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1 **Towards the development of efficient electro-Fenton reactors**
2 **for soil washing wastes through microfluidic cells**

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10 **Abstract**

11 This work focuses on the coupling of three different approaches into the same reactor at
12 the same time: microfluidic cells, anodic oxidation with diamond anodes and an electro-
13 Fenton process. In order to supply oxygen a jet aerator was used and a CB/PTFE
14 Duocel[®] Al foam cathode was installed to promote the formation of hydrogen peroxide.
15 This novel concept is applied for the direct treatment (without the addition of salts or
16 other reagents) of soil washing wastes obtained in the remediation of soil spiked with
17 clopypalid. Results obtained pointed out that this approach can increase the efficiency of
18 the process by folds as compared to traditional treatment technologies. The chemical
19 analysis of the intermediates showed different reaction mechanisms: anodic oxidation,
20 electro-Fenton and a negligible contribution of coagulation. The coupled system studied
21 in this work present several advantages such as high treatment efficiency and short
22 treatment time which indicates that the development of electrochemical reactors for
23 diluted liquid wastes is progressing in an adequate direction.

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5 25 **Keywords**
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8 26 Microfluidic cells; electro-Fenton; diamond anodes; anodic oxidation; soil washing
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10 27 wastes.
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1. Introduction

Soil remediation is a major interest topic nowadays, since its large impact on the water reservoirs preservation for human consumption ¹. One of the major pollutants in soils and water reservoirs are herbicides because they are widely applied in industrialized countries to control weeds in agricultural and non-agricultural systems. However, those compounds are often toxic and persistent; hence, a correct application is required to avoid their presence in the environment ².

In case of acute accidental emissions, rapid excavation and soil washing is a very interesting choice to avoid the diffusion of the pollution and limit the extension of the problem in the very first moments ³⁻⁵. This process produces a liquid waste (so-called soil washing waste) from the soil washing fluid (SW) used to extract the pollutants. This fluid is either water, when the pollutant is highly soluble in water, or more complex formulations (for instance, water plus a surfactant) when the solubility of the pollutant is low.

Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid) is an organochlorinated compound commonly used as herbicide. The principal characteristics of this herbicide is the high persistence in soil and also a high-water solubility. Because of this, it has frequently been detected in natural environments, including drinking water. Its high solubility in water represents an advantage when it comes to be removed from polluted soils because it is amenable to be extracted via a conventional soil washing techniques, with no other solvent than water as the washing fluid ⁶

Once the pollutant is transferred from the soil to the liquid phase, the treatment of this soil waste fluid is the important stage ⁷⁻¹³. Depending on the nature of the pollutant, conventional and economic treatments such as biological oxidation or coagulation-

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3 56 flocculation can be applied. However, many anthropogenic pollutants are bio-refractory
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5 57 and/or do not successfully coagulate. Under these circumstances, advanced oxidation
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7 58 processes (AOPs) are of great interest. Among them, electrochemical AOPs (EAOPs)
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9 59 are gaining interest in the last decades because of their outstanding performance¹⁴⁻¹⁶

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12 60 A great deal of effort has been put in order to development new processes¹⁷⁻²⁰. In this
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14 61 context, the electrochemical cell design has a major role on the performance of the
15
16 62 electrochemical processes and hence in its efficiency²¹⁻²³. Until now, little scientific
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18 63 attention has been paid to the development of efficient reactors (most of it comes from
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20 64 companies) and most of the works devoted to wastewater treatment in the literature use
21
22 65 stirred-tanks cells or parallel-plate flow-by reactors^{24, 25}.

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24
25 66 Recently, parallel-plate flow-by microfluidic (MF) electrochemical cells have been
26
27 67 evaluated for the treatment of wastewater containing bio-refractory organic pollutants^{18,}
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29 68²⁶. The main advantage of a micro-fluidic cell is the minimum ohmic drop in the
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31 69 electrolyte thanks to an inter-electrode gap in the order of micrometers. Therefore, this
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33 70 cell configuration provides flexibility to achieve reasonable cell voltage even when it
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35 71 comes to treat low-conductive effluents. The main limitation comes from the
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37 72 operational problems derived from the high friction in the inter-electrode gap and the
38
39 73 concomitant high pumping costs and low electrolyte flows^{17, 27}. It also leads to an
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41 74 accumulation of gases on the electrode surface and within the inter-electrode gap,
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43 75 especially at high current densities which are desirable to intensify the treatment^{28, 29}

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48 76 In this context, a new design has been lately proposed to solve this drawback: the
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50 77 micro-fluidic flow-through cell^{17, 27}. This reactor is aimed not only to produce a
51
52 78 minimum ohmic drop in the electrolyte but also for maximizing mass transfer.
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54 79 Importantly, the high forced circulation of electrolyte through the three-dimensional
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56 80 electrodes strips the gases out of the IE gap, minimizing the aforementioned drawbacks

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3 81 of microfluidic reactors. The microfluidic flow-through with a conductive-diamond
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5 82 mesh anode was applied to the treatment of a synthetic solution requiring from 4 to 10
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7 83 times less electric charge and 6 to 15 times less energy consumption at 10 and 100 mA
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9 84 cm^{-2} , respectively, as compared to a conventional flow-by reactor ^{17, 27}.

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11
12 85 If an appropriate cathodic material is selected ^{30, 31}, hydrogen peroxide (H_2O_2) can be
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14 86 electrogenerated at the cathode via oxygen reduction reaction in a process generally
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16 87 known as Electro-Fenton (EF) ^{23, 32}. Given that anodic oxidation takes places in the
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18 88 anode and the production of the Fenton reagent is a cathodic process, they can be
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20 89 combined in the same reactor in such a way that both electrodes contribute to the
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22 90 pollutant abatement, thus increasing the overall efficiency ³³. One of the key aspects of
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24 91 EF reactors is to produce H_2O_2 at a high rate and current efficiency which is, in turn,
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26 92 determined by the low solubility of oxygen under room conditions ³⁴. In a series of
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28 93 previous works, some of the authors studied the jet aerator (JA) as a new compressor-
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30 94 free system to produce H_2O_2 in electrolytic cells ^{31, 35, 36}. As a result, this system feeds
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32 95 the cathode with large oxygen flow rates thanks to the saturation of the medium and the
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34 96 formation of air bubbles, promoting a fast and efficient H_2O_2 generation. This state-of-
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36 97 the-art system can be used to aerate a microfluidic flow-through cells because the
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38 98 bubbles are easily stripped away from the inter-electrode gap, in contrast to what would
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40 99 occur in a conventional microfluidic cell.

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45 100 In summary, the jet-aerated microfluidic flow-through (MF-FT) reactor used in this
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47 101 work presents three new features to improve the treatment: *i*) combines the anodic
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49 102 oxidation and the EF processes using state-of-the-art 3D electrodes *ii*) a cell design with
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51 103 a low inter-electrode gap and an enhanced mass transfer conditions *iii*) aeration via a
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53 104 compressor-free system. ³⁶.

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3 105 With this background, this work focuses on the application of the jet-aerated MF-FT
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5 106 reactor to treat a complex and real waste with a low natural conductivity. This effluent
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7 107 is obtained after the application of soil washing technique to a soil polluted with the
8
9 108 herbicide clopyralid. It is very important to highlight that this waste directly undergoes
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11 109 electrolysis after the extraction, without the addition of salts to artificially increase the
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13 110 conductivity, because this practice leads to a secondary pollution by inorganic ions
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15 111 which are less hazardous but a more persistent type of pollution causing environmental
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17 112 issues such as rivers salinization^{37, 38}.

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20 113 Several tests were carried out to study the influence of several parameters and isolating
21
22 114 the different removal processes that may contribute to the overall abatement of organic
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24 115 pollutants, with especial emphasis on reactions mechanisms, in order to obtain valuable
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26 116 information for the scale up of this promising reactor design.
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31 32 118 **2 Material & Methods**

33 34 35 119 **2.1 Reagents and Chemicals**

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38 120 Double de-ionized water (Millipore Milli-Q system, resistivity: $18.2 \mu\Omega \text{ cm}^{-1}$ at 25 C)
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40 121 was used to prepare water solutions. Clopyralid (3,6-Dichloro-pyridine-2-carboxylic
41
42 122 acid), methanol and formic acid (HPLC grade) were used to prepare the mobile phase in
43
44 123 HPCL analysis (Sigma-Aldrich, Spain). Sulfuric acid (H_2SO_4) used to adjust the pH and
45
46 124 iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) used as iron source in electro-Fenton test were employed as
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48 125 received from Panreac (Barcelona, Spain).
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50 51 52 126 **2.2 Soil washing**

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3 127 The soil used in this study was obtained from a quarry located in Toledo (Spain). It is
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5 128 characterized by its inertness, low hydraulic conductivity (10^{-8} cm s⁻¹) and lack of
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7 129 organic content ¹². The soil was contaminated with a water solution of clopyralid
8
9 130 aleatory distributed over the clay surface and subsequently aerated for 1 day, obtaining a
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11 131 clopyralid concentration in soil of 100 mg kg⁻¹ soil. Then, the soil was washed with de-
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13 132 ionized water in a discontinuous stirred tank reactor (1 dm³ capacity) for 4 h at 100 rpm.
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15 133 Finally, the bi-phasic mixture soil-washing effluent was separated by decantation for 24
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17 134 h.

135 **2.3 Experimental set-up.**

136 The core of the experimental setup used during this work is a micro-fluidic flow-
137 through electrochemical cell (inter-electrode gap of 150 μm) coupled to a jet aerator, as
138 previously described ³⁶. The wastewater is continuously fed to the electrochemical cell
139 from the reservoir tank by a centrifugal pump (Heidolph KrP 25/4). The reservoir tank
140 is equipped with a cooling jacket for temperature control and which was kept constant
141 (25 °C) by means of an external water bath. Electro-oxidation tests were carried out
142 using a 3D-niobium mesh boron-doped diamond (Diachem[®]) supplied by Condias
143 GmbH (Germany) as the anode and a perforated-plate stainless steel as the cathode,
144 both of them with a wet cross section of 33 cm². In the electro-Fenton tests, the cathode
145 was replaced by an aluminium sponge (Duocel[®], supplied by ERG Materials &
146 Aerospace) with a deposition of carbon black (Vulcan XC72) and
147 polytetrafluoroethylene (Teflon[®]) prepared as described in a previous work ³⁶. 0.50 mM
148 of Fe were added and the pH adjusted to 3 at the beginning of tests, a typical
149 experimental conditions employed in EF ^{39, 40}

150 **2.4 Analytical techniques**

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2
3 151 Clopyralid and intermediates concentration were measured via High Performance
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5 152 Liquid Chromatography (HPLC) using an Agilent 1200 series coupled a DAD detector
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7 153 and a ZORBAX Eclipse Plus C18 analytical column³⁷. Degradation of clopyralid was
8
9 154 also followed by measurement of Total Organic Carbon (TOC) concentration using a
10
11 155 Multi N/C 3100 Analytik Jena analyzer. The pH and conductivity were measured using
12
13 156 a CRISON pH25+ and CRISON CM35+. The anions present in the wastewater were
14
15 157 detected and quantified via ion chromatography with a Shimadzu LC-20A system. The
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17 158 iron concentration in EF tests was measured by inductively coupled plasma atomic
18
19 159 emission spectroscopy (ICP-AES) in a Varian Liberty RL sequential ICP-AES
20
21 160 equipment. The oxidants generated was quantified iodometrically by potentiometric
22
23 161 titration with thiosulphate in acidic media. This method analyze all oxidants capable to
24
25 162 oxidize iodide (I^-) to iodate (IO_3^-)⁴¹

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29 163 The studies of electrode surface were obtained by means of Scanning Electron
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31 164 Microscope (SEM) FEI model QUANTA 250 working under low vacuum with a
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33 165 detector of secondary electron (LFD) or a backscattered electrons detector (BSED). The
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35 166 Energy Dispersive Analysis X-Ray (EDAX) analyses were performed with an Apollo X
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37 167 (Ametek, U.S.A.) coupled to the previous SEM system.

3. Results and Discussion

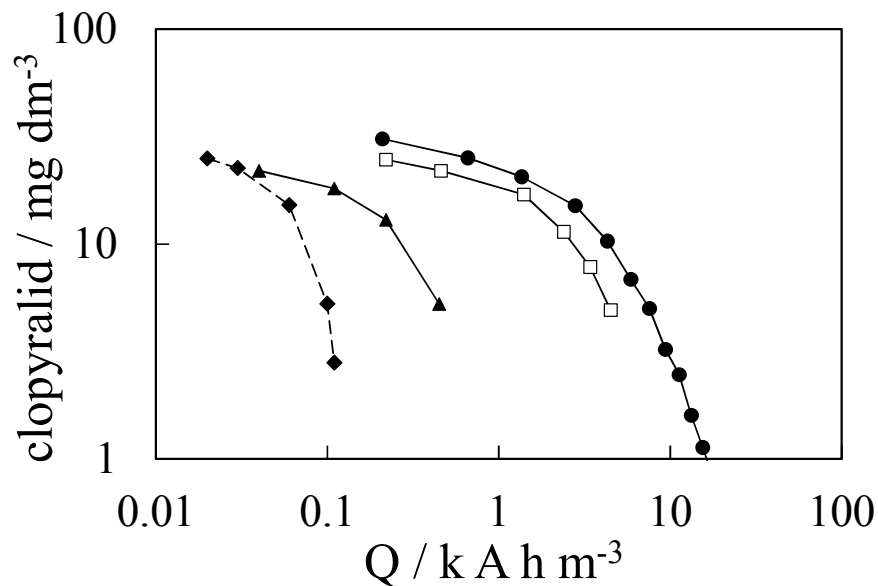
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43 169 As described in the introduction, in the search of more efficient cells for the treatment of
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45 170 wastewater, microfluidic cells are an interesting alternative. Reducing the inter-
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47 171 electrode gap minimize ohmic drops in the electrolyte and, therefore, leads to a
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49 172 reduction of cell voltage and energy consumption. In addition, a high mass transfer is
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51 173 expected in the MF-FT due to the local turbulence induced by mesh-electrodes and their
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53 174 larger surface area with respect to plate electrodes^{22,27}.

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3 175 Figure 1 shows the decay of the clopyralid contained in soil washing fluids during
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5 176 different electrolytic test carried out at the same current density (10 mA cm^{-2}):
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7 177 commercial flow-by electrochemical cell with plate diamond electrodes MF-FT
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9 178 equipped with a conductive-diamond mesh as anode and the latter equipped with a
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11 179 cathode (CB/PTFE-Al) to produce H_2O_2 in the presence of catalytic amounts of soluble
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13 180 Fe (II) (EF process).

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16 181 Experimental results obtained in these three tests are compared to the theoretical 100%-
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18 182 efficiency performance for the mineralization of clopyralid. In every case, the soil
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20 183 washing fluid was the same, obtained by washing 400 g of soil polluted with 100 g kg⁻¹
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22 184 of clopyralid with 1.0 dm³ of Milli-Q water.

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25 185 This process produces a real waste with a conductivity of 0.75 mS cm^{-1} that differs to
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27 186 previous experiments prepared it with a typical ion composition and higher conductivity
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29 187 (1 mS)¹⁷. In these experiments also the ions concentrations were measured (only the
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31 188 most important species are shown): 6 mg Cl⁻ dm⁻³, 150 mg SO₄²⁻ dm⁻³, 8.5 mg NO₃⁻
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33 189 dm⁻³, 4 mg Na⁺ dm⁻³.

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37 190 At this point, it is important to take into account that, as explained before, using real
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39 191 wastes without doping them with salts is an important challenge. Thus, although this
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41 192 addition could be positive in economic terms (lower cell voltage and improved
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43 193 production of oxidants at the anode surface), in fact, what it is introduced is really a new
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45 194 type of pollution in the waste, less hazardous but much more persistent³⁷.



195

196 **Figure 1.** Removal of clopyralid from soil washing fluids (no electrolyte added). (●)
197 commercial Diacell[®] equipped with diamond anodes; (□) microfluidic reactor; (▲)
198 microfluidic reactor with electro-Fenton process; (◆) theoretical 100% efficiency
199 curve.

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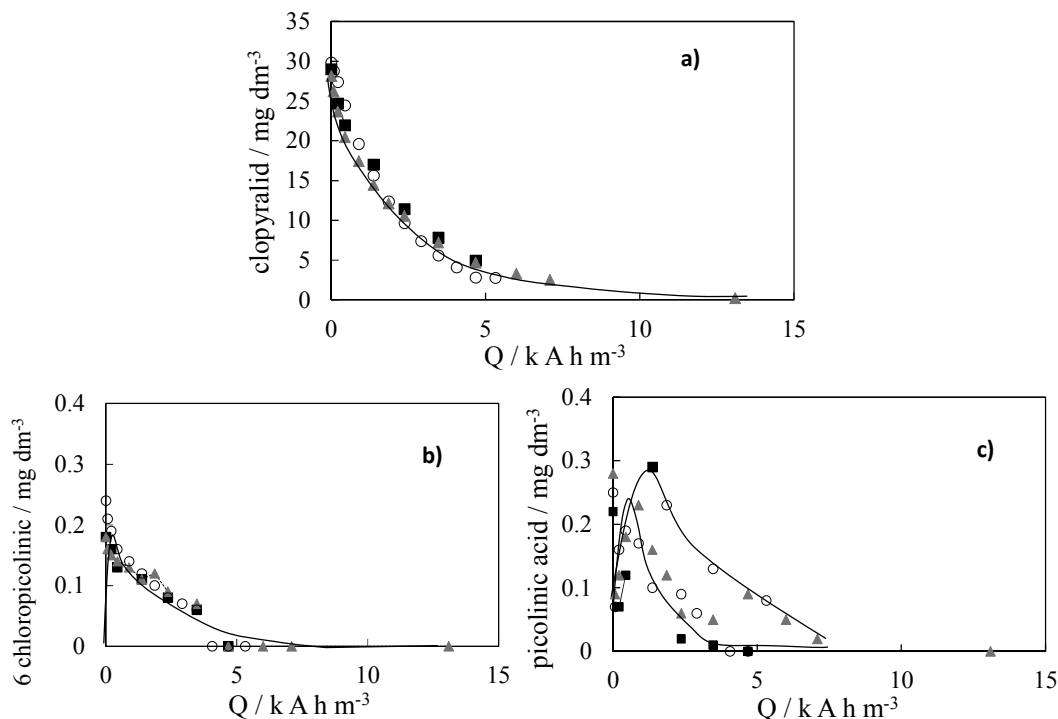
201 Results are represented in log-log plot because of the very different time-scales obtained
202 for the degradation of the same waste. As stated before, these data confirm that by
203 changing the cell configuration, an important improvement might be obtained. In
204 particular, the largest improvement was obtained by promoting the Fenton reaction
205 inside the cell with the addition of iron and the production of hydrogen peroxide. In
206 every case, the same current density was employed, 10 mA cm^{-2} , a value low enough to
207 get a high efficiency, even in a system controlled by diffusion. For comparison purpose,
208 the electrical charge required to attain around 80% of clopyralid removal the electrical
209 charge required is 6.0, 4.0 and 0.4 kA h m^{-3} in the case of using conventional cell, MF
210 reactor or MF electro-Fenton reactor, respectively. This means that an outstanding

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3 211 reduction of operation cost of more than one log can be attained by using this novel
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5 212 approach.

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10 214 In the MF-FT cell, the wastewater flows through the electrodes to improve mass
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12 215 transfer and, hence, to minimize diffusional limitations of the reagents towards the
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14 216 electrodes (pollutant to the anode and oxygen to the cathode). As seen in Figure 2, there
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16 217 are almost no differences in the treatment of the same soil washing waste at different
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18 218 flow rates (0.4, 1.0 and 1.6 L min⁻¹ corresponding to 3.77, 9.43 and 15.1 cm s⁻¹
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20 219 considering the dimensions of the cell) at a fixed current density, which suggests that
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22 220 the microfluidic cells are not limited by mass transfer under those conditions.

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26 221 Figure 2 also shows that removal of the intermediates is practically not influenced by
27
28 222 the flow rate. Only two intermediates were measured at appreciable concentrations: 6-
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30 223 chloropicolinic acid and picolinic acid, although traces of 3- chloropicolinic acid were
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32 224 also observed. These intermediates generated during the electrooxidation of washing
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34 225 fluids in undivided cell may be promoted from the dehalogenation of the clopyralid
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36 226 molecule, which can occur mainly on the surface of the cathode ^{42, 43}. Regarding the
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38 227 concentration profile, a continuous decrease in the concentration of 6- chloropicolinic
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40 228 acid with time is observed up to its complete removal. On the other hand, picolinic acid
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42 229 undergoes a rapid increase up to a maximum and then a decrease, which indicates that
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44 230 the electrochemically-assisted dechlorination seems to go primarily through this
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46 231 intermediate instead of 6- chloropicolinic acid and 3-chloropicolinic acid
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233 **Figure 2.** Influence of the flowrate in the removal of clopyralid (a), 6 chloropicolinic
234 acid (b) and picolinic acid (c) using a microfluidic reactor. (○) 0.4 L min^{-1} ; (■) 1.0 L
235 min^{-1} ; (▲) 1.6 L min^{-1} .

236 The main difference expected to be produced by the current density is the formation of
237 oxygen bubbles at large current densities, which may have a negative impact on
238 conventional microfluidic cells because of the short inter-electrode gap^{28,29}, preventing
239 their use. To observe this the MF-FT can be operated at high current densities. A value
240 of 100 mA cm^{-2} was selected for the next tests. In addition, a less concentrated waste
241 (obtained after the washing of 0.2 kg per each dm^3) was used in order to magnify the
242 effect of diffusional limitations.

243 As seen in Figure 3, only the raw clopyralid and the dehalogenation intermediate
244 picolinic acid were detected by HPLC. However, what seems to be more important is
245 the huge difference between the results obtained in the two tests. As in previous cases,

the total removal of organics is attained but with important differences in efficiency. It was observed that by increasing the current density from 10 to 100 mA cm⁻² in the same electrochemical cell, the efficiency decays more than 20 times (the current charge required is more than 20 times higher for the same result), because of the promotion of side reactions that do not contribute to clopyralid degradation and the diffusion control of the clopyralid elimination rate⁴⁴. Thus, these results confirm the relevance of the use of a suitable current density with this type of cells.

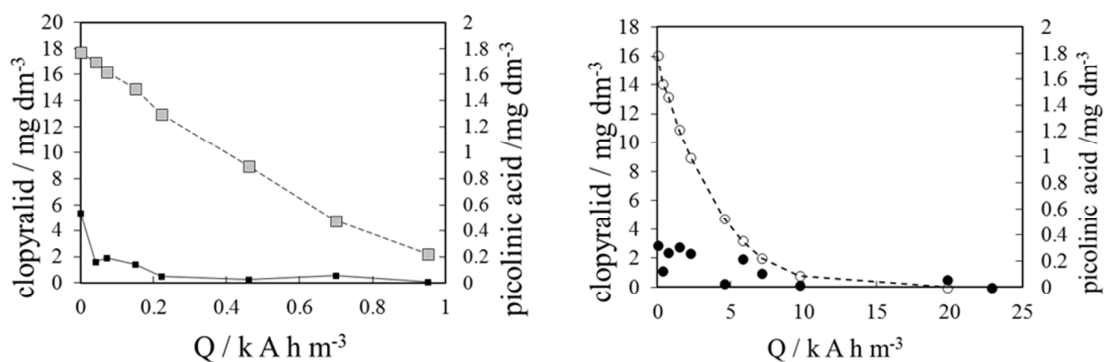
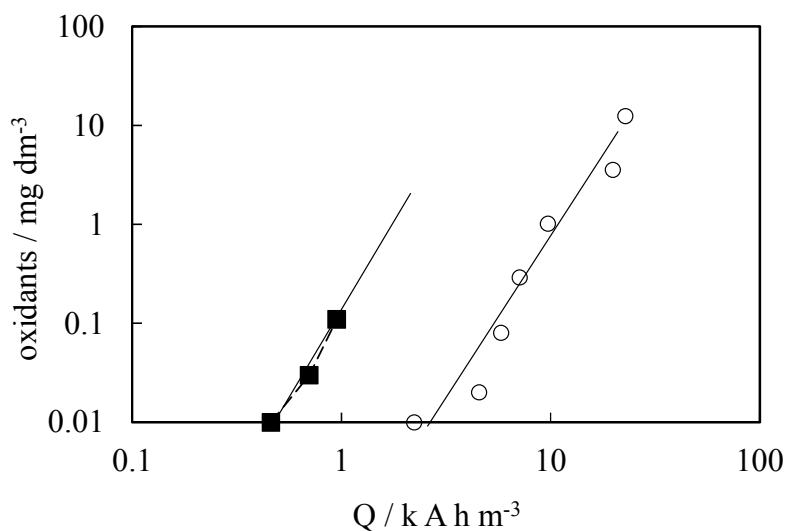


Figure 3. Changes in the concentration of clopyralid (□,○) and picolinic acid (■,●) during the electrolysis of a soil washing waste obtained with a ratio soil / SWF of 0.2 kg soil / kg⁻¹ of SWF. a) 10 mA cm⁻² b) 100 mA cm⁻².

As shown in Figure 4, the formation of oxidants does not seem to be promoted, only delayed by operating at such high current densities. Thus, at 10 mA cm⁻² the production of oxidants is important, even at low applied current charges and this production only becomes important operating at high current densities at much higher charges, indicating the preferential formation of oxygen instead of valuable oxidants when operating at very high current densities.

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266

267 **Figure 4.** Changes in the concentration of oxidants during the electrolysis of a soil
268 washing waste obtained with a ratio soil / SWF of 0.2 kg soil / kg⁻¹ of SWF at 10 mA
269 cm⁻² (■) and 100 mA cm⁻² (○).

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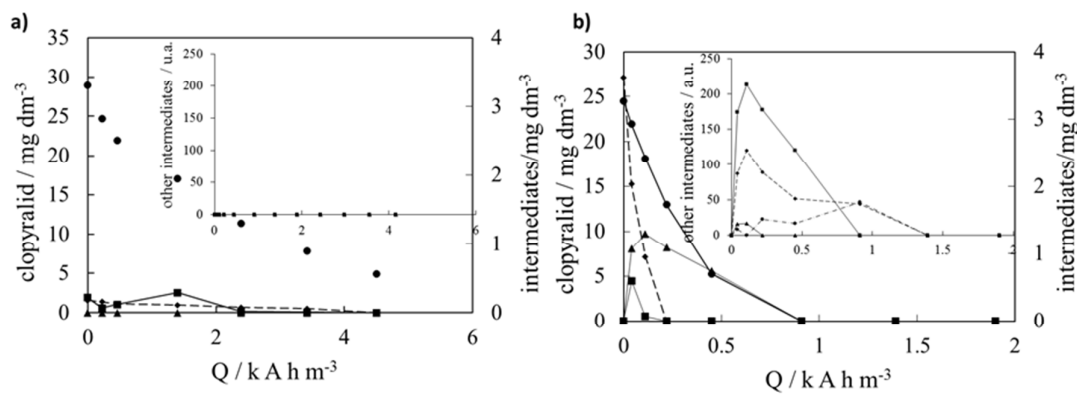
271 Those results point out that no operational problems are observed working in this
272 microfluidic reactor at high current densities, but still work has to be done to
273 homogenize the current distribution to increase the efficiency.

274 Once evaluated the efficiency of the MF-FT architecture as an anodic oxidation reactor,
275 the next step was to optimize the efficiency of the microfluidic cell using a cathode to
276 produce H₂O₂ and promote the Fenton reaction.

277 Figure 5 shows the main changes observed when a soil washing fluid polluted with
278 clopyralid is treated in a microfluidic reactor, with and without promotion of the Fenton
279 reaction by addition of Fe (II) into the electrolyte. As seen, results are completely
280 different being much efficient the system in which iron is added. This configuration

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3 281 depletes organic concentration is less than 1.5 Ah dm^{-3} , while the other electrolytic
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5 282 system needs 4 times more current charge to achieve the same removal. This proves that
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7 283 the promotion of the Fenton reagent is highly effective. It is probably due to the fact that
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9 284 this mechanism takes places in the bulk and, thus, in the absence of diffusional
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11 285 problems. It is particularly important the differences observed in the concentration of
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13 286 picolinic acid, which is known to be a typical difficult-to-oxidize species in the single
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15 287 electrolytic test and which shows a clear profile of intermediate during the oxidation.

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17
18 288 With respect to by-products, four intermediates were detected. Those molecules do not
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20 289 correspond to the dehalogenation compounds but are probably compounds formed by
21
22 290 oxidation. Those species were not observed in the single electrolytic system proving the
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24 291 existence of different mechanisms in the Fenton-assisted process. At this point, it is
25
26 292 important to highlight that the behavior observed in the MF-FT cell as anodic oxidation
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28 293 reaction, in which no oxidative intermediates are detected, is characteristic of the anodic
29
30 294 oxidation of diluted wastes and it has been described in many other previous papers ⁴⁵⁻
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32 295 ⁴⁸. It is explained in terms of the strong oxidative conditions produced by the anodic
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34 296 oxidation technology with diamond anodes (weakly physisorbed HO• radicals and the
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36 297 promotion of an oxidative cocktail that promotes different oxidation mechanism at the
37
38 298 same time) which leads to the complete mineralization. However, Fenton mechanisms
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40 299 accelerates the process by producing the oxidants in the bulk but lead to the occurrence
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42 300 of other intermediates (namely dihydroxypyridin-2 carboxylic acid, oxalic acid, tartronic
43
44 301 acid and oxamic acid during our experience).



302

303 **Figure 5.** Treatment of soil washing fluids containing clopyralid in microfluidic reactor

304 (a) and microfluidic electro-Fenton (b). (●) clopyralid; (■) picolinic acid, (▲) 3-

305 chloropicolinic acid; (□) 6-chloropicolinic acid. Onsets: intermediates formed by

306 electrolytic processes: (●) dihydroxypyridin-2 carboxylic acid; (■) oxalic acid; (▲)

307 tartronic acid; (□) oxamic acid.

308

309 Fenton reactions are known to combine oxidation and coagulation mechanisms, because

310 the separation of Fe from the treated effluent is accomplished by increasing the pH and

311 promoting its precipitation in the form of insoluble $\text{Fe}(\text{OH})_3$. A similar mechanism can312 take place on the cathode due to the formation of OH^- in the reduction of water to

313 hydrogen. However, in the case of clopyralid coagulation is not expected to have a great

314 significance because it is dissolved and not in the form of colloid. As it is known, in that

315 case only the inefficient adsorption mechanisms can play a role in coagulation processes

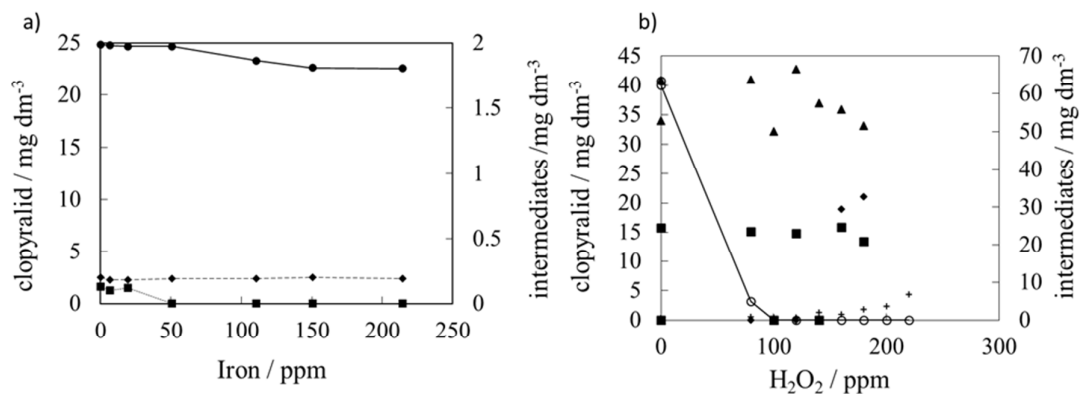
316 ⁴⁹.

317 In order to confirm this hypothesis, and hence to evaluate the effects of the coagulation

318 on the removal of the species involved in the degradation of clopyralid, a jar test was

319 carried out by adding different doses of iron coagulants to a solution containing

320 clopyralid and the three dehalogenated derivatives. The results are shown in Figure 6.



323

324 **Figure 6.** a) Coagulation of clopyralid with iron chloride: (○) clopyralid, (■) picolinic
 325 acid and (□) 6-chloropicolinic acid at pH 7. b) Fenton experiment of clopyralid
 326 solution: (○) clopyralid, (■) picolinic acid, (□) oxalic acid, (Δ) tartaric acid and (▲)
 327 oxamic acid at pH 3.

328

329 The adsorption of these pollutants onto the growing flocs is not very important even at
 330 the highest concentration tested, which is largely superior to the one added in the
 331 electro-Fenton test. Therefore, the coagulation mechanism is negligible and confirms
 332 that the important improvement in the performance obtained by adding iron to the
 333 microfluidic cell must be associated to oxidative processes (Fenton reaction).

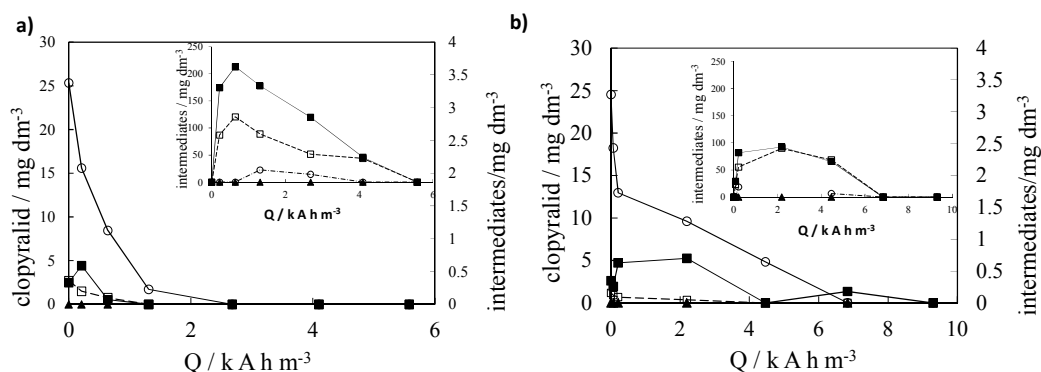
334 On the other hand in Part b, it can be seen the results obtained in the degradation of
 335 clopyralid by a chemical Fenton process, obtained by adding different concentrations of
 336 H₂O₂ (within range 80-240 ppm) and 0.5 mM Fe at pH 3.0 to the raw wastewater at a
 337 constant temperature of 25°C for 24 hours. The reaction time was expanded up to 24 h.
 338 to ensure total conversion of hydrogen peroxide. As can be seen, the reaction products

339 (picolinic acid, oxalic acid, tartaric acid and oxamic acid) were nearly the same than in
 340 the electroFenton process. The occurrence of carboxylic acids as the final by-product is
 341 typical in those processes¹.

342

343 In order to gain insight into the electro-Fenton process, two additional test were carried
 344 out at higher current densities to observe if the effect of increasing of current density is
 345 detrimental also in the case of the coupled approach.

346 Figure 7 shows the time course of clopyralid and intermediates of the electrolysis
 347 carried out at higher current densities (30 and 50 mA cm⁻²). They supplement the
 348 information given in Figure 5b in which the results of the same process, operated at 10
 349 mA cm⁻² were shown.



350

351 **Figure 7.** Electro-Fenton of a SWF carried out at 30 mA cm⁻² (a) and 50 mA cm⁻² (b).

352 (○) clopyralid; (■) picolinic acid; (▲) 3-chloropicolinic acid; (□) 6-chloropicolinic
 353 acid. Onsets: Fenton Oxidative intermediates: (○) dihydroxypyridin-2 carboxylic acid;
 354 (■) oxalic acid; (▲) tartronic acid; (□) oxamic acid.

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3 356 In comparing the x-axis of the three panels, it is evident that the increase in the current
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5 357 density leads to a more inefficient treatment and the differences are important as in the
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7 358 case of the single electrolysis. In this case, the range of study was not as broad but even
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9 359 so, the process become much less efficient at high current densities and required a much
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11 360 larger current charge to obtain the same degree of pollutant removal. The reason behind
12
13 361 this behavior is mainly the inefficient production of H₂O₂ at such current densities. As
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15 362 demonstrated in previous works ^{31, 34}, current density and oxygen transport to the
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17 363 cathodic surface must be balanced for an efficient production. An excess of current
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19 364 density results detrimental for H₂O₂ generation due to the promotion of parasitic
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21 365 reactions, particularly the reduction of H₂O₂ to H₂O, as discussed previously ³⁰. A
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23 366 further improvement on this regard may be the use of a pressurized-jet aerator to
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25 367 provide larger oxygen flow rates to the MF-FT cell ⁵⁰.

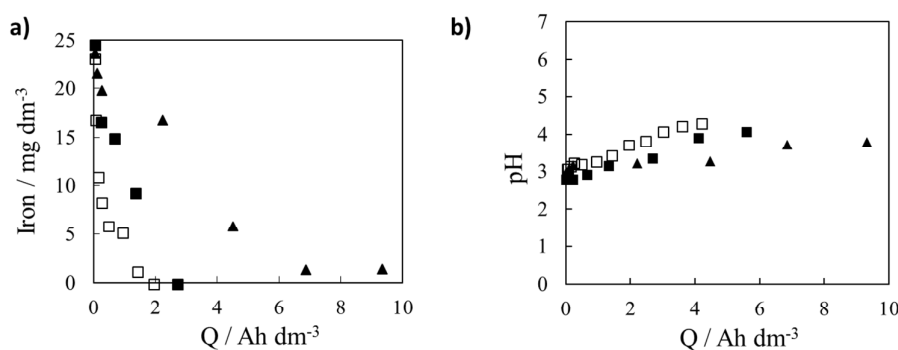
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29 368 Regarding intermediates, it has to be pointed out that the formation of carboxylic acids
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31 369 (tartronic, oxalic and oxamic acids) is in agreement with the mechanisms proposed in
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33 370 the literature and that finally are transformed into carbon dioxide, which becomes an
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35 371 important difference.

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38 372 A last important point that should be highlighted is that the concentration in the bulk of
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40 373 soluble iron added to promote the Fenton reaction was steadily decreasing over time
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42 374 (Figure 8). Considering that clopyralid is removed at early stages and also the
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44 375 carboxylic acids are generated, the final removal of these compounds can mostly be
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46 376 promoted by anodic oxidation due to the depletion of soluble iron that inactivates the
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48 377 Fenton reaction.

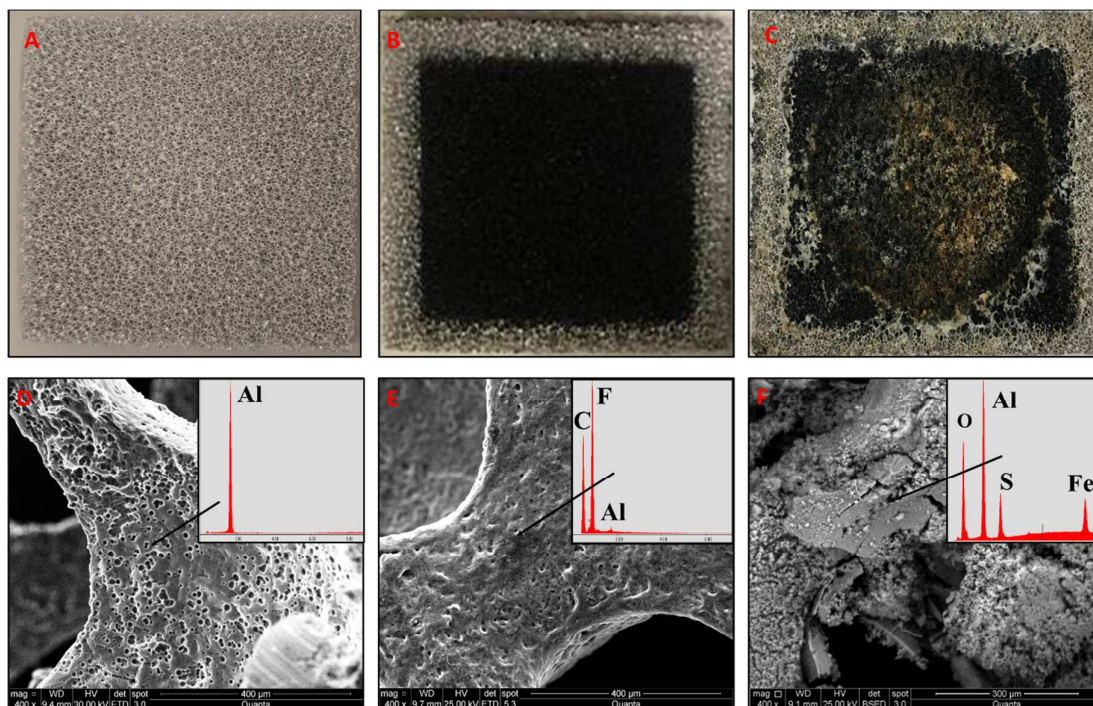
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51 378 The most plausible explanation for this fact is the formation of insoluble iron hydroxide
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53 379 due to the basic local pH on the cathode and the low value of the solubility product
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55 380 constant of Fe(OH)₃. In fact, the occurrence of red particles over the cathodes surface

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3 381 over the treatment support this hypothesis (Figure 9). Images A, B and C in this figure
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5 382 shows the aspect with the naked eye of the Al foam prior to CB/PTFE deposition, once
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7 383 deposited and after the EF tests, respectively. In the latter, red-colored particles
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9 384 deposited onto the surface can be seen.

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12 385 The nature of this deposition was further investigated by a post-mortem characterization
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14 386 by SEM images combined with EDAX analysis. As shown in images D, E y F, the raw
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16 387 material is composed mainly by Al, whereas after the deposition the surface is covered
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18 388 by carbon and fluorine, the components of the CB and PTFE. In contrast, in the last
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20 389 image the presence of amorphous structures composed mainly of Fe, O and also Al
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22 390 observed. The presence of Fe and O is attributed to the presence of insoluble $\text{Fe}(\text{OH})_3$,
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24 391 thus confirming that iron was deposited onto the cathodic surface. Interestingly, also
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26 392 aluminum is detected. It may come from either the dissolution of the Al foam used as
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28 393 cathode or from the Al foil used as current collector. The Al in the bulk may also
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30 394 precipitates in the form of hydroxide due to the low solubility of this compound in basic
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32 395 medium, as in the case of iron hydroxide. This information is quite interesting to
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34 396 continue the development of the reactor by improving the reusability of the cathodic
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36 397 materials by eliminating or substituting those components that may lead to the current
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38 398 of undesirable operational problems.



400 **Figure 8.** Changes iron concentration (a) and pH (b) during the electro-Fenton
 401 technology with microfluidic reactors. □ 10 mA cm⁻²; ■ 30 mA cm⁻²; ▲ 50 mA cm⁻²



402
 403 **Figure 9.** Photographs of aluminum cathode a) before and b) after deposition CB/PTFE
 404 and c) after the test with soil washing fluid. SEM photographs and EDAX analysis of
 405 the cathode d) before and e) after deposition CB/ PTFE and f) after the test with soil
 406 washing fluid.

407 4. Conclusions

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

- 409 • Clopyralid is removed faster in the MF-FT than in a commercial flow cell at 10
 410 mA cm⁻². Likewise, at this current density, flow rate does not have a great
 411 influence on the organic degradation indicating that under this condition it is not
 412 mass transfer controlled.

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3 413 • The combined use of boron-doped diamond as anode and a CB/PTFE Duocel[®]
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5 414 Al foam as cathode in the presence of catalytic amounts of Fe (0.5 mM) leads to
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7 415 synergistic effect for clopyralid removal. Dehalogenation of raw molecule seems
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9 416 to be quite relevant, while coagulation does not seem to play an important role.
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11 417 • The higher the current density the lower is the efficiency of both anodic
12
13 418 oxidation and electrofenton processes.
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15 419 • Improving current distribution and optimization of the aeration system could
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17 420 result in an improvement of the reactor. The main drawback to be solved is the
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19 421 deposition of iron or aluminium particles on cathodic surface.
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45 431 **5. Bibliography**

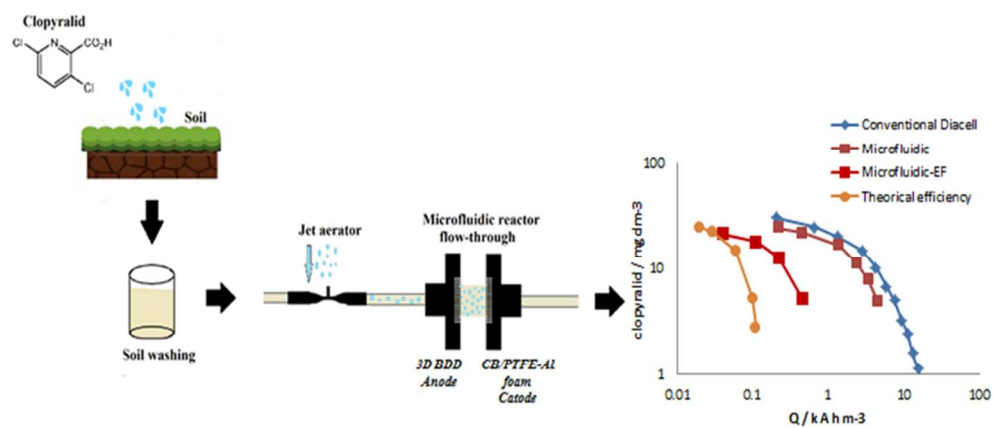
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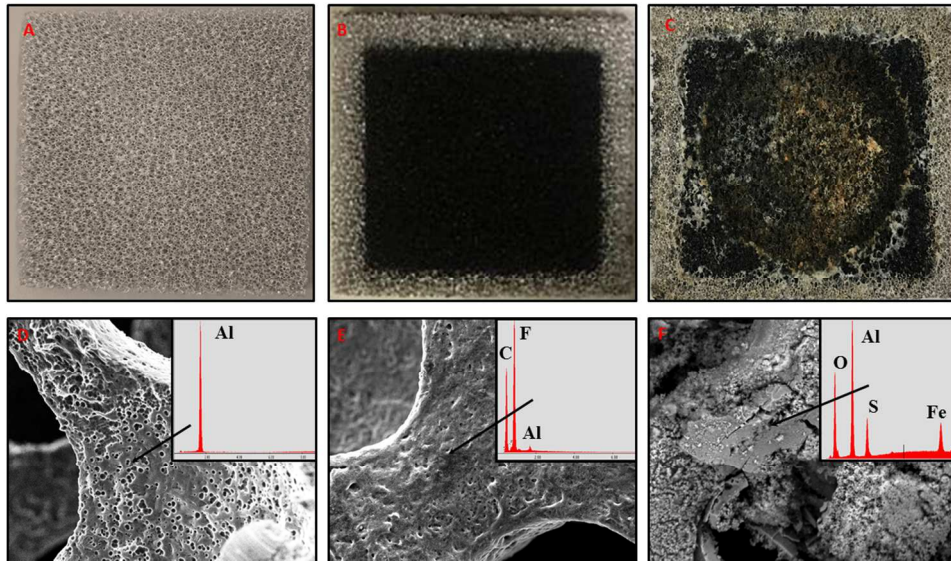
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Graphical Abstract

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