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

R. López-Vizcaíno[1], C. Risco[2], J. Isidro[2], S. Rodrigo[2], C. Saez[1], P. Cañizares[1], V. Navarro[3], M.A. Rodrigo[1,*]

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

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

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

Abstract

This work describes the application electrokinetic fence technology to a soil polluted with herbicides in a large prototype containing 32 m^3 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

25 different distribution of species and even to a very different evolution of the resulting

26 current intensity. 2-D maps of the main species at different relevant moments of the test

27 are discussed and important information is drawn from them. Ions depletion from soil

28 appears as a very important problem which should be prevented if the effect of natural

29 bioremediation and/or phytoremediation on the removal or organics aims to be accounted.

30

31 **Keywords**

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

33 **Highlights**

34 -   In EK soil remediation technology, size of the experimental setup matters

35 -   Same processes occurring, different observations made because of the dimensions

36 -   Increase in the intensity over the experiment due to the conductivity and pH

37 -   Depletion of ions from soil and concentration in the nearness of electrode wells

38 -   Rapid dynamic response: almost no relevant changes after a 15-day treatment

39

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

89   processes), which also coexists with other chemical processes (such as ion exchange

90   reactions such as precipitations, etc.) and physical processes (hydraulic fluxes,

91   evaporation, etc.). The prevalence of any of these mechanisms over the others can lead to

92   a very different performance of the technology (Alshawabkeh et al., 1999; Yuan et al.,

93   2006; Karagunduz et al., 2007; Yuan et al., 2007; Buchireddy et al., 2009; Li et al., 2016)

94   and it is worth to evaluate how the size of the experimental setup influences on these

95   mechanisms if results carried out at small scale aims to be extrapolated for full-scale

96   applications.

97   This work reports important information about the scale-up of electrokinetic fence

98   (EKF) technology for the remediation of soil polluted with herbicides, by comparing

99   results obtained in a prototype of 32 m^3 with those obtained in a mockup of 175 L. These

100   lower-scale results were obtained in different works previously published in the literature

101   (Risco et al., 2015, 2016e), within a wider-scope research program in which different

102   electrodes placement were compared for the efficient removal of pesticides from soil

103   (Risco et al., 2016a, 2016b, 2016c, 2016d). At this point, a preliminary work about scale-

104   up informs about the many inputs that should be accounted for proper scale-up study

105   (López-Vizcaíno et al., 2016). Within this general scope, Part I is focused on the

106   description of the processes that affect to inorganic species contained or produced in soil

107   during the application of the remediation technology.

108   **2. Materials and Methods**

109   **2.1. Materials**

110   The soil used in this work is provided from a region of Castilla la Mancha (Spain),

111   with important agrarian activities. This soil has been used in others works carried out to

112   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 m^3, 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 m^2 (4 m $\times$ 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

137   167.8 cm (Fig. SM-2). The electrodes used were cylinders of graphite (15 cm in diameter

138   and 100 cm in length). The wells used were PVC cylinders with lateral perforations (31.5

139   cm in diameter and 140 cm in depth) to facilitate the flow and transport of electrolytes.

140   To monitor the different parameters during the test, thermocouples, tensiometers

141   water and pressure sensors (or "divers") were located at different positions into the soil.

142   Moreover, a complete distribution of twenty micro-boreholes were disposed into the soil

143   for sampling and to monitor the pH, electrical conductivity, pressure and temperature of

144   the pore (Fig. SM-2).

145   Additionally, a system designed to extract the volatilized pesticide composed of

146   extractor hoods and a blower was connected to the prototype. This setup drives the gases

147   produced in the electrolyte wells to an absorber tank, which contains with 10 g L^{-1} of SDS

148   (Fig. SM-3) to retain the pesticides volatilized.

149   To obtain a soil with hydro-mechanical properties similar to those of a real soil in

150   the environment, the following procedure was applied:

151   -   Installation of a first layer of gravel (height 0.2 m) and a second layer of river sand

152   (height 0.1 m) separated with a geotextile to avoid mix of the particles with

153   different size. These layers act as a drain support.

154   -   Installation the soil into the reactor by compaction of six layers of controlled

155   height (layers 1 to 4, 0.2 m; layer 5, 0.15 m and layer 6, 0.11 m). The compaction

156   were carried out with an INCOINSA 21215 vibrating plate with a compaction

157   surface of 0.2 m^2. To check the compaction process, after of dispose each layer,

158   several samples of soil were extracted to analysis its water content and dry density

159   -   Installation a surficial layer of sand that acts as a capillary barrier to minimize

160   evaporation losses.

161   -   Construction of the electrolyte wells and instrumentation of the plant.

162   These steps were extensively explained in a previous work focused on scale-up of

163   electrokinetic remediation processes (López-Vizcaíno et al., 2016). After these stages, an

164   accidental pesticide spill was simulated by the discharge of 10 L of two aqueous

165   emulsions containing 50.8 g L^{-1} of 2,4D and 50.8 g L^{-1} Oxyfluorfen, respectively, for one

166   day. This concentration corresponds to an initial target concentration of 20 mg kg^{-1}_{soil} if

167   the pesticides were homogeneously distributed throughout the soil . The test starts when

168   the power supply (MAGNA POWER ELECTRONICS (7.5 Kw: 0-1000 V and 0-25 A))

169   was turned on with a constant voltage of 168 V (1.0 V cm^{-1}).

170   **2.3. Lab-scale soil remediation column**

171   For comparison purposes, a small lab-scale column was used (in addition to a

172   pilot-scale mockup whose results were described in the literature and that it is not going

173   to be described in this section). The lab-scale cell was made of transparent methacrylate

174   and divided into five compartments. A scheme is shown in Fig. SM-4.

175   The width of the plant was 3 cm. The central compartment, where the soil is

176   located, has a length of 15 cm and it was compacted manually and separated of the

177   electrode compartments by a nylon mesh (0.5 mm). This compaction was carefully done

178   to avoid the formation of heterogeneities zones in the soil, which can result in preferential

179   paths for the fluid transport. Likewise, the compaction procedure was carried out with the

180   target to obtain a similar water content and dry density than in the prototype. One of these

181   compartments served as anode and other as cathode. Graphite bar electrodes (10 cm $\times$ 1

182   cm $\times$ 1 cm) were used as anode and cathode. Each electrode compartment was connected

183   to an additional compartment to collect the liquid overflowing from the wells. The

184   experiments were performed in a potentiostatic mode, setting a voltage at 1.0 V cm^{-1}.

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185   **2.4. Analytical techniques**

186   The water content (w) and dry density (ρ_d) of natural soil were determined based

187   on standards ASTM D2216 (*International*, 2010b) and ASTM D7263 (*International*,

188   2009). Particle size distribution from a size smaller than silt was obtained using a laser

189   diffraction particle size analyzer with an aqueous module. Temperature, suction and

190   phreatic level were monitored with thermocouple PT-100, tensiometers T5X from UMS

191   and divers sensors from Eijkelkamp. pH, conductivity and temperature of the liquid pore

192   were measured with a multiparametric analyzer sensION+ MM150 DL from Hach.

193   **3. Results and discussion**

194   The electrokinetic fence (EKF) prototype evaluated in this study was operated for

195   more than one month keeping an electric field of 1.0 V cm^{-1} between consecutive

196   electrodes. Resulting current intensity informs about the development of electrochemical

197   processes on the surface of the anode and cathode and, in its turn, these electrochemical

198   processes drive the rest of the processes that are occurring into the soil.

199   Fig. 1 shows the changes observed in this parameter over the experimental period

200   studied in this work. As it is observed, current intensity increases from an initial value

201   below 10 to a value over 20 A. This value is reached for the first time in less than 2 d,

202   and from that moment on is approximately maintained during the whole experimental

203   period (average final value 20.43 A)
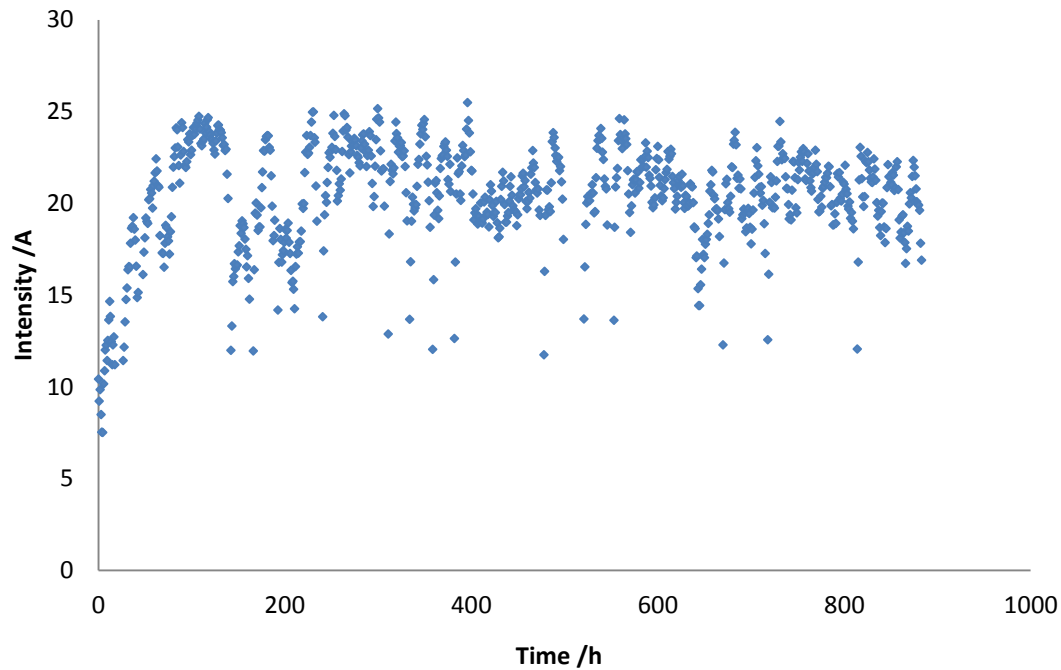
Figure 1. Time-course of the changes of the intensity during the EKF tests carried out in the prototype.

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

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219   which it is then maintained until the end of the test, while the observation in the lower

220   scale facilities indicates just the opposite trend: ohmic resistance increases during the test

221   up to a constant value.

222   According to the values obtained, obviously, the intensity is not directly related to

223   the amount of soil contained in the setup (or size), because the ratio between mass of soil

224   in both setups is near to 182, while the increase in the resulting intensity from the mockups

225   to the prototype is only 81 times. Likewise, there is not a direct relationship to the ratio

226   between total electric fields applied, which is below 13 (which also match with the ratio

227   between the distances of electrodes, because the same electric field was applied in the

228   two studies). This means that simple extrapolation of this parameter for the pre-design of

229   the scale up is not an easy task in this type of soil remediation technologies. Opposite, a

230   much more complex study has to be carried out. Initially, two inputs should be considered

231   to determine this value: the water content of the soil and the ionic conductivity.

232   In the case of the mockup, the current intensity evolution could not be explained

233   in terms of the changes in the water content of the soil. This content increases from an

234   initial value of 16 % up to a final value around 19%, and, hence, this parameter does not

235   allow to explain an increase in the resistance by the increase in the volume of partially

236   saturated zones. At this point, it is worth to take in mind that the increase in the water

237   content obtained in the EKF mockups was explained in terms of the electroosmotic fluxes

238   generated in the soil, because the water content decreases in same setup down to the

239   nearness of 11% when no electric field was applied (due to evaporation).

240   For this reason, the decrease in the conductivity has to be explained in terms of

241   the dragging of the ions contained in the groundwater from the soil to the electrodes wells

242   by electromigration, which resulted in a depletion of ions in the soil. The concentration

243   of these ions increased significantly in the wells and helped to compensate the productions

244   of hydroxyl ions in the cathode and protons in the anode. With respect to a reference

245   experiment in which no electric field was applied, the removal of conductivity from water

246   contained in soil was found to be of 23.4%, value that can explain the changes in the

247   resulting current intensity observed in the mock-ups. It is worth to say that the same soil

248   was used in both setups and that the same procedures were applied to prepare it (obviously

249   adapted to the final size).

250   In the case of the 32 m^3 - prototype, water content behaves in a different fashion

251   that in the mock-up, although always in values that correspond to partially saturated soil.

252   Water content of the soil was risen from 6.4% to saturation in 24.6% before the

253   remediation test, which was the target value to start the experiment. During the

254   electrochemical test, it decreases from this initial value of 24.6% down to 23.14%. This

255   final value is over the 19% water content obtained in the mockups (overcomes it by 20%)

256   and, obviously, this is positive to explain the lower resistance of the soil. Fig. SM-5 shows

257   the maps corresponding to the average water content and to the distribution in the soil by

258   height, dividing the soil into three horizontal layers in the plane xy.

259   It should be taken into account that the range of colors used in Fig. SM-5 goes

260   only from 20 to 25%. Taking into account this narrow zone, it is easy to observe that there

261   is not a large change of water content in soil but simply a zone near to one of the cathodes

262   in which water content is a little bit lower than in the rest, in particular in the bottom layer

263   of the soil in this zone. Small non-homogenies in the soil can help to explain these

264   differences, because, according to the symmetry of the system, they were not expected

265   and, hence, they do not have a clear explanation.

266   At this point, it is worth to describe that this type of prototype underwent previous

267   tests to characterize evaporation and sealing. Both tests were described in a previous

268   manuscript (Lopez-Vizcaino et al., 2016) and clearly indicated that the system had no

269   leaking and water contained in the soil can be easily evaporated. Anyhow, although

270   evaporation is also expected to occur during the remediation process carried out in the

271   prototype scale, the water content of soil is much higher than in the mock-ups.

272   In order to explain the differences, one very important observation to explain

273   moisture is related to the electroosmotic flowrates, as it was pointed out before. While in

274   the two mockup systems it was obtained net electroosmotic fluxes of 1.8 and 0.8 cm d^{-1},

275   they were negligible in the prototype system because no extra water was collected in the

276   cathodes and /or needed to be added in the anodes during the complete one-month long

277   test. The only way to explain these results is by assuming a compensation between the

278   electroosmotic and the hydraulic fluxes in the prototype. At this point, it was considered

279   interesting to perform one test in a very small lab-scale plant in which the same soil was

280   placed. Results obtained are shown in Fig. SM-6 and they demonstrate the importance

281   of the driving force in these systems (pressure for hydraulic and electric field for

282   electroosmotic flowrates) and they also clearly indicate that electroosmotic fluxes

283   increases in small devices for the same electric field applied. Thus, in the smallest scale

284   plant, for 1.0 V cm^{-1}, electroosmotic flux corresponds to 183.27 cm d^{-1} value that it is two

285   log-units above the one obtained in the mockups. From the comparison of the plots shown

286   in Fig. SM-6, it can be drawn that this electroosmotic flux can be compensated by the

287   hydraulic flux, with simply a water column difference as low as 3 cm. This difference is

288   a relevant value for the lab-column, but it is completely negligible in the case of the

289   prototype and, of course, non-detectable under the operations conditions used. In the case

290   of the pilot mockup, differences of this magnitude are also difficult to be monitored and,

291   although in a lower extension, this balance of the two type of fluxes can stand for the

292   lower value observed of the net electroosmotic flux as compared to the obtained in the

293   lab-scale column.

294   Regarding conductivity of the groundwater, the other parameter that affects the

295   ohmic resistance of the system, Fig. 2 shows the changes observed in the conductivity of

296   the anode and cathode wells, as well as the 2-D map of the conductivity changes in soil

297   during four representative moments of the test.
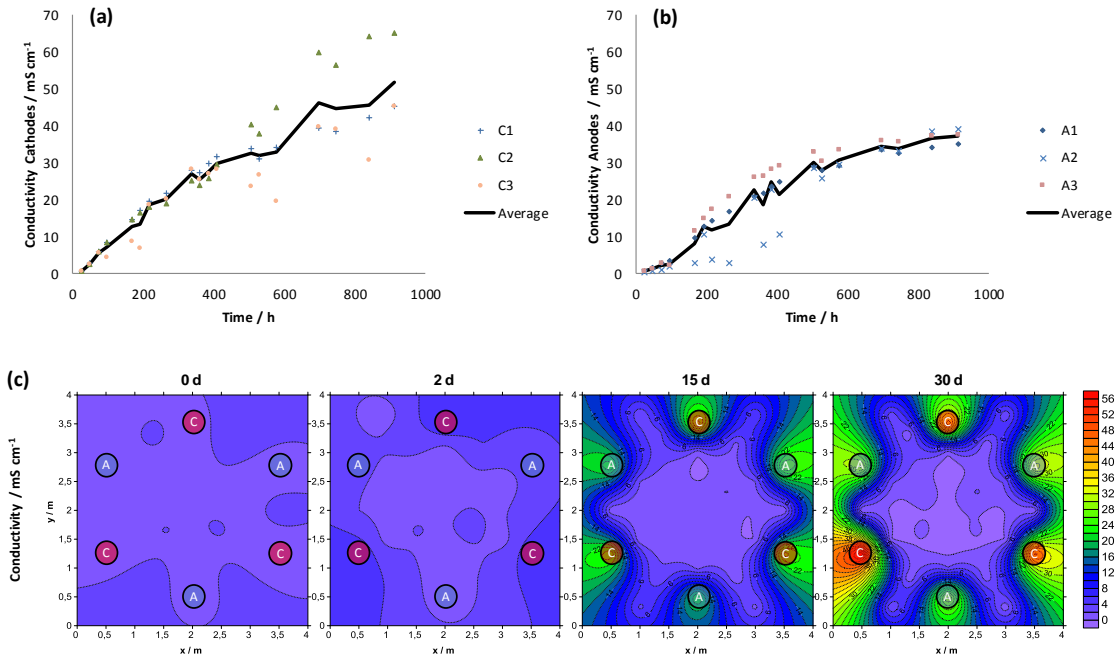
299   Figure 2. Changes in the conductivity of the (a) cathodic and (b) anodic wells. (c) 2-D

300   maps of conductivity distribution in four representative times of the test.

301   As observed, there is a large increase in the conductivity of the fluids contained

302   in the three anodic and three cathodic wells up to values around 40 mS cm^{-1}. No great

303   differences are observed between results obtained in each well, as compared to the results

304   obtained in the other two wells with the same polarity of electrode. Meanwhile, the

305   average value of conductivity in the soil changes from 1.79 (day 0) up to 10.73 mS cm^{-1}

306   (day 30) (with values at days 2 and 15 of 2.76 and 7.82, respectively, that indicates a

307   continuous increase over the duration of the test). ~~In comparing these values with the~~

308   ~~values obtained in the mockups, a very different trend is observed, because in that case~~

309   ~~the conductivity of soil decreases during the tests by 23.4%.~~ Obviously, to explain the

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310 increase in conductivity of the soils not only the transport of ions from soil to electrodes

311 of different charge should be considered, but also the variations of pH has to be taken into

312 account. Otherwise, increases in the conductivity in soil and electrode wells are hard to

313 be explained.

314   Regarding the pH, it is worth to remember that it produces one of the most

315 important changes expected. Oxidation and reduction of water (which develops in the

316 anode and cathode of the prototype, respectively), producing oxygen, hydrogen, protons

317 and hydroxyl ions according to Eq (1) and (2).

318    $$H_2O - 2e^- \longrightarrow 1/2\ O_2 + 2\ H^+ \qquad (1)$$

319    $$H_2O + e^- \longrightarrow 1/2\ H_2 + OH^- \qquad (2)$$
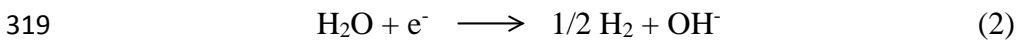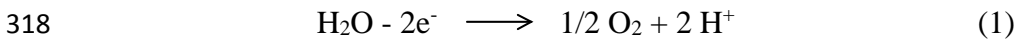
320   Amount of gases produced is negligible as compared to the magnitude of the

321 prototype and both hydrogen and oxygen are dissipated in the atmosphere without being

322 necessary any further safety evaluation because of the small quantity produced and the

323 gas extraction system connected to each one of the electrolyte well. However, protons

324 and hydroxyl ions remains for a longer time in the place where they are produced, because

325 they are more slowly transported, having a great importance in many other processes

326 occurring in the soil.

327   As it can be seen in Fig. 3a and 3b, pH in the three anode wells decreases down to

328 extreme values (lower than 1) while pH in the three cathodes increases up to values

329 around 12, not finding further differences between any of the anolyte or catholyte wells

330 respect to the others of the same polarity. Transport of protons from the anode to the

331 cathode (acidic front) and from the cathode to the anode (basic front) is then established

332 and, in less than two days of operation, clear profiles of pH are formed around the

333 electrodes wells as the 2-D maps shows (obtained at four representative times of the test).

334 Obviously, the acidic and basic fronts neutralize to each other at a given distance of the

335 electrodes and as it can be observed in Fig. 3c (green color), the amount of soil with a

336 non-extreme pH is almost maintained from the second day of the EKF test. Hence, only

337 two-three days period is enough not only to stability the intensity but also the pH profiles

338 thorough the soil and in the wells.
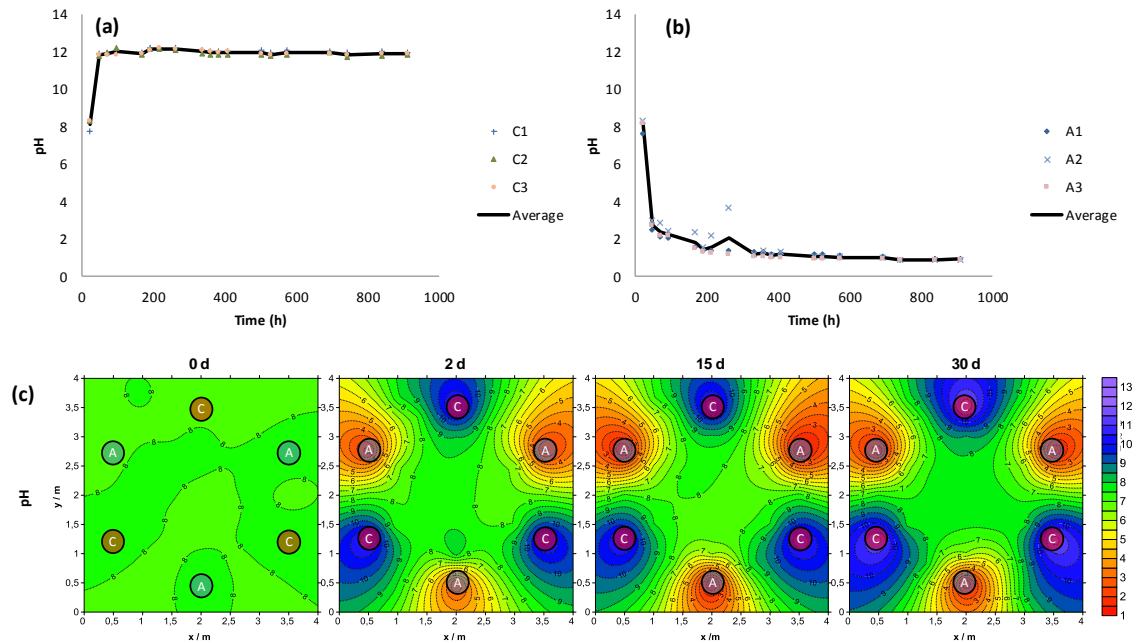
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340 Figure 3. Changes in the pH of the (a) cathodic and (b) anodic wells. (c) 2-D maps of pH

341 distribution in four representative times of the test.

342   Thus, the amount of soil in which pH is kept within the range 6 to 8 is close to

343 70%, value much higher than those obtained with the same technology in the mockup

344 scale, which were 45% (EKF test with oxyfluorfen) and 10% (EKF test with 2,4-D).

345 Differences can be easily explained by the very different distances between electrodes

346 and the different transport rates associated, which obviously should have an influence on

347 the final map. At this point, it has to be taken into account that protons and hydroxyl ions

348 are not only transported by migration but also by many other processes (dragged with

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349 electroosmotic and hydraulic fluxes, diffusion, etc.) and, hence, size of the experimental

350 facility is a factor of the major significance.

351 In order to confirm that the scale of the setup (in which it is carried out the

352 assessment of the EKF) has a definitive influence on results, Fig. 4 shows the results

353 obtained during electrokinetic tests carried out to evaluate the transport of 2,4-D and

354 oxyfluorfen in a typical lab-scale column (the same that was used in the evaluation of the

355 hydraulic and electroosmotic fluxes). More results about these tests will be discussed

356 afterwards because those tests were not carried out for evaluating the pH fronts but with

357 the aim of evaluating the mobility of pesticides in setups of different sizes.
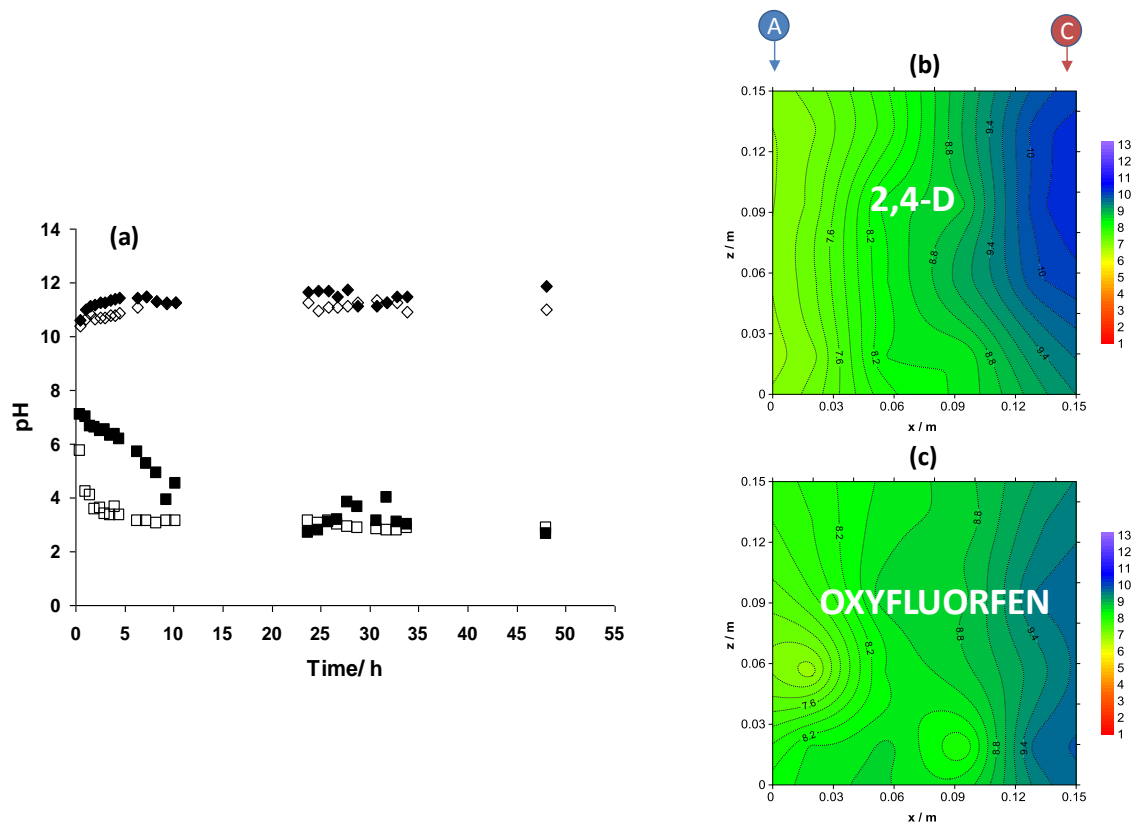
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359 Figure 4. a) Changes in the pH of the electrolyte wells and in the pH distribution during

360 the electrokinetic treatment of pesticides in a lab-scale plant. (Full points: oxyfluorfen;

361 Empty points: 2-4-D). Final pH distribution : b) 2,4-D, c) Oxyfluorfen.

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362   The 2-D map of pH in the soil shows a soil that it is kept within the neutral pH

363   range in more than 80% and in which only the zone closer to the cathode well shows an

364   alkaline pH. It is important to take in mind that in this case not the xy plane but the xz

365   plane is represented, which is more representative for this setup taking into account the

366   geometry of electrodes. Regarding the evolution of the pH in the wells, cathode wells

367   meet almost the same value of that obtained in the prototype (and also in the mockups),

368   while in the anode wells, the pH only decreases down to 2.7. This means that in this short

369   distances, neutralization of the pH fronts is more intense and in fact, the basic front is

370   avoiding any negative effect of the acidic front, helping to attain than a very high ratio of

371   the soil is kept at close neutral pHs (between 6 and 8). Another important observation is

372   that pH in the electrodes wells reach a constant value in less than one day, and hence,

373   stabilization in this parameter is confirmed to be rapidly meet in electrokinetic soil

374   remediation systems.

375   Hence, the increase in the intensity during the EKF test can be explained by the

376   increase in the conductivity, which in turns, it is explained by the very important effect

377   of the pH changes produced on the electrodes.

378   Electromigration is the main process to explain the transport of protons and

379   hydroxyl anions and it is also the key the explain the mobility of ions because

380   electroneutrality should be maintained over time in every point of the soil. Fig. 5 shows

381   how the 2-D map of the changes in the concentration of three different anions during four

382   representative moments of the test. These three anions (chloride, sulfate and nitrate) are

383   typically contained in most soils and they have a great relevance in life associated to soil

384   as they act as nutrients for microorganisms and plants and their exhaustion may have a

385   very negative impact on the soil characteristics. In addition, in the case of nitrate (and

386   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.
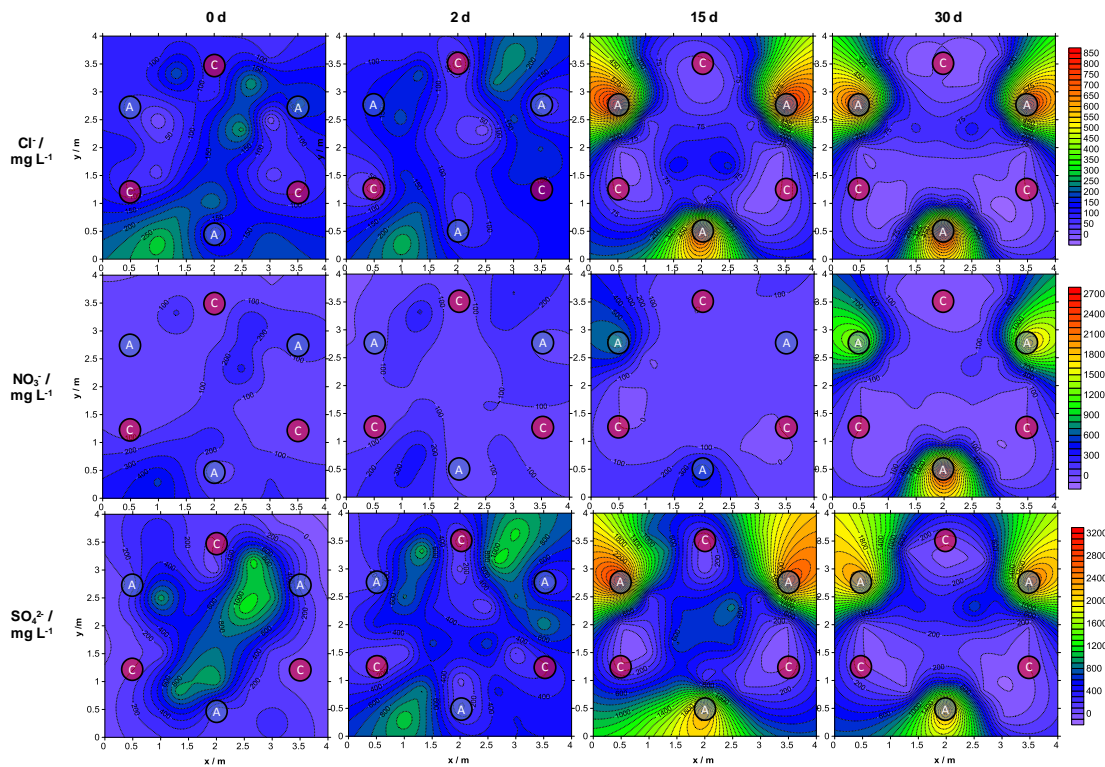
Figure 5. Changes in four representative moments of the 2-D maps of anions monitored

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

19

402 should be considered and tried to be minimized, by using technique such as the periodic

403 polarity reversal. Opposite to changes observed in the pH or in the resulting current

404 intensity, stabilization of the concentrations according to the 2-D maps takes more than

405 two days. For the case of the sulfate and chloride it seems to be reached before the 15th

406 day of operation. The slower response of nitrates may be related to their much more

407 complex chemistry, which involves their very easy cathodic reduction to ammonium and

408 the electrochemical production of nitrogen oxides, as well as their expected significant

409 ion exchange with soil, which is expected to be promoted in the vicinity of electrodes

410 because of great changes in the concentration of proton and hydroxyl ions.

411   The same general conclusions can be drawn from the 2-D maps of the two cations

412 monitored, that are shown in Fig. 6.
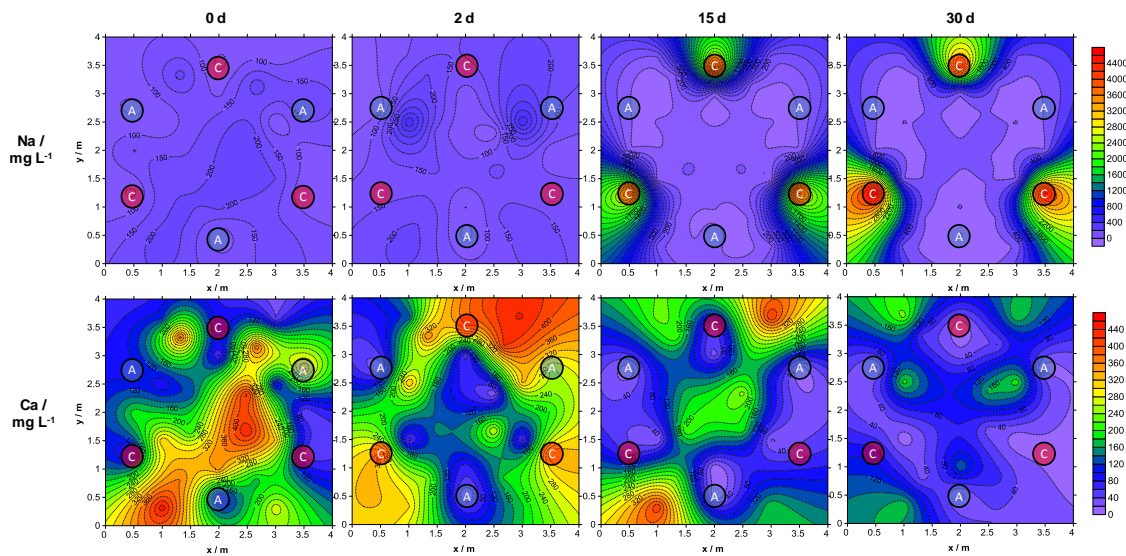
413

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

415 during the EKF tests.

416   In this case, the cations are concentrated in the nearness of the cathodes and as it

417 can be seen in the plots corresponding to sodium, not great differences are obtained

418 between the 15th and the 30th day of operation, indicating that transport of ions in

419   electrokinetic soil remediation processes is very rapid and it does not need longer times

420   to be completed. A very interesting observation is what it seems a "disappearance" of

421   calcium, which it is not real but just the expected result according to the strongly basic

422   pH in the nearness of the cathode: calcium is immobilized in the soil matrix and hence it

423   is not present as a free species in the water taken during the monitoring. Obviously, this

424   fixation of calcium is also negative from the viewpoint of natural biological processes

425   that may occur in soil, and it must have a negative impact on natural bioremediation and

426   phytoremediation of organic pollutants because fixed calcium is not available as nutrient.

427   This negative impact may be easily prevented by adding acids to the catholyte, although

428   this strategy should be very carefully assessed because this addition may produce other

429   negative consequences on soil.

430   A last common observation that it is worth to point out from all 2-D maps shown

431   in this work (pH, conductivity, anions and cations) is the boundary effects produced by

432   the walls of the prototype, which explains the accumulation of conductivity and ions

433   (including protons and hydroxyl ions produced electrodically) just in the rear part of the

434   wells (that part outside the electrokinetic zone). This accumulation is clearly a

435   consequence of the walls, and almost surely the main difference which can be found with

436   respect to a full-scale application. Obviously, it will not be found in a full-scale

437   application, for which the physical constraints produced by the walls do not exits.

438   **4. Conclusions**

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

440   −   Size of the experimental setup used to study soil remediation processes is key

441   to understand their performance. Despite the same processes are occurring at

442   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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563

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

R. López Vizcaíno[1], C. Risco[2], J. Isidro[2], S. Rodrigo[2], C. Saez[1], P. Cañizares[1], V. Navarro[3], M.A. Rodrigo[1,*]

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

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

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

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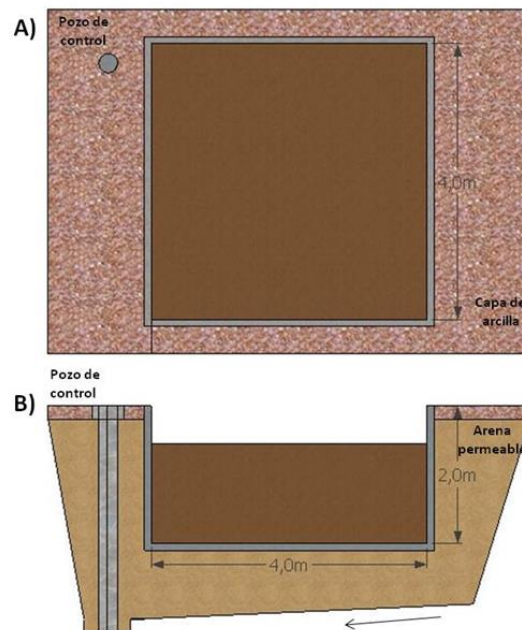
Figure SM-1. Scheme of (A) Plan view and (B) section of EKR reactor.
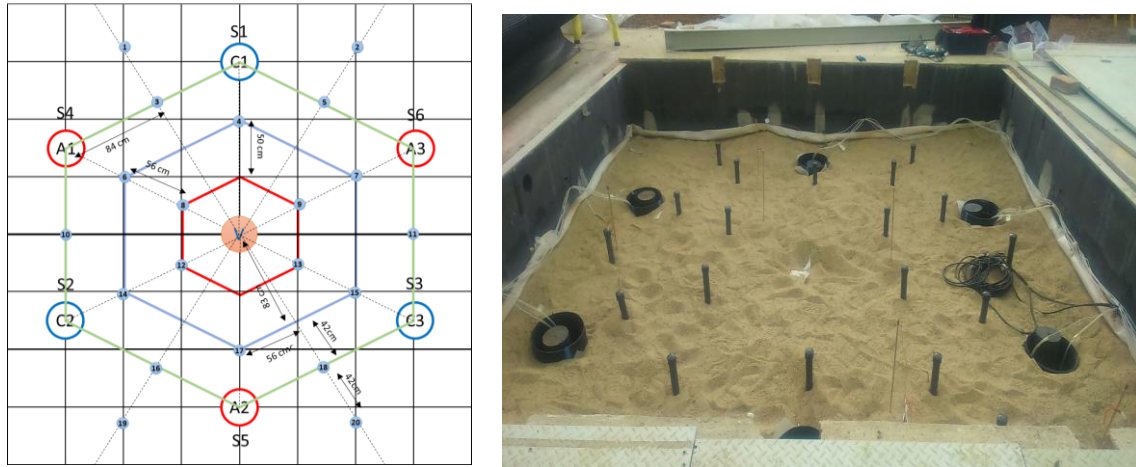
Figure SM-2. Positioning of electrode wells and of the main instrumentation used and picture of the setup
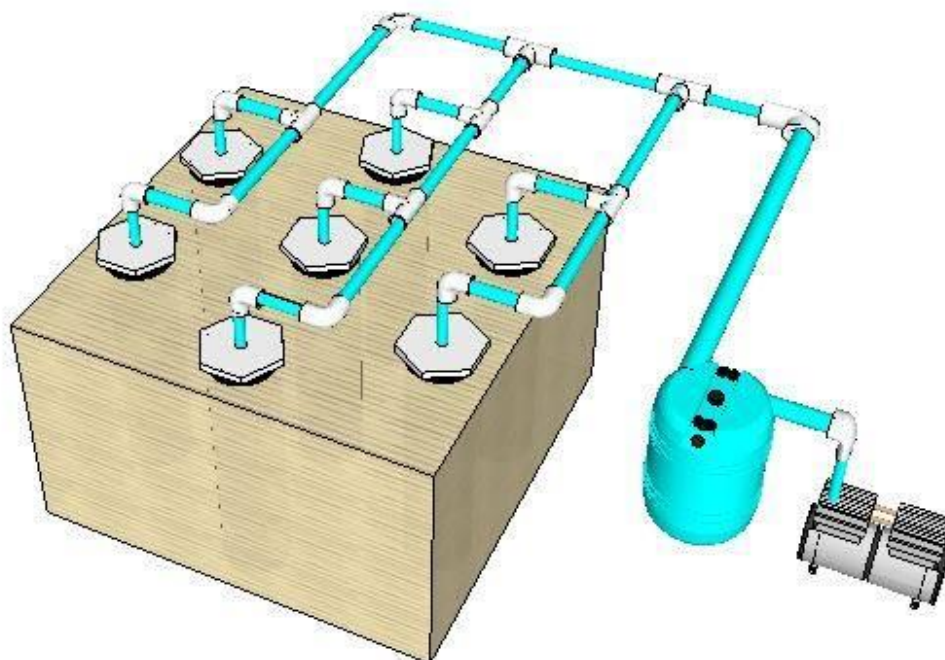

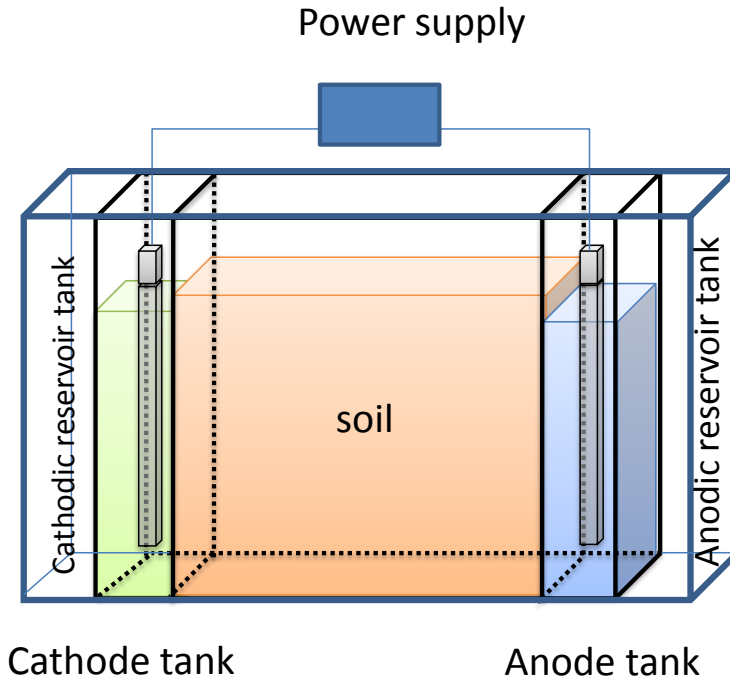**Figure SM-3**. Gas extraction system coupled to the soil remediation prototype

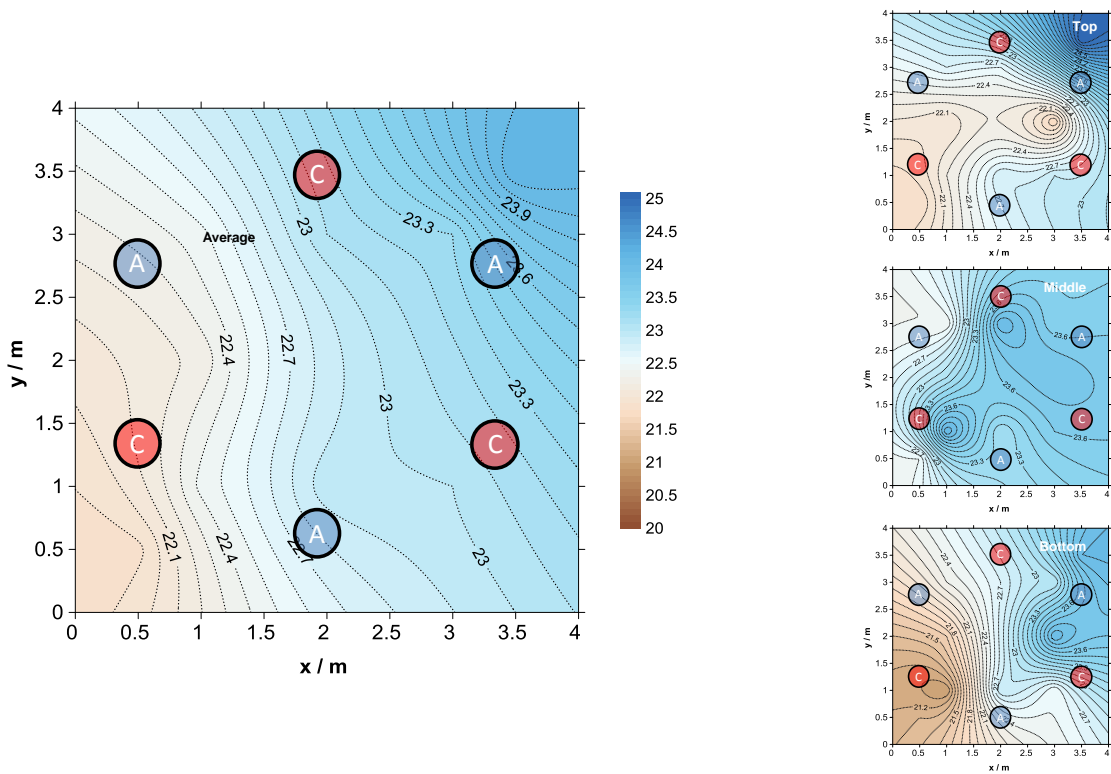**Figure SM-4**. Scheme of the lab-scale soil remediation cell

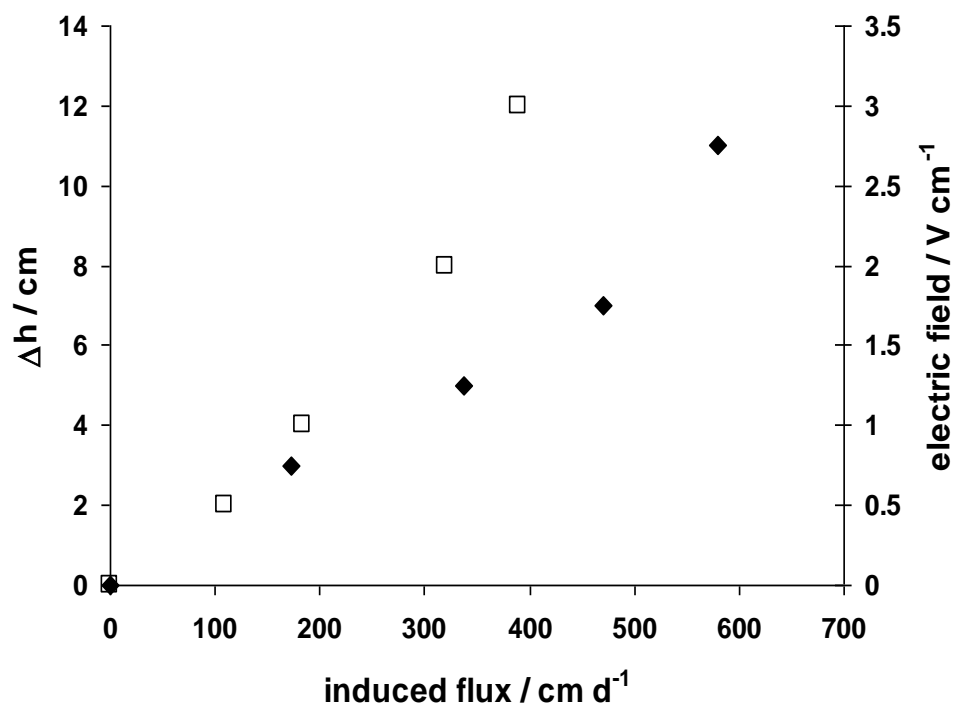**Figure SM-5**. Water content distribution after the EKF test

Figure SM-6. Effect of the height (full points) and electric field (empty points) on the flowrates produced in the lab-column setup