic treatment and no water was added during the 800
283 h of control-test. After this time, the water content of the reference test decreased from
284 the initial value of 11% to 9%. Similar results were attained in previous works carried out
285 in the same experimental set up (opened to atmosphere) and under similar operation
286 conditions (initial soil moisture and room temperature) but using different model
287 pollutants (Risco et al., 2016b; Risco et al., 2016c). According to these studies, the loss
288 of water only can be related to side processes such as evaporation or filtration. On the
289 other hand, and as expected, the water content in the soil that underwent EKAB and
290 REKAB increases, due to the continuous addition of water to anodic wells. Results show
291 that this increase is 8 % higher in the REKAB test than in the EKAB (26 % vs. 18 %),
292 indicating that during EK process the accumulation of water in the soil is favored and that
293 the water fluxes are influenced by the use of reverse polarity. In fact, the water demand
294 of the REKAB test to maintain liquid level in anodic wells was 70% higher than that of
295 the EKAB test (71.0 L added during operation of REKAB test vs. 41.4 L added during
296 operation of EKAB test). Likewise, the amount of water extracted from cathodic wells
297 was also around 48% higher in case of using reverse polarity (41.7 L extracted during
298 operation of REKAB test vs. 28.2 extracted during operation of EKAB test). Moreover,
299 the evaporation flux (estimated by mass balance) was also higher in the REKAB test (7.2
300 % vs 1.6 % of EKAB test). This difference in the evaporation flux could be related to the
301 temperature reached in each test. However, at the light of the average temperature
302 registered in each case (Figure 6), this different evaporation flux cannot be explained

303 attending to the average temperature of the soil registered during both processes, as it was
304 only 3 °C higher during the EKAB test (average values of 31 and 28°C in EKAB and
305 REKAB, respectively).



306
307 Figure 4. 2-D plots of the final moisture of the soil after the reference (a), EKAB (b) and
308 REKAB (c) tests. ● Pollution point, ● Cathodic wells, ● Anodic wells, ■ PRB.

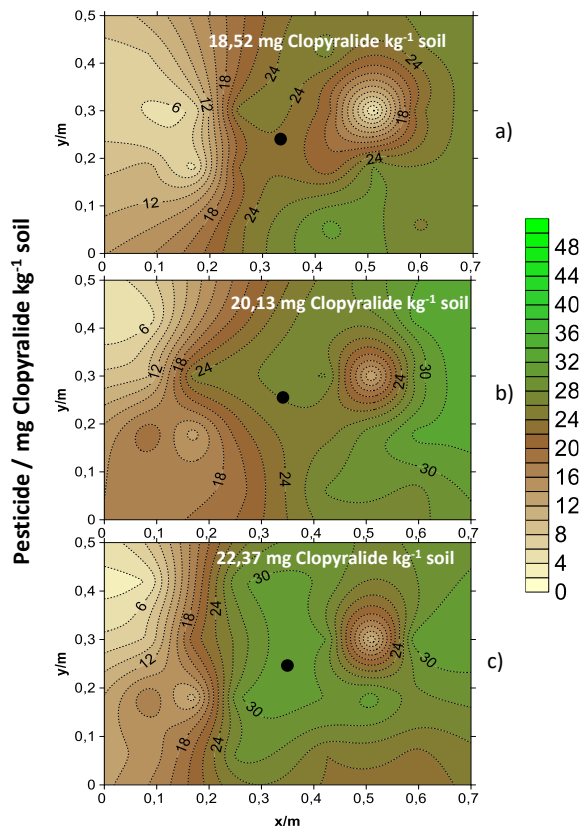


309
310 Figure 5. Time course of the average temperature during the REKAB and EKAB tests.

311
312 The 3-D plot of clopyralid remaining in the soil after the reference tests and the two
313 electrokinetic processes evaluated (EKAB and REKAB) are shown in Figure 6-8. During
314 the reference test, soil does not undergo electrokinetic treatment after the application and
315 dispersion of the simulated accidental spill and, therefore, the losses of clopyralid inform
316 about the contribution of non-electrokinetic transport mechanisms such as volatilization.

317 As it can be observed in Figure 6, after 30 days from the leakage, the distribution of
318 clopyralid in the soil is not homogeneous, on contrary of that obtained in the reference
319 experiments carried out with 2,4-D and oxyfluorfen in previous works (Risco et al.,
320 2016e). In the present work, the accidental spill was not superficial as in the previous
321 studies but it was simulated to a certain depth (10 cm from the surface), in order to
322 minimize the volatilization of herbicide during the leakage (Lopez-Vizcaino et al., 2016).
323 On the other hand, it can be observed that the highest amount of herbicide is accumulated
324 near the point of contamination and the average concentration in the upper, intermediate
325 and lower zone are 18.5, 22.4 and 22.8 mg clopyralid g⁻¹ dry soil, respectively. According
326 to this analysis, of the 3,000 mg introduced during the accidental spillage, 2,904 mg of
327 clopyralid remained in the soil after 30 days, and thus only 3% of the total amount of
328 clopyralid was transferred to the atmosphere or transformed by the action of species
329 contained in the soil. In fact, in literature it is proposed that iron particles naturally
330 contained in soil matrix can promote the dehalogenation of chlorinated pollutants (Bocos
331 et al., 2014). According to chemical characterization of the soil, the natural soil used in
332 this work contains a 3% of FeO₃ (Lopez-Vizcaino et al., 2014a), which can place a
333 relevant role on the dehalogenation of the clopyralid molecule. Unfortunately, apart from
334 clopyralid, no organics were detected in the soil-samples analysed after the tests. This
335 indicates that this side process does not take place or that the concentration of the
336 dehalogenated molecule is under the detection limit of the analytic technique used.
337 Simultaneous, to verify the role of evaporation flux, the transfer rates of clopyralid from
338 the liquid (100 mg of clopyralid dm⁻³) to the gaseous phase were estimated in a close
339 system. Based on the obtained clopyralid flux (0.00012 mg (cm² h)⁻¹), the maximum loss
340 expected for clopyralid in the electrokinetic reactor (assuming 48 x 68 cm² of surface area
341 of the electrokinetic reactor) is 280 mg. This value is slightly higher than that obtained in
342 the reference test (around 100 mg) but it can be considered as a primary estimation of the

343 volatilization rate of clopyralid. Likewise, the capillary barrier located at the top of the
344 soil helps to prevent the transfer to the atmosphere. Comparing this reference experiment
345 with those of 2,4-D and oxyfluorfen (Risco et al., 2016b; Risco et al., 2016c), it can be
346 noted that the loss of clopyralid by volatilization was very low (3 % vs. 49 and 7.5 %
347 observed during the reference tests of soils polluted with 2,4-D and oxyfluorfen). These
348 great differences can be explained attending to significantly lower vapour pressure of
349 clopyralid ($1.36 \cdot 10^{-9}$ mPa at 25°C) in comparison to that of 2,4-D (0.020 mPa at 25°C)
350 and oxyfluorfen (0.026 mPa at 25°C). In addition, it should also be related to the way in
351 which accidental spill was simulated (at 10 cm depth and not directly on the surface as in
352 the previous studies) and to the thicker capillary barrier placed on the top of the soil
353 surface in the test carried out with 2,4-D (1 cm of capillary barrier vs. 3cm used in the
354 other cases).



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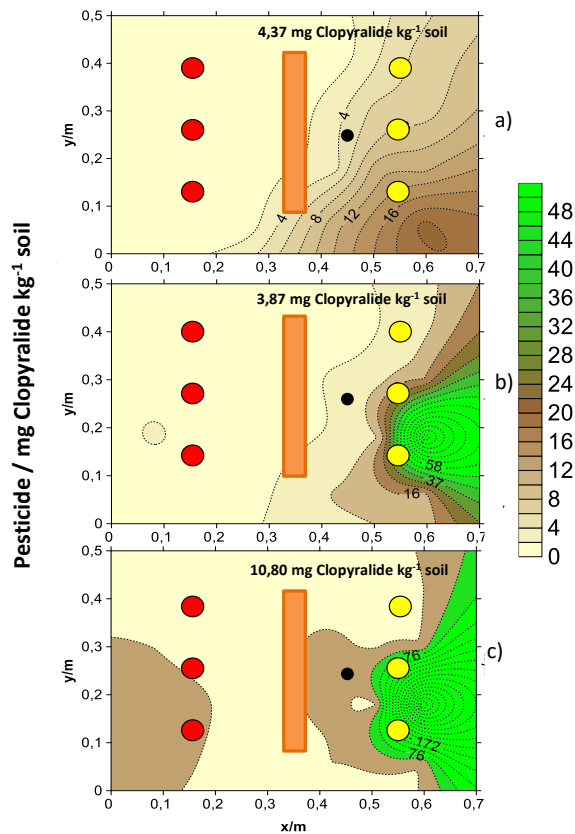
356 Figure 6. 3-D plots of clopyralid concentration (mg kg^{-1} of soil) in the soil after the
 357 reference test. ● Pollution point. a) Upper zone, b) Middle zone, c) Bottom zone.

358

359 Regarding EKAB test (Figure 7), the amount of clopyralid remaining in the soil is
 360 1639.32 mg and differences between the distributions of the herbicide in the three layers
 361 are relevant. In this point, it is important to remark that the greater concentration is
 362 detected in the bottom layer, which can be associated with a higher transport of the
 363 pesticide associated to gravity flux. In fact, the maximum clopyralid concentration
 364 (concentration peaks of 529 mg clopyralid kg^{-1} soil) is obtained near to the anodic well
 365 sited close to extraction valve. This seems to indicate that the mobility of the clopyralid

Comentado [MARR1]: Cuidado, los datos estan con la coma decimal

366 by electro-osmosis is not the primary transport mechanism. In fact, the amount retained
367 in the reactive barrier is 196.28 mg, and only 1.42 mg is mobilized towards the wells. In
368 this case, clopyralid is not detected in cathodic wells. This indicates that clopyralid
369 mobilized by electro-osmosis is retained in the PRB before reaching the cathode wells.
370 On the other hand, it is important to point out that clopyralid is a negatively charged
371 molecule and thus it can be moved towards the positively charged well (anode) by
372 electromigration fluxes. Similar result was obtained in the case of 2,4-D (18.7 % was
373 mobilized to anodic wells) (Risco et al., 2016a), whereas in the case of oxyfluorfen (Risco
374 et al., 2016c), it was mainly dragged by electroosmotic flux (19.2 % in the cathodic wells
375 vs. 0.4 in the anodic wells). In addition, it should be mentioned that a large amount of
376 contaminant is collected by gravity flow 888.1 mg. Then, the amount of clopyralid
377 transferred to air can be estimated by mass balance: 277.88 mg (9.16% of total amount).
378



379

380 Figure 7. 3-D plots of clopyralid concentration (mg kg^{-1} of soil) in the soil after the EKAB
 381 test. ● Pollution point, ● Cathodic wells, ● Anodic wells, ■ PRB. a) Upper zone, b)

382 Middle zone, c) Bottom zone.

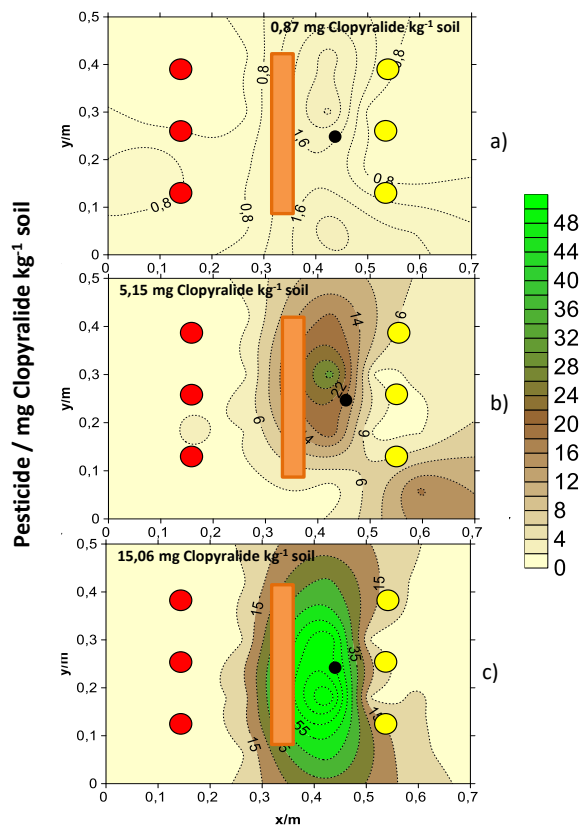
383

384 On the other hand, in Figure 8 it can be observed that after 30 days of treatment in the
 385 REKAB test, 1260.36 mg of clopyralide (12% less than EKAB), while the amount
 386 retained in the reactive barrier was 374.12 mg (10% more than EKAB). Due to the daily
 387 reversal of polarity, electroosmotic and electromigration flux also changed, and the
 388 changes in the direction of both fluxes seem to favor the mobilization of clopyralid
 389 through the reactive barrier and therefore its retention. In fact, on the contrary of that

Comentado [MARR2]: Lo mismo con las comas

390 observed in EKAB test, clopyralid remained in soil after REKAB process is accumulated
 391 in the bottom layer and around the PRB. The amount of clopyralide that is extracted with
 392 the gravity flow is 766 mg, while the amount transferred to the air (estimated by mass
 393 balance) is 598.18 mg.

394



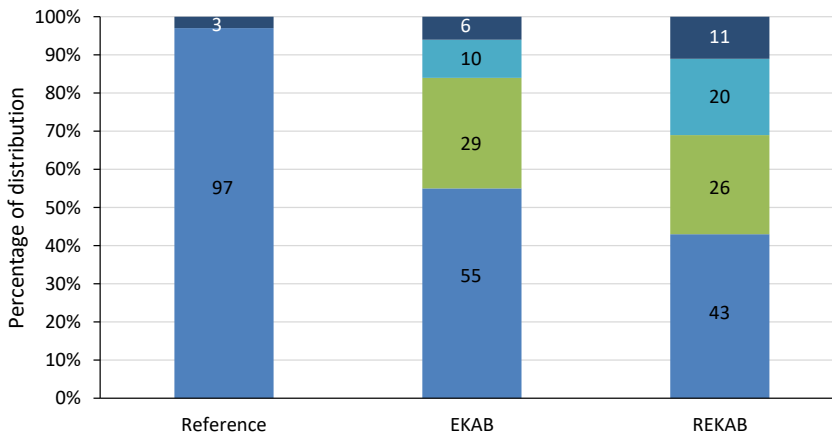
395

396 **Figure 8.** 3-D plots of clopyralid concentration (mg kg^{-1} of soil) in the soil after the
 397 REKAB test. ● Pollution point, ● Cathodic wells, ● Anodic wells, ■ PRB. a) Upper
 398 zone, b) Middle zone, c) Bottom zone.

399

400 For comparison purposes, Figure 9 summarizes the final distribution of clopyralid in the
401 three test carried out. As can be observed, after 30 days of treatment the amount of
402 clopyralid extracted from the soil (estimated as sum of amount retained in PRB and
403 amount extracted with flushing fluids) is 46 and 39 % of the initial amount in the case of
404 REKAB and EKAB processes, respectively. Moreover, the total removal of clopyralid by
405 EKAB is 45% while it reaches 57% in the case of REKAB. These percentages are close
406 to that attained in the EKSF of 2,4-D polluted soil (76.2 %) although in that case around
407 23% of the 2,4-D was transferred to the atmosphere. Moreover, it is important to remark
408 that the use of reverse polarity seems to be a good strategy to favour the retention of
409 organics in activated carbon-PRB. On base of these results, REKAB process appears as
410 a good alternative for the remediation of soil polluted with soluble pesticides (such as
411 clopyralid, used as model compound in this study). Moreover, the daily polarity reversion
412 allows not only to attain an improved efficiency but also to control pH (avoiding acidic
413 and basic fronts).

414



415

416 Figure 9. Final distribution of clopyralid after 30 days of treatment. ■ Remained in soil,
417 ■ extracted with flushing fluid, ■ adsorbed in PRB, ■ Volatilized.

418

419

420 **Conclusions**

421

422 From this work, the following conclusions can be drawn:

- 423 – EKAB and REKAB involves not only adsorption but also electrokinetic transport
424 and evaporation as the main mechanisms that explain the removal of pollutants.
- 425 – Adsorption of clopyralid is a very important removal mechanism in both EKAB
426 and REKAB and polarity reversion attains an improved efficiency of this process
- 427 – Important differences between REKAB and EKAB. Better control of pH
428 (avoiding acidic and basic fronts) and higher water content of soil when using
429 REKAB.
- 430 – After one month of operation, the removal of clopyralid by EKAB is 45% while
431 it reaches 57% in the case of REKAB.

432

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434

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438

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