

# Enhanced electrolytic treatment for the removal of clopyralid and lindane

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## Abstract

In this work, it is evaluated the more critical point of a new electrochemical technology for the removal of organic pollutants based on the regeneration of granular active carbon (GAC) (that can be used efficiently to concentrate aqueous wastes) with methanol and in the electrochemical treatment of methanol with conductive diamond electrochemical oxidation (CDEO). The system proposed was studied with lindane and clopyralid. Results show that it is possible the complete removal of the raw pesticides and intermediates formed by electrolyzing these species in methanol media and that both sodium chloride and sodium hydroxide can be used as supporting electrolyte to increase the conductivity of methanol. The cell voltages obtained are quite similar to those obtained during the electrolysis of aqueous wastes. The electrolysis of these dilute solutions does not generate significant concentrations of intermediates and the depletion of the raw pollutant fits well to a pseudo-first order kinetic model. Oxidants capable to oxidize iodide to iodine are produced during the electrolysis in methanol media and they have an important influence on the degradation of the pollutants. The new technology, based on the concentration of the pollutant before electrolysis, allows to remove completely pollutants from soil and soil washing fluids in a more efficient way, although the concentration of pollutant

25 attained and, hence, the efficiency of the overall removal process depends on the  
26 adsorption equilibria of the pollutant in aqueous and methanol media.

27

## 28 **Keywords**

29 Clopyralid; lindane; electrochemical oxidation; GAC adsorption, **BDD**

30

## 31 **Highlights**

- 32 – Lindane and clopyralid can be removed electrolytically from methanol solutions
- 33 – Intermediates formed in the electrolytic process are also depleted
- 34 – Sodium hydroxide or chloride should be added to methanol in order to get an  
35 efficient process
- 36 – Oxidants capable to oxidize iodide to iodine are produced during the electrolysis  
37 in methanol media.

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## 48 **1. Introduction**

49 Treatment of wastes containing low concentration of organic pollutant using anodic  
50 oxidation is frequently very inefficient because of diffusional limitations that occurred in  
51 the electrochemical cell when operated with such wastes (Sirés et al., 2014; Martínez-  
52 Huitle et al., 2015). Nowadays, one of the key challenges for the environmental  
53 electrochemical technology is to overcome these limitations. This may help to make this  
54 technology much more efficient than most of the competing advanced oxidation  
55 processes and it will help to focus the interest of companies, currently having a wait-and-  
56 see position for the application of the very promising electrochemical technologies  
57 (Bebelis et al., 2013; Dewil et al., 2017).

58 Changes in the cell design, promotion in the production of oxidants increasing the  
59 mediated anodic oxidation and/or activation of oxidants electrogenerated (typically by  
60 irradiation of UV light or application of ultrasounds) are the most investigated methods  
61 to overcome this performance limitation (Martínez-Huitle and Brillas, 2009; Panizza and  
62 Cerisola, 2009; Sires and Brillas, 2012; Feng et al., 2013; Oturan and J.J., 2013; Brillas,  
63 2014; Brillas and Martínez-Huitle, 2015; Trelly et al., 2016). However, at this point, it is  
64 important to take in mind that electrolysis of diluted wastes fits well to first order kinetics  
65 (Aquino et al., 2014). This means that reduction of a given percentage of the initial  
66 concentration (f.i. 99%) requires the same applied electric charge, regardless of the value  
67 of the initial concentration. Hence, the more concentrated is the waste, the more efficient  
68 is going to be the electrolytic process. For this reason, another alternative to improve the  
69 performance of the anodic oxidation consists of the pre-concentration of the pollutant.  
70 Our lab is trying to develop this promising alternative using different approaches and, up  
71 to now, we have demonstrated the feasibility of several of them. Thus, the application of

72 coagulation for the concentration of colloids (Muñoz et al., 2017) and the use of  
73 electro dialysis for the concentration of ionic species (Raschitor et al., 2017) have been  
74 successfully evaluated. In this line, a previous rapid communication suggested a new  
75 process based on the concentration of organics by adsorption with GAC and their later  
76 desorption in methanol, shedding light on a new way to enhance the electrolytic treatment  
77 (MuñozMorales et al., 2018). This process was based on a previous observation: removal  
78 of organics in methanol media is feasible (Martin de Vidales et al., 2012, 2013) . In fact,  
79 we noticed that when we evaluated the use of electrochemical oxidation for the removal  
80 of progesterone and triclosan, surprisingly, the removal was very efficient because of the  
81 difficulties in the oxidation of the methanol molecule. This means that methanol could  
82 recover and re-use in the overall treatment in the search of cost-efficient process.

83 This work aims to enlarge the conclusions of this first communication (Muñoz-Morales  
84 et al., 2018) using two different compounds and a more exhaustive characterization. Thus,  
85 it focuses on the electrolytic removal of clopyralid and lindane from methanol solutions,  
86 trying to shed light on this novel proposal of treatment, in order to use it for the  
87 regeneration of GAC (Bouwer and McCarty, 1982; Luekittisup et al., 2015) used for the  
88 treatment of gaseous effluents or for the concentration of diluted wastes through  
89 sequential adsorption- electrolysis. To do this, two pollutants have been chosen because  
90 of their very different polarity: clopyralid ( $C_6H_3Cl_2NO_2$ ) and lindane ( $C_6H_6Cl_6$ ). Both  
91 compounds are common pesticides that are causing serious problems in the environment  
92 due to its high solubility, in the case of clopyralid (Sojic et al., 2009), or in the case of  
93 lindane, because there are many areas very affected by uncontrolled dumping of this  
94 carcinogen pesticide (Dominguez et al., 2018c). In order to increase the ionic conductivity  
95 of methanol up to values in which it may be suitable for the use of electrolysis 3000 mg  
96  $L^{-1}$  of sodium chloride or 2000 mg  $L^{-1}$  of sodium hydroxide were added. In the first case,

97 chloride ions are ionic species contained in the electrolysis while in the second,  
98 methanoate and hydroxyl radicals are the ionic species that explains the ionic conductivity  
99 and promotion of oxidants. Degradations attained during the electrolysis in methanol  
100 media are compared to those that are obtained in the electrolysis in aqueous media.

## 101 **2. Materials & methods**

### 102 **2.1. Chemicals and reagents**

103 Lindane ( $C_6Cl_6$ , >98%), Sodium Dodecyl Sulphate (SDS) (used as solubilizing agent) and  
104 Ethyl Acetate HPLC grade were obtained from Sigma Aldrich (Madrid, Spain) and used  
105 for GC-ECD and GC-MS. Clopyralid were obtained from Cymit Quimica (Barcelona,  
106 Spain) and was used as received. Granular Active Carbon (GAC) was obtained from  
107 Chemviron (Feluy, Belgium). Methanol was obtained from VWR and formic acid  
108 (Sigma-Aldrich, Spain) was used for the mobile phase of HPLC. Sodium chloride and  
109 sodium hydroxide were analytical grade (Sigma Aldrich, Spain). Helium and nitrogen (Air  
110 Air Liquide España, S.A) were used in gas chromatography and helium was filtered by a  
111 Hydrocarbon Cartridge Filter (Thermo Fisher Scientific) previous to its use. Double  
112 deionized water (Millipore Milli-Q System, resistivity: 18.2 M $\Omega$  cm at 25°C) was used to  
113 prepare aqueous solutions.

### 114 **2.2. Analytical techniques**

115 To determine lindane concentration in the liquid phase, an L–L extraction process was  
116 used before the analysis. Aqueous samples (2.0 mL) were analysed following extraction  
117 with ethyl acetate (2.0 mL) for 2 min using a vortex stirrer and 10 minutes with a  
118 centrifugal pump at 4000 rpm for the separation of the phases. Then, organic phase was  
119 transferred to a GC vial. All lindane samples extracted from electrolyzed solution were

120 filtered with 0.22  $\mu\text{m}$  nylon filters before analysis. Likewise, to measure lindane in  
121 methanol, 3 mL of sample was mixed with 3 mL of ethyl acetate using a vortex stirrer for  
122 2 min and an aliquot was transferred to a GC vial. The removal of lindane was quantified  
123 by Gas Chromatography Electron Capture Detector (GC-ECD) with the same conditions  
124 explained in previous paper of this group (Muñoz-Morales et al., 2017). For the  
125 determination of degradation by-products originated in the electrolysis treatment of  
126 lindane a gas chromatography with a mass detector (GC-MS) was used (Thermo Fisher  
127 Scientific DSQ II) using capillary, HP-5MS column with length and diameter of 30 m  
128 and 0.25 mm respectively. The concentrations of the clopyralid and their intermediates  
129 were quantified by HPLC (Agilent 1200 series) using a ZORBAX Eclipse Plus5 C18  
130 analytical column as we reported in our previous work ((Cotillas et al., 2017)). The  
131 concentration of oxidants species was determined iodometrically according to Kolthoff  
132 & Carr (Kolthoff and Carr, 1953) and Standard methods (APHA-AWWA-WPCF, 1998).

### 133 **2.3. Adsorption tests**

134 The adsorption capacity of the GAC was tested with a solution of 100  $\text{mg L}^{-1}$  of pollutants  
135 in methanol and milli-Q water as solvents. These solutions were mixed with different  
136 quantities of GAC (from 0.01 to 0.1  $\text{g L}^{-1}$  with clopyralid and 0.5 to 15.0  $\text{g L}^{-1}$  in the case  
137 of lindane) to obtain the different isotherms. Additionally, in lindane aqueous solutions  
138 10  $\text{g L}^{-1}$  of SDS are added to increase the solubility of this compound (water solubility  
139 limit is 7.3  $\text{mg L}^{-1}$  at 25°C [28]). Both experiments were carried out in closed glass bottles  
140 of 100 mL placed in an incubating orbital shaker (VWR) with a stirring speed of 180 rpm  
141 for 24 h to guarantee the thermodynamic and kinetic equilibrium.

### 142 **2.4. Electrochemical oxidation of synthetic solutions**

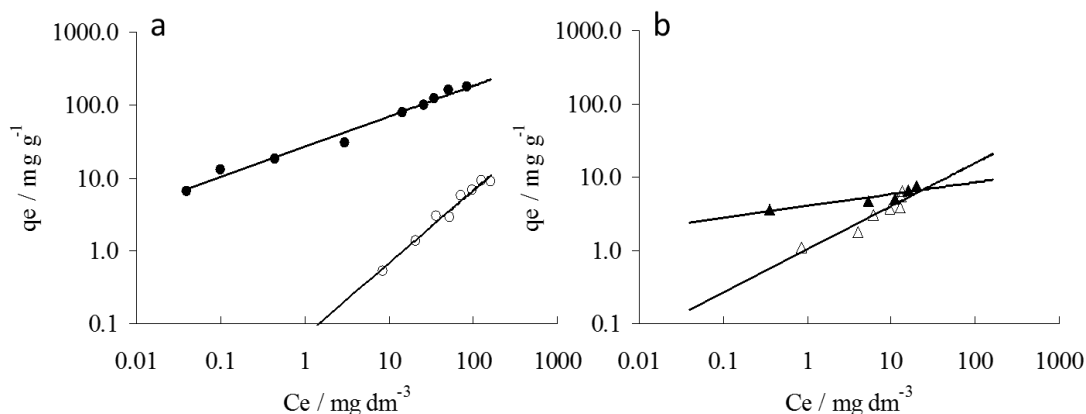
143 Synthetic solutions were prepared with 100 mg L<sup>-1</sup> of the pollutant and 50 mmol of  
144 electrolyte (NaCl and NaOH) in methanol and water to determine the depletion of lindane  
145 and clopyralid. Batch tests were conducted in a 1 L cylindrical glass reactor in a bench-  
146 scale electrochemical setup described elsewhere (Cotillas et al., 2017), using a peristaltic  
147 pump at flow rate of 60 L h<sup>-1</sup>. A condenser with circulating water at 25 ± 1 °C was used  
148 to prevent the loss of volatile organic compounds (VOCs) to the gas phase. The anode  
149 was a 78 cm<sup>2</sup> BDD film (Adamant Technologies, Switzerland), (500 ppm of B, 2.25 µm  
150 thickness) and p- type Si as support and a stainless steel of similar size was the cathode.  
151 The interelectrode gap was 1.6 mm. The electric current was provided by a Delta  
152 Electronika ES030-10 power supply (0-30 V, 0-10 A). Current density applied in  
153 galvanostatic mode was in the range of 20- 30 mA cm<sup>-2</sup> according with typical values  
154 studied in previous works (MuñozMorales et al., 2018). Prior to use, the electrode was  
155 polarized for 10 min in a 0.035 M Na<sub>2</sub>SO<sub>4</sub> solution at 15 mA cm<sup>-2</sup> to remove any  
156 impurities from its surface. Samples (0.02 L) were collected in the glass reactor.

157

### 158 **3. Results and discussion**

159

160 **Capability of GAC adsorption to concentrate pollutants.** Fig. 1 shows the adsorption  
161 isotherms of clopyralid and lindane onto GAC in water and methanol obtained at room  
162 conditions for the sake of comparison.



163

164 Figure 1. **a.** Adsorption isotherms of clopyralid in milli-Q water (●) and methanol (○) on  
 165 GAC particles. **b.** Adsorption isotherm of lindane with 20g L<sup>-1</sup> SDS in milli-Q water (▲)  
 166 and methanol (△) on GAC particles.

167 As seen, in both cases, the experimental data fit well Freundlich isotherm models (see  
 168 (1), where  $q_e$  is the quantity of pollutant adsorbed per gram of GAC and  $C_e$  is the  
 169 concentration of the pollutant in the liquid phase), especially in the case of clopyralid,  
 170 being the fitting parameters and the regression coefficients shown in Table 1.

171 
$$q_e = k c_e^{\frac{1}{n}} \quad (1)$$

172 Table 1. Freundlich fitting parameters of clopyralid and lindane isotherm in water and  
 173 methanol.

	k	n	R <sup>2</sup>
Clopyralid in water	0.08	1.0	0.97
Clopyralid in methanol	26.51	2.23	0.98
Lindane in water	1.04	1.70	0.89
Lindane in methanol	4.07	6.20	0.81

174

175 The adsorption capacity depends significantly on the solvent, being much higher in  
 176 aqueous media than in methanol. This is especially important for the case of clopyralid,



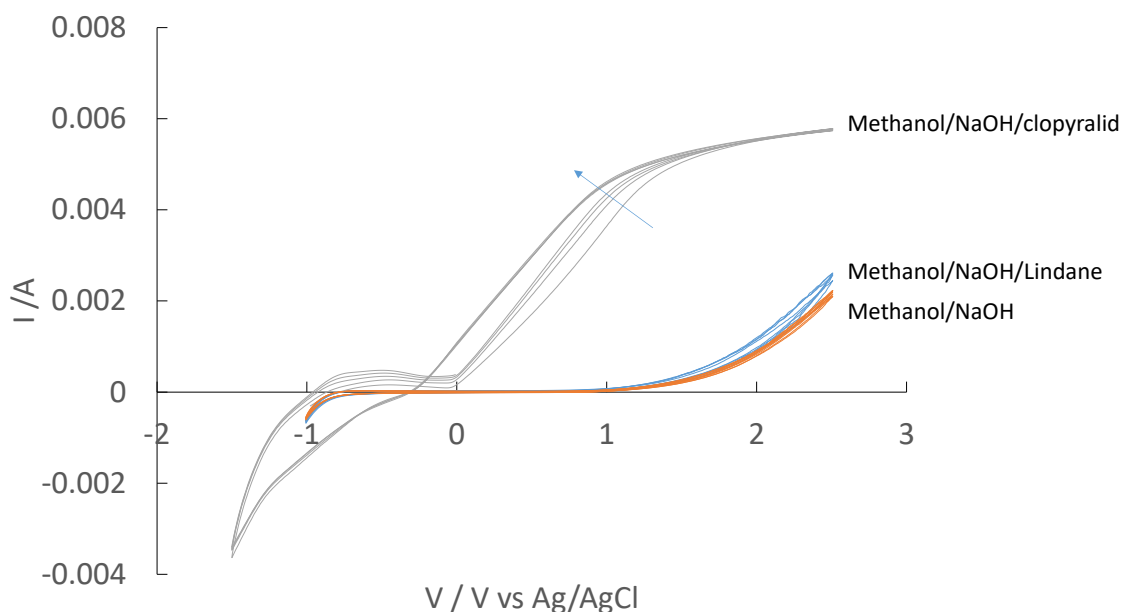
177 in which more than two log units pointed out the very different interaction of the surface  
178 of GAC with the organic in the presence of water or methanol. Regarding lindane,  
179 differences are more important for low concentration, but adsorption capacities are  
180 overlapped in the higher range. At this point, it is worth to take in mind the low solubility  
181 of lindane in water that make necessary to be emulsified with sodium dodecyl sulfate  
182 (SDS) in order to reach these concentrations. Hence, the process is not a pure adsorption  
183 but a much more complex process, which involves interactions of GAC particles with  
184 free lindane, free SDS and different types of lindane-SDS micelles. However, results  
185 clearly point out that in the solubility range the behavior is just the same of that observed  
186 for clopyralid. Hence, GAC can be used to concentrate these pollutants and desorption of  
187 GAC used in the treatment of gaseous effluents in methanol is a potentially good choice.

188

189 **Electrolysis of chlorinated organics in methanol supporting electrolyte.** Once  
190 demonstrated that GAC adsorption can be used to concentrate pollutants, the next step in  
191 the evaluation of the chlorinated hydrocarbon removal technology consists of the  
192 electrolysis of the methanol solutions.

193 Fig. 2 shows the voltammetric response of the diamond electrodes in three different  
194 electrolytes: methanol/NaOH, alone, with 100 mg L<sup>-1</sup> of clopyralid and with 100 mg L<sup>-1</sup>  
195 of lindane.

196



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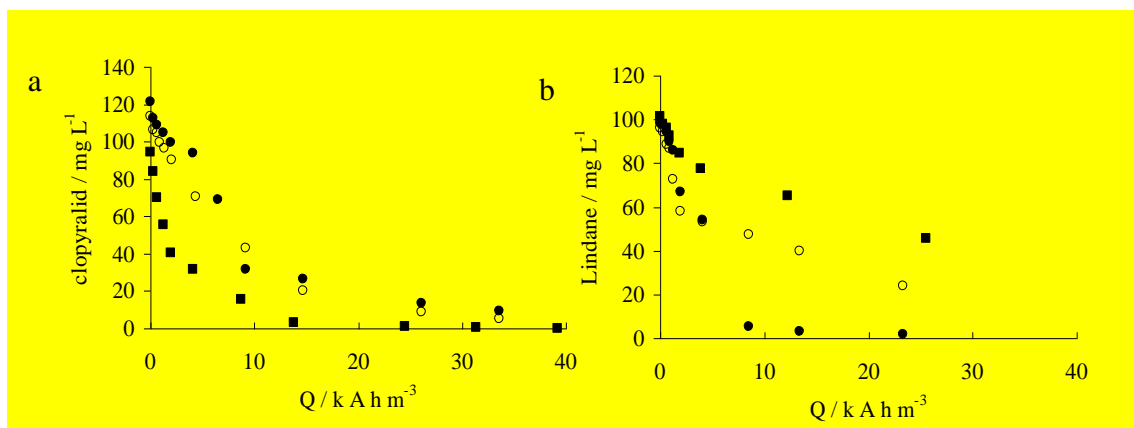
198 Figure 2. Cyclic voltammograms (5 cycles) on p-Si/BDD electrodes of CH<sub>3</sub>OH/NaOH  
 199 (orange line), CH<sub>3</sub>OH/NaOH/lindane (blue line) and CH<sub>3</sub>OH/NaOH/clopyralid (grey  
 200 line). Pollutant concentration: 100 mg L<sup>-1</sup>. Auxiliary electrode: Pt; Reference electrode:  
 201 Ag/AgCl. Scan rate: 50 mV s<sup>-1</sup>.

202

203 As it can be seen, there is an exceptionally large electrochemical window for the  
 204 electrolysis with diamond electrodes of methanol solutions, which is closely similar to  
 205 that observed in aqueous solutions (Rodrigo et al., 2001). In addition, in both cases, the  
 206 addition of the pollutant to the CH<sub>3</sub>OH/NaOH solution leads to an increase in the  
 207 intensity, clearly pointing out that there is, at least, a direct oxidation pathway to explain  
 208 the degradation of this chlorinated hydrocarbons. It is particularly important the  
 209 differences observed between clopyralid and lindane, with a much higher response in the  
 210 former case. This indicates that the direct electrochemical reactivity of this molecule is  
 211 much higher, although lindane also undergoes important changes. A possible explanation  
 212 can be the great reactivity of the pyridine group of clopyralid.

213 Fig. 3 shows the removal of the two studied pollutants during the electrolysis of methanol  
214 solutions containing 120 and 100 mg of clopyralid and lindane, respectively. Results  
215 obtained during the electrolysis of aqueous solutions with the same concentration of  
216 chlorinated hydrocarbon species are also shown for comparison purposes, although it  
217 should be taken into account that in a real application the concentration of the pollutants  
218 in methanol media would be much higher than in water, especially in the case of  
219 clopyralid. The first important observation that can be made is that both, clopyralid and  
220 lindane, can be completely removed not only in aqueous but also in methanol media. In  
221 addition, opposite to what it could be expected, the oxidation of lindane in aqueous media  
222 is not more efficient than those obtained in methanol, despite in this later case hydroxyl  
223 radicals mediated-oxidation is not the key to explain the removal of the organics, because  
224 simply they are not produced in methanol media. This may be related to the presence of  
225 SDS, which is required to increase lindane solubility thanks to the formation of micelles.  
226 These SDS-lindane micelles do not seem to be so accessible to oxidants as lindane in  
227 methanol solution. The degradation of both clopyralid and lindane in this organic media  
228 is a very important outcome and, in fact, as it was described above, there are very few  
229 references (Martín de Vidales et al., 2012b; Martín de Vidales et al., 2012a) in which the  
230 electrolysis of organics in methanol as supporting electrolyte had been studied.

231



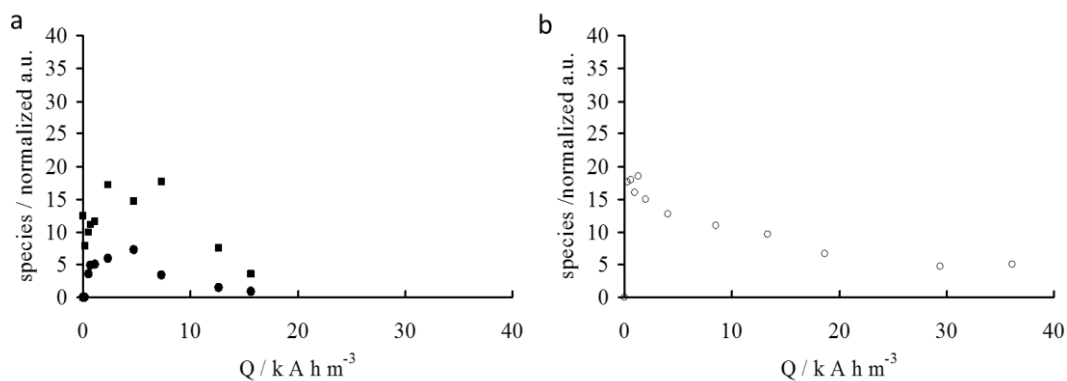
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233 Figure 3. Electrolysis of clopyralid (part a) and lindane (part b) in aqueous or organic  
234 media: (■) Aqueous media (with 3000 mg NaCl L<sup>-1</sup> in figure 3a and 20 g L<sup>-1</sup> of SDS in  
235 figure 3b), (●) methanol media with 3000 mg NaCl L<sup>-1</sup>, (○) methanol media with 2000  
236 mg NaOH L<sup>-1</sup>. Current density: 250 A m<sup>-2</sup>.

237 A very important observation is that in each case, the decay fits well to first order kinetic,  
238 not only in aqueous but also in methanol media. In aqueous media, this is an expected  
239 behavior for the electrolysis of diluted solutions of organics, which is explained in terms  
240 of a mixed oxidation mechanisms that includes the diffusion control of the direct  
241 processes and mediated oxidation. Opposite, in methanol media the mechanisms are not  
242 as studied as in aqueous media but the good mathematical fitting of results suggests that  
243 both mechanisms can be also responsible of the decay of the organics in this media. The  
244 first order kinetics constants of the decays are shown in Table SM-1. As it can be seen,  
245 for the oxidation of clopyralid, the pseudo-first order kinetic constants are similar in  
246 methanol media and this value increases up to the double in aqueous media. However,  
247 results are reverse for lindane. In this case, the less efficient process is the degradation in  
248 aqueous media with a very low value of the pseudo first kinetic constant. This parameter  
249 increases importantly in the electrolysis of methanol with sodium hydroxide as supporting  
250 electrolyte and even more importantly in the case of methanol with sodium chloride. In  
251 any case, what it is important to point out is that kinetic constants in methanol are quite  
252 close among them and that there are not major differences with those obtained in water.  
253 Hence, kinetic constants obtained using methanol solvent are higher than those obtained  
254 by Dominguez et al (Dominguez et al., 2018b) in the degradation of lindane solutions by  
255 electro-Fenton, confirming the high capability of electrolysis with diamond electrodes  
256 (Dominguez et al., 2018a).

257

258 One very important point are the intermediates formed in methanol media. We used GC-  
259 ECD and GC-MS to monitor the concentration of the raw molecule and reaction products  
260 in the case of lindane and HPLC-UV in the case of clopyralid. It is important to note that  
261 the total organic carbon (TOC) is not monitored because the huge concentration of  
262 methanol represents a much more high value than the contribution from the pollutant  
263 (MuñozMorales et al., 2018). Changes during the electrolysis are shown in Fig. 4 for  
264 lindane and in Fig. 5 for clopyralid. The first important observation: the oxidation of  
265 lindane in aqueous media leads to two intermediates (1,3 dichlorobenzene and 1,1,3,3-  
266 tetrachloro 2-propanone) with a very low area as compared with the that of the raw  
267 lindane, and that finally disappear, indicating that the technology can destroy completely  
268 the compound. Lindane intermediates were identified and confirmed with GC-MS after  
269 comparing the matching percentage with NIST library. This is not the case of the  
270 electrolysis in methanol media, where harsher conditions were clearly reached: no  
271 intermediates were found in methanol with sodium chloride and only one intermediate  
272 (3,4,5,6 tetrachlorocyclohexene, and at a very low concentration) was found in the  
273 electrolysis with hydroxyl ions (Fig. SM-3). This means that oxidation carried out in this  
274 media should be very aggressive and once lindane molecule starts its oxidation it proceeds  
275 even in a faster way in methanol than in water, up to the complete removal of the  
276 pollutants. Results obtained are according to the study carried out by Dominguez et al  
277 (Dominguez et al., 2018c) where a plausible reaction pathway for lindane oxidation has  
278 been proposed based on the identified chlorinated and hydroxylated intermediates and the  
279 resulting short-chain carboxylic acids.

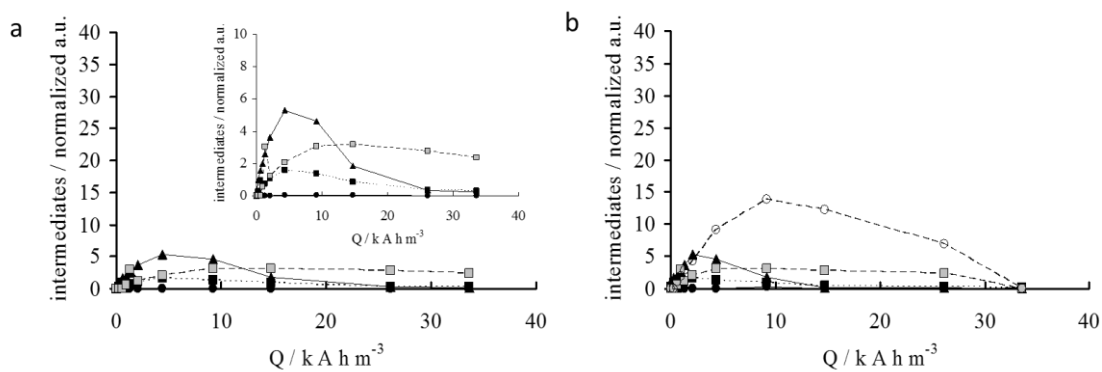


280

281 Figure 4. Main intermediates detected by GC-MS during the electrolysis of Lindane in  
 282 aqueous media with 20 mg SDS L<sup>-1</sup> (part a) and in methanol with 2000 mg NaOH L<sup>-1</sup>  
 283 (part b): (●) 1,3-dichlorobenzene, (■) 1,1,3,3-tetrachloro 2-propanone, (○) 3,4,5,6-  
 284 tetrachlorocyclohexene. Current density: 250 A m<sup>-2</sup>.

285

286 In the electrolysis of clopyralid up to four intermediates (carboxylic acids) were found in  
 287 methanol supporting electrolyte, all of them in rather low concentrations and degraded  
 288 during the electrolysis. As expected the most important are the oxalic and the oxamic  
 289 acids and this can be explained in terms of their well-known lower oxidizability by AOPs.  
 290 In fact, in literature (Da Pozzo et al., 2005; Ozcan et al., 2010) it is reported that clopyralid  
 291 suffers a rapid dechlorination process in the cathode with the subsequent release of  
 292 chlorine anions. Then, pyridine ring is oxidized leading to the generation of aliphatic acids  
 293 as main reaction intermediates (Fig SM-4). The area of intermediates is very low as  
 294 compared to that of the initial clopyralid and this supports the previous comment on the  
 295 harsher oxidation conditions generated that it is typically observed when treating low  
 296 concentrated wastes.



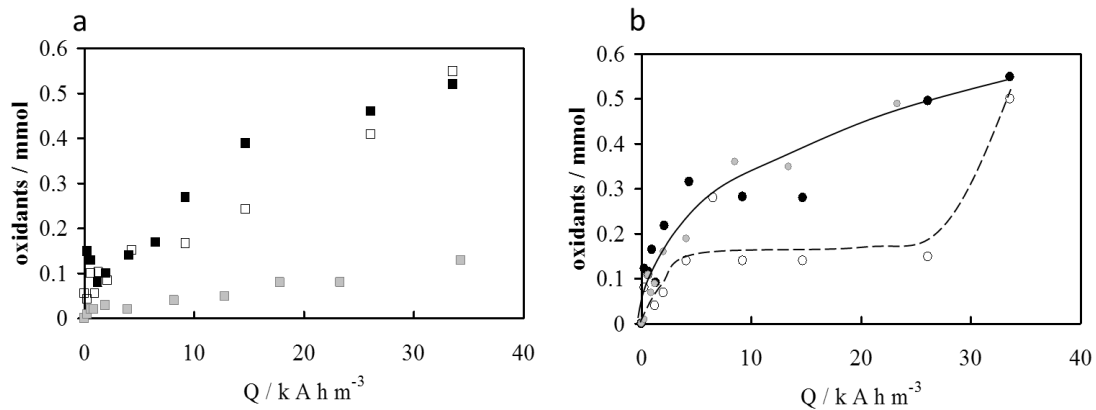
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298 Figure 5. Main intermediates detected by HPLC during the electrolysis of Clopyralid in  
 299 methanol with 3000 mg NaCl L<sup>-1</sup> (part a) and 2000 mg NaOH L<sup>-1</sup> (part b): (▲) tartronic  
 300 acid, (■) oxalic acid, (◼) oxamic acid, (●) non-identified intermediate, (○) non-  
 301 identified intermediate. Current density: 250 A m<sup>-2</sup>.

302

303 A very important point regarding the mechanisms may come from the comparison of the  
 304 production of oxidants in the electrolyte in the presence and absence of organics, which  
 305 is shown in Fig. 6. The differences have to be explained in terms of the reactivity of these  
 306 oxidants with the organics contained in the electrolyte, which in turn, have to depend on  
 307 the nature of the organics. In the studies carried out here, it can be seen that there is a net  
 308 consumption of oxidants in the electrolysis in methanol media (Fig. 6), which is very  
 309 important for lindane in the case of methanol with hydroxyl ions and for clopyralid in the  
 310 case of methanol with chloride. Many of these compounds are oxychlorinated species,  
 311 which have a paramount importance in all the oxidation process with NaCl (Dominguez  
 312 et al., 2018a). In the first case, methanoate and hydroxyl ions can produce small amounts  
 313 of hydrogen peroxide while in the second case gaseous chlorine can be the responsible  
 314 for the observed change observed. Additionally, the plane zone may be related to the  
 315 formation of intermediates and their reactivity with oxidants formed. This behavior

316 confirms the differences found in the oxidizability of the organic by each of these  
317 oxidants promoted.



318  
319 Figure 6. Oxidants produced during the electrolysis of methanol solutions with 2000 mg  
320 L<sup>-1</sup> of NaOH (part a) or NaCl (part b): (■, ●) without organic, (□, ○) with clopyralid,  
321 (■, ●) with lindane. Current density: 250 A m<sup>-2</sup>.

322  
323 A final point regarding the evaluation of the technology is the cell voltage. In Fig. SM-1,  
324 the time course changes of the cell voltage in the different experiments carried out in this  
325 work are shown. As it is well-known, in electrolytic processes, the operating cost (in  
326 particular, the energy spent) is directly related to it and one of the main potential  
327 weaknesses of using a non-aqueous media may be the low ionic conductivity and,  
328 consequently, the important ohmic losses associated with this low value. It is important to  
329 consider that this important parameter is related to many inputs of the electrochemical  
330 process, including not only electrolyte but also cell configuration, current feeders, etc.  
331 Anyhow, as seen, the changes in the cell voltage during the electrolysis in the three  
332 supporting electrolytes indicates that the supporting media does not play a very important  
333 role. Thus, except for the initial high value observed in the electrolysis of lindane in  
334 methanol/ sodium hydroxide as supporting electrolyte, differences (once the cell is in  
335 operation) are not very important and even, in the case of clopyralid they are in favor of



336 using methanol media. This confirms that this technology is not only promising but a real  
337 challenge in the treatment of organics using electrochemical oxidation.

338

#### 339 **4. Conclusions**

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

- 341 – Clopyralid and lindane can be efficiently removed from methanol solutions using  
342 anodic oxidation with diamond anodes.
- 343 – Similarly to aqueous solution, the electrolysis of these dilute solutions does not  
344 generate significant concentrations of intermediates and the raw pollutant is  
345 depleted completely from the electrolyte, fitting well to a pseudo first order kinetic  
346 model.
- 347 – Oxidants capable to oxidize iodide to iodine are produced during the electrolysis  
348 in methanol media and they have an important influence on the degradation of the  
349 pollutants.
- 350 – Both sodium chloride and sodium hydroxide can be used to increase the  
351 conductivity of methanol and cell voltages obtained are quite similar to those  
352 obtained during the electrolysis of aqueous wastes.

353

#### 354 **5. Acknowledgements**

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358

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