ZVI - Reactive Barriers for the Remediation of Soils Polluted with Clopyralid: Are They Really Worth?

J. Vidal¹, C. Saez², P. Cañizares², V. Navarro³, R. Salazar¹ y M.A. Rodrigo^{2,*}

¹ Departamento de Química de los Materiales. Facultad de Química y Biología. Universidad de Santiago de Chile. Chile

² Departamento de Ingeniería Química. Facultad de Ciencias y Tecnologías Químicas. Universidad de Castilla La Mancha. Campus Universitario s/n. 13071 Ciudad Real. Spain.

³ University of Castilla-La Mancha - Institute of Technology, Campus Universitario s/n, 16071 Cuenca, Spain

Abstract

In this work, the remediation of soil spiked with clopyralid is evaluated using two types of zero valent iron (ZVI) barriers coupled with electrokinetic soil flushing (EKSF). These barriers consist of soil merged with iron particles. In one of the tests conducted, granular milimetric iron was used, whereas in the other, iron was placed in the form of nanoparticles. The performance of this novel technology is compared to that of single EKSF technology. Tests were carried out in bench scale mockups (175 L) and they lasted one month. Over this period, soil underwent the application of an electric field of 1.0 V/cm between a row of three anodes and a row of three cathodes. Results indicate that ZVI barriers seriously affect electrokinetic flushes by preventing the mobility of pollutants to the electrode wells. However, they achieve a larger dehalogenation of clopyralid than single EKSF. There are no significant differences between the results obtained using the two sizes of ZVI and the volatilization of pollutants associated to thermal effects was almost prevented by means of capillary barriers implemented on top of the mockups. After the treatment, most of the

clopyralid not removed is concentrated near the anodes wells and a very important fraction can be easily extracted by excavating a very small percentage of the soil, because the pollutant has been concentrated in very specific points during remediation. Results are significant for the design of full-scale applications for the remediation of soils polluted with soluble chlorinated hydrocarbons.

Keywords

Soil remediation; electrokinetic soil flushing; reactive barriers; iron; clopyralid

Highlights

- ZVI barriers combined with EKSF can be used to treat soil spiked with herbicide clopyralid
- ZVI barriers influence electrokinetic flushes, discouraging the mobility of pollutants
- Placement of ZVI barriers yields a larger dehalogenation than single EKSF
- Volatilization of the pollutants was almost prevented using capillary barriers
- After the treatment, most of the remaining pollutant is concentrated in a narrow zone

*Author to whom all correspondence should be addressed: manuel.rodrido@uclm.es

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46 **Introduction**

47 Soil pollution is becoming a very serious environmental problem [1-4]. As other
48 environmental issues, it may significantly affect human health and biodiversity. Fortunately,
49 society is becoming more aware of the need to prevent and remediate soil pollution, and this
50 is reflected in more strict regulations in developed countries.

51 However, the technical evaluation for soil remediation cannot be compared to that of other
52 environmental problems. The majority of the environmental problems in liquid phase can be
53 assessed successfully at the lab scale, but soil is a heterogeneous media in which the solid,
54 liquid and gas phases have to be considered in order to understand what occurs in the system.
55 Use of small devices to try to draw conclusions about the performance at full scale does not
56 always lead to satisfactory and reliable answers to the existing questions and often, there is a
57 huge difference between results and hypotheses. In spite of that, most of the studies about
58 soil remediation conducted today are carried out at very small lab-scale [5, 6].

59 Electrokinetic remediation of soils is based on the application of an electric field between
60 two or more electrodes immersed in the soil to induce transport phenomena: electromigration,
61 electro-osmosis and electrophoresis, which are responsible of the mobilization of the species
62 (ions, water, charged particles, respectively) contained in contaminated soil. In previous
63 works, our group evaluated the performance of different electrokinetic remediation processes
64 at different scales [7, 8]. The results obtained in these works pointed out that the scale of the
65 plant was very important, since the larger the scale tested, the less important were the
66 electrokinetic processes and, in turn, the more important were the processes caused by the
67 temperature rise associated to electric heating. Pilot plants of more than 100 kg of soil were
68 found to be the minimum size to obtain successful soil remediation conclusions. However,

even in those cases, many cautions have to be taken before extrapolating conclusions to full-scale applications from those results, and thus the use of higher scales was strongly advised when possible.

In addition, previous studies[8, 9] showed that, almost no reactive processes were involved in the remediation treatments, due to the material used for the electrodes (graphite), which promoted their consumption (self-combustion) before any type of reactivity with pollutants contained in soil-flushing fluids could be developed. The only reactive approach has been addressed through the promotion of simultaneous bioremediation with electrochemically assisted processes [10, 11] but, even in those cases, no chemical reactions were promoted.

A reactive barrier (RB) is an in situ remediation method that combines a passive chemical, physical or biological treatment zone with subsurface water flow. The pollutants are either degraded or retained in the barrier material, which may need to be replaced periodically. Reactive barriers can consist of zero –valent iron (ZVI), activated carbon, chelator, sorbents or microorganisms beds [5, 12]. Among them, ZVI-barrier is suggested as a key technology for a rapid partial treatment in which the hazardousness of the halogenated pollution contained in soil is decreased by the transformation of the halogenated pollutants into less-hazardous (but still risky) non-halogenated species [13-16].

Iron is known to be a good reagent for the dehalogenation of chlorinated hydrocarbons. This reaction proceeds according to the process summarized in eq. 1[17, 18].

The reaction has been successfully evaluated for many different chlorinated hydrocarbons including atrazine derivatives, lindane, perchloroethylene and chlorophenols among others [15, 19-26].

In this work, the performance of ZVI RBs coupled with EKSF is going to be evaluated for the treatment of clopyralid, an herbicide that, to the knowledge of authors, has not been treated before with ZVI. The main reactions involved in this target compound can be summarized in eqs 2 and 3, which lead to the formation of 3-chloropicolinic acid, 6-chloropicolinic acid (eq.2) or fully dechlorinated picolinic acid (eq.3)

The size of the iron particles used for the dehalogenation is a topic of utmost interest, because dehalogenation is a heterogeneous process that depends on the iron surface in contact with the chlorinated organic [14, 17, 27]. The smaller the particles used, the larger the surface area in contact with the chlorinated hydrocarbon and hence, the higher efficiency expected in dehalogenation. Therefore, in comparing the effects of the particle size, it is expected a better performance when using the smaller size iron particles.

This work aims to evaluate the significance of this dehalogenation process by implementing it into reactive barriers (RB), included in an electrokinetic soil flushing (EKSF) treatment process in bench-scale plants (175 dm³). The ZVI RB contributes with the dehalogenation of the pollutant and the EKSF treatment process induces the mobilization of ions, water, clopyralid and its intermediates to the anodic and cathodic wells. To this end, the performance of a standard EKSF process will be compared first to a modification of the EKSF in which a nano-ZVI RB is placed next to a row of anode wells, and second to a third

system in which the RB does not contain iron nanoparticles but iron milimetric granules. The same accidental spill will be simulated in three mockups and results will be compared in terms of pollutant distribution and reactions products in the three mockups.

2. Materials and methods

Materials. In order to reproduce actual conditions and increase the reliability of results, we used a natural soil from a quarry located in Mora (Toledo, Spain), whose mineralogical composition (Quartz 7%, Feldspar 15%, Calcite 4%, Kaolinite 26%, Smectite 28%, Illite 20% and Organic content 0%) was determined by X-ray diffraction analysis. The commercial herbicide model Clopyralid (CAS number: 1702-17-6, $C_6H_3Cl_2NO_2$, 72% of purity, solubility > 1 g/L at 20 °C, $Kow = 2.34 \cdot 10^{-3}$ at pH 7 and 20 °C) was used as received. Two types of iron were tested: micro iron ($\geq 99\%$), reduced, powder (fine) purchased from Sigma Aldrich and Nanofer Star (NanoIron, Czech Republic), a dry air-stable nZVI powder used as received.

Experimental design. The experimental installation consists of a methacrylate reactor with an useful capacity of 175 dm³ described elsewhere [28]. The volume of total soil used in each reactor is 139.6 dm³, composed of four layers that from bottom to top are:

- 1) 27.0 dm³ of coarse gravel (that acts as a draining agent, simulating the groundwater table of a real soil),
- 2) 5.4 dm³ of sand, followed by
- 3) 101.2 dm³ low permeability soil (clay) and, finally,
- 4) 5.4 dm³ of sand (that acts as a barrier minimizing evaporation from the surface of the system).

Finally, to obtain a degree of compaction more similar to a soil in its natural state, a Proctor compaction test has been carried out for every 30 kg of aggregate clay, achieving the application of constant compaction energy to obtain a soil with homogeneous compaction. The metal hammer has an approximate weight of 2.5 kg and is adapted to the interior of a tubular guide so that the height of the free fall is approximately 305 mm.

Three tests were run simultaneously. In the three systems used, the electrodes are positioned in semipermeable electrolyte wells to facilitate the extraction of the effluents generated in the process. The configuration of electrodes consists of two rows with three wells facing one another and separated by 38 cm (Figure SM1). The reactive barrier of zero-valent iron with dimensions of 1 x 38 x 16 cm³ in width, length and depth is positioned at a distance of 2 cm from the anodic wells (Figure SM2). In the first system, it consisted of 366.83 g of ZVI nano-particles and 1100 g of soil. In the second system, the barrier contained 398.91 g of fine grain ZVI particles (596 µm) and 1197 g of soil. Finally, the third system consists of an electrokinetic soil-flushing without a reactive barrier. The electrode materials used, in anodes as in cathodes, are graphite rods with dimensions 1x1x10 cm³. The electrolyte wells have coupled a level control system connected to the feed tank to regulate the volume of water added to the soil. In cathode wells, level controls connected to peristaltic pumps have been introduced to extract surplus water. After the installation of the wells, tensiometers are inserted to analyze the amount of water that the soil has in continuous, as well as thermocouples to monitor the temperature. In addition, to collect the contaminant from the evaporation flows, a cylindrical adsorption column of 1 cm in diameter and 20 cm in length filled with activated carbon was connected. Once the assembly is complete, from a tank the soil is contaminated drop by drop with an equivalent of 20 mg of clopyralid / kg of soil, leaving a day for the contaminant to disperse through the reactor.

To begin operating, the electrolyte wells were saturated, therefore, water was added manually to the wells until the level obtained allowed the flow of electric current. Electric current is supplied by a power supply SM 400-A R-8 DELTA ELEKTRONIKA BV in potentiostatic work mode applying 30 Volts and with variable intensity. The electrokinetic experimentation lasts approximately 850 hours. Over this time, it is controlled the amount of electrolyte that is supplied in anodes and collected in cathodes and samples are extracted every day in the cathode collectors. At the end of the experiments, the soil underwent a postmortem analysis, being divided in order to obtain surface and depth maps of pH, conductivity, humidity, clopyralid concentration and intermediates [4, 29].

Apparatus and analytical procedures. Clopyralid and intermediates were measured by HPLC as described elsewhere [30] using Agilent 1260 Infinity equipment. To determine the concentration of organics in solid samples, a solid-liquid extraction (S-L) process was carried out using milli-q water as a solvent with a polluted soil/solvent ratio of 0.4 (w/w). The mixture was mixed vigorously on a VV3VWR multi-tube agitator for 2 minutes. After agitation, phase separation was accelerated by the use of a Cencom II P-elite angular rotor centrifuge (for 20 minutes and 4000 rpm). Finally, they were filtered and measured by HPLC. The pH and conductivity were measured with the help of a Crison GLP 22 pH meter and a Crison Ecmeter Basic 30+ conductivity meter. During the postmortem analysis, soil samples were taken and the pH and conductivity were measured with the same S-L extraction procedure previously described. The humidity was measured using different procedures depending on whether the measurements were carried out continuously or discontinuously. The discontinuous measurements were made by thermogravimetry whereas the continuous measurements were made indirectly by analyzing the suction that the soil presents [31]. The suction values are determined by a set of tensiometers model T5 (UMS GmbH, Munich,

Germany) inserted directly on the ground, and connected to a datalogger model DL6 (UMS GmbH, Munich, Germany) that automatically stores data with an interval of 20 minute sampling. The temperature of the soils was obtained through the insertion of ECT model thermocouples (Decagon Devices, Pullman, USA). The data collection was carried out by connecting these sensors to an Em5B datalogger (Decagon Devices, Pullman, USA) that has 5 acquisition channels and automatically stores data with a sampling interval of 20 minutes. The particle size measurements for the ZVI nanoparticles were made in a ZETA SIZER Nano series MALVERN Instruments. The fine-grained particles of ZVI were measured by the sieving method using sieves opening of 0.5, 0.6, 0.71, 0.85, 1, 1.4 and 2 mm.

3. Results and Discussion

The operation of the three mockups for one entire month points out important differences not only in the intensity, but also in the electroosmotic flux (EOF) and temperature induced by the electric field applied between the two rows of electrodes contained in each plant (1.0 V cm⁻¹). They can be seen in Figures 1 (intensity) and 2 (EOF and temperature).

Figure 1. Time-course of the changes observed in the intensity exerted in the three systems with the application of an electric field of 1.0V cm^{-1} . ▲ no RB ◆ nano-ZVI RB ■ granular iron RB.

The intensity follows a decreasing pattern, always from an initial value, which is very close in the three setups (0.4 A). This value is very similar to the values registered in previous electro-remediation tests in which other technologies were evaluated [3, 4, 31-35]. In comparing the three curves, it can be stated that the decrease seems to be magnified by the presence of the reactive barriers (RBs). Thus, the average intensity in the system with no RB was 0.38 A , while this average value decreases down to 0.33 and 0.35 A in the case of the systems with the nano-ZVI and the granular iron barriers. The decrease trend observed in all cases may be related to changes in pH and soil conductivity [3, 4, 31-35].

Figure 2. Time-course of the changes observed in the EOF (part a) and temperature (part b) in the three systems with the application of an electric field of 1.0V cm^{-1} . ▲ no RB ◆ nano-ZVI RB ■ granular iron RB. For temperature changes in the mockups: full points (inner electrokinetic zone); empty points (outer zone).

Electro-osmotic flows are also disturbed by the RB, with the system in which the nano-ZVI particles were placed being more affected. It is important to know that the EOF decreases in the case of the two mockups with RB but not in the case of the system without RB (Figure 2a), opposite to what it could be observed with intensity (which is assumed as the driving force of the system). This can affect the dragging of pollutant to cathodic wells. Regarding temperature (Figure 2b), the first important observation is related to the difference between the temperature inside the zone delimited by the electrodes wells (inner electrokinetic zone) and the outer zone, which points out the relevance of the ohmic heating of soil during electrokinetic remediation tests. Difference is higher than 2°C in the three cases, which is very important taking into account the short distances and also that the outer zone is also affected (although in a lower extension) by the electrochemically induced processes. In addition, although the three mockups were run simultaneously in the same room, the average temperature reached by the mockup with the nano-ZVI RB (26 °C) is slightly higher than that registered by the system without RB (25.7 °C); and both systems reached a temperature higher than that attained in the mockup with the micro-ZVI RB (24.6 °C). According to previous works [7, 8, 11] the electric heating is expected to be more intense in the nearness of electrodes and its effect increases with the size of the plant.

EOFs have an impact on the water content of soil as it can be observed in Figure 3. Thus, the water content in the system without a RB is much higher than in the other two systems with average water content of 0.208 L kg⁻¹ dry soil in the first case and 0.182 and 0.187 L kg⁻¹ for the nano-ZVI and granular iron RBs. The lower water content is particularly important in the case of the system equipped with the nano-ZVI, which is consistent with the higher expected

volatility caused by the higher temperature and with the lower EOF registered during the treatment.

Figure 3. Distribution of water content in the three mockups after the remediation test. Top: upper layer of soil; Medium: middle layer of soil and Down: lower layer of soil. Water content is expressed in %.

Figure 4 shows the water balances in the three setups after the one-month operation period. As seen, the main difference observed in the fluxes is associated with electro-osmosis, and this difference is consistent with the higher EOF found in the system without RB, which opposes almost with the same values of hydraulic fluxes registered in the three mockups. The higher EOF has an impact on the water accumulated in the soil, which almost doubles in the case of the systems with no RB. This means that RB disturbs EOF very importantly, but not the hydraulic flows (which are not horizontal but vertical).

Figure 4. Water distribution in the three mockups at the end of the electrochemical tests (30 days of operation).

This is important because the RB is placed just inside the main current lines produced in by the two rows of electrodes. In fact, iron particles could behave as bipolar electrodes and, hence, they can modify importantly the fluxes inside the cell. In fact, it can be seen how the water content is much higher in the zone next to the anodes in the two systems with RB, being this value more relevant when iron granules are used. However, this larger mobility of water has not an impact on the water evaporated, which is more related (as seen in the onset) to the temperature rise originated by the ohmic losses.

Concentration of clopyralid decreases in an important way during treatment but the mechanisms are completely different in the three mockups as in can be seen in Figure 5, where the mass balances are plotted in bar graph. In the system with no RB, an important fraction of the pollutant is dragged (45.6%), value that is much higher than the value dragged in the two systems equipped with RB (14.5 and 27.6 for the nano-ZVI and mili -ZVI RB, respectively).

Figure 5. Clopyralid distribution in the three mockups at the end of the electrochemical tests (30 days of operation). Onset: dehalogenated intermediates.

These ratios can be easily explained by comparing the flows generated in each system, which were of 33, 18 and 21 $\text{dm}^3 \text{kg}^{-1}$ soil for ESKF, nano-ZVI RB and granular iron RB tests, respectively. Likewise, the percentages of clopyralid volatilized are related to the water evaporated in each case: thus, 6.5, 11.4, 8.5 % of the clopyralid initially contained in the soil is transported to the gas phase in the ESKF, nano-zvi and granular iron RB tests. These values are consistent with the percentages of water evaporated in those experiments (which are 26.6, 42.4 and 26.4%, in the same cases). Finally, the most relevant information that can be drawn from this plot is given by dehalogenation. As can be seen, even in the case of ESKF, there is a partial dehalogenation of clopyralid into picolinic acid, with a non-negligible transformation of 5.8% of the initial content of the pollutant, which can be explained by the iron content of the soil (0.6%). This process has been confirmed by means of a soil washing test carried out in our lab and it is important because it states that if soil contains iron (which is a common case), natural processes can induce a partial detoxification [13]. However,

dehalogenation is promoted with both RB increasing the transformation ratio up to 11.1 and 12.4% for the nano-ZVI and granular iron RBs. In this case, in addition to the formation of picolinic acid, the partial dehalogenation to 6-Chloropyridine-2-carboxylic acid and, more important, to 3-Chloropyridine-2-carboxylic acid is observed.

As expected, distribution of clopyralid after the treatment is not uniform. In fact, most of the clopyralid is concentrated in the vicinity of the anodes wells, as it can be seen in Figure 6. One month seems to be a rather short period for the complete remediation of the soil. In fact, the aim of this work was not to remediate soil completely, but to a point in which the main mechanisms involved could be clearly discerned. However, results demonstrate that the treatment was more effective than initially expected and, after that month, only remained in soil 42.1, 64.1 and 52.0% of the initial clopyralid spilled in the EKSF, nano-zvi and granular iron RB tests, respectively. In addition, what it is more important is that 87, 78.5 and 60.8% can be easily extracted by excavating only 15, 20 and 15% of the soil, because the pollutant has been concentrated in very specific points during remediation.

Figure 6. Distribution of clopyralid after one month of application of the three technologies.

Initial concentration dosed was enough to obtain a uniform distribution of 20 mg Kg⁻¹. Units of the plot are mg clopyralid Kg⁻¹ soil.

RBs are supposed to have a great impact on results. The amount of iron contained in the RB was important: 366.83 g of nano-ZVI in 1100 g of soil in one of the barriers and 398.91 g of granular iron in 1196.73 g of soil in the other. These amounts are stoichiometrically more than enough to dehalogenate completely the clopyralid spilled in the soil. In the Figure 7, the post-mortem characterization of the barrier indicates that dehalogenation was uniform (not dependent on the position) and that 3-chloropicolinic acid and picolinic acid are the key final products. In addition, they are produced in similar ratios with both types of RBs. This result is contrary to what occurred to the rest of the soil, in which picolinic acid is the primary (and almost unique) product. In the three mockups, the production of the 6-chloropicolinic acid is negligible. In addition, it is important to compare these results with those obtained in

soil washing tests in which 300 g of the same soil are mixed with 30 g of nano-ZVI (test 1) and with 30 g of granular iron (test 2). In the first case the speciation of the products was 11.59, 17.19 and 71.22% of picolinic, 3-Chloropyridine-2-carboxylic acid and 6-Chloropyridine-2-carboxylic acid while in the second the products speciation changes to 71.50, 4.15 and 24.35%, respectively. These results show the great variability, which should be a consequence of the different soil/iron ratios and perhaps other side processes.

Figure 7. Post mortem characterization of the RB. Full points: nano-ZVI RB. Empty points: mili-ZVI RB. ▲ Clopyralid, ◆ picolinic acid, ● 3-chloropicolinic acid, ■ 6-chloropicolinic acid

Distribution of picolinic acid in the soil is more uniform than that of clopyralid (Figure 8). This is also the case of the distribution of the other two dehalogenated molecules shown in the supplemental materials of this work (Figures SM3 and SM4). It is important to take into account that the values are much lower than in the case of the parent pollutant and the picolinic acid is not only be formed in the RB but also in the whole soil by reaction of the dispersed clopyralid with the iron contained in the soil.

Figure 8. Distribution of picolinic acid after one month of application of the three technologies. Initial concentration of clopyralid dosed was enough to obtain a uniform distribution of 20 mg Kg⁻¹. Units of the plot are mg picolinic acid Kg⁻¹ soil.

Other important parameters in the comparison of the three technologies tested in this work are pH and the ionic conductivity. As seen in Figure 9, there are no significant differences in the distribution maps, and this fact indicates that the RB does not influence the quality of the soil, from the viewpoint neither of pH nor for the ions distribution. This is important because dehalogenation of clopyralid consumes protons according to reactions 2 and 3, but this consumption is negligible in comparison with the production of proton in the anode wells. Likewise, the pH in the nearness of the cathodes becomes more alkaline although the profile generated is not particularly important.

Figure 9. pH and conductivity distribution after one month of application of the three technologies.

Conclusions

From this work, the following conclusions can be drawn:

- ZVI reactive barriers combined with EKSF may achieve the dehalogenation of clopyralid in soils
- ZVI barriers achieve a larger dehalogenation than single EKSF, although they seriously affect to the electrokinetic flushes, preventing the mobility of pollutants to the electrode wells and hence exhibiting a non-favorable behavior as compared to the EKSF.
- There are no significant differences between the treatment performances obtained with the two sizes of ZVI.
- Volatilization of the pollutants associated with the thermal effects was almost prevented with capillary barriers implemented on the top of the mockups.
- After the 1-month treatment most of the clopyralid not removed is concentrated in the vicinity of the anodes wells and more than 60% can be easily extracted by excavating only 15 % of the soil, because the pollutant has been concentrated in very specific points during remediation.

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