



25 **Keywords**

26 Conductive diamond, ultrasound irradiation, electrolysis, herbicide, 2,4-D

27 **Highlights**

28 - Total mineralization can be successfully attained by electrolysis with bipolar  
29 electrodes

30 - Combined US irradiation and electrolysis lead to a very efficient process

31 - Lower cell voltages in the US irradiation process reduce the energy demand

32 - US irradiation promotes to production of chlorates and not perchlorates

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38

## 40 **Introduction**

41 Electro-oxidation has been extensively studied in recent years for the remediation of  
42 wastewater [1, 2]. Its main advantages compared to other advanced oxidation processes  
43 are robustness and high efficiency [3-6]. The optimum performance of this technology  
44 depends on many factors, including electrode material, cell arrangement, waste  
45 composition parameters (pH, supporting electrolytes) and operating conditions  
46 (temperature and current densities) [7]. Most papers found in the literature focus on the  
47 influence of waste composition and operating conditions on treatment results; the  
48 presence of chloride in the waste and the significance of current density as the main  
49 operating parameter are largely unexamined [8, 9]. Likewise, in comparing materials, the  
50 most promising electrode material is conductive-diamond coating on a p-Si support [10].  
51 These electrodes have demonstrated very good properties, which lead to high production  
52 of hydroxyl radicals and many other oxidants [11-13].

53 In comparing cell arrangement, most studies have been performed at bench scale with  
54 simple cells with anodic area varying from 3 to 140 cm<sup>2</sup>. However, there is a lack of  
55 assessment of cell design and scaling up reactors using commercial cells [14]. In  
56 particular, the use of bipolar electrodes is a promising for scaling up the remediation of  
57 wastewater [15, 16]. Likewise, the combination of ultrasound irradiation and  
58 electrochemical oxidation is a promising alternative worth studying [17-20]. Ultrasonic  
59 irradiation effectiveness is based on cavitation and improvements in mass transfer. The  
60 hydrodynamic cavitation process involves the formation, growth, and sudden collapse of  
61 micro-bubbles. These gas bubbles in aqueous solution lead to the thermal dissociation of  
62 water molecules into  $\cdot\text{H}$  and  $\cdot\text{OH}$ . This powerful oxidant is responsible for harsh  
63 oxidation conditions [21-25]. Ultrasound irradiation combined with electro-oxidation can

64 be very effective for the removal of different organic pollutants such as dyes [26-28],  
65 phenolic compounds [29-31], organo-chlorinated species [32], pharmaceutical products  
66 [23, 33, 34], phthalates [25, 35] and herbicides [24, 36]. Regarding herbicides, Bringas  
67 [24] evaluated the degradation kinetics of diuron using low-frequency ultrasound  
68 irradiation coupled to electrochemical oxidation with a boron-doped diamond anode.  
69 Synergistic behavior was observed when both processes were combined, improving the  
70 mineralization kinetics by 43 %. Escaplez [32] reported higher degradation efficiency of  
71 trichloroacetic acid using a sono-electrochemical process with platinized titanium (Pt/Ti)  
72 mesh as the anode material. Garbellini [30] demonstrated that the highest levels of decay  
73 of pentachlorophenol were attained using sono-electrolysis rather than silent electrolysis  
74 using a diamond anode. These results can be explained by increased mass transport,  
75 minimization of inactivation electrode effects and the simultaneous generation of  
76 hydroxyl radicals by both ultrasound irradiation and the polarized BDD surface.

77 Herbicide remediation is a major problem, and various technologies are currently being  
78 developed to solve it [37-39]. This work aims to assess the performance of a combined  
79 US irradiation - electrolytic treatment for the removal of soluble organic herbicides from  
80 water. A commercial electrochemical cell Diacell type 401, equipped with bipolar boron-  
81 doped diamond electrodes and a US horn, was used to demonstrate the scalability of the  
82 system and the role of US irradiation in this promising technology. Synthetic wastewater  
83 consisted of solutions of 2,4-D herbicide with sodium chloride. Two reactions are  
84 expected to develop simultaneously in the reactor: the depletion of an organic herbicide  
85 and the oxidation of chlorides to perchlorates. This later reaction prevents the application  
86 of this technology, and thus, the aim is not to optimize the environmental remediation  
87 process (obviously, in such an application, production of perchlorate should be prevented)  
88 but simply to increase knowledge about the scalability of this type of process, taking

89 advantage of the simultaneous occurrence of both reactions during the electrolysis of  
90 synthetic wastewater. The well-known oxidation of chloride with diamond anodes will  
91 help to obtain relevant conclusions about the influence of electro-generated oxidants.

## 92 **Materials and methods**

### 93 **2.1. Chemicals**

94 All chemicals, including sodium sulfate and sodium chloride (Fluka, Spain), 2,4-  
95 D (dichlorophenoxyacetic acid), hydroquinone, 1,4-benzoquinone, 4-chlororesorcinol, 2-  
96 chlorophenol, 2,4-dichlorophenol (Sigma-Aldrich, Spain), were analytical grade and used  
97 as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used as the mobile  
98 phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 M $\Omega$  cm at 25  
99 °C) was used to prepare all solutions.

100

### 101 **2.2 Experimental setup**

102 All electrolysis was conducted in a DiaCell® type 401 supplied by Adamant  
103 Technologies (Switzerland). The DiaCell® module can be assembled with one, two, three  
104 or four compartments, each of them fed with wastewater by internal parallel inlets. The  
105 boundary electrodes are monopolar Si/BDD, and when multiple compartments are in use,  
106 the separating electrodes are floating bipolar Si/BDD electrodes. All electrodes were  
107 circular (100 mm diameter) with a geometric area of 70 cm<sup>2</sup>. The inter-electrode gap was  
108 approximately 9 mm. The BDD coating had a film thickness of 2 mm and a resistivity  
109 100 m $\Omega$ •cm. The boron concentration was 500 ppm, and the ratio sp<sup>3</sup>/sp<sup>2</sup> >150. The BDD  
110 electrode was cleaned for 10 min in a 1 M Na<sub>2</sub>SO<sub>4</sub> solution at 15 mA cm<sup>-2</sup> prior to  
111 electrolysis assays. Sono-electrochemical experiments were performed in the electrolysis  
112 set up using the same fluid-dynamic conditions. For US, the electrolysis cell was equipped

113 with an ultrasound generator UP200S (Hielscher Ultrasonics GmbH) equipped with a  
114 titanium glass horn measuring 40 mm in diameter and 100 mm in length. The output used  
115 was continuous wave mode with percentage of cycle of 100% emitting 24 kHz, and 200  
116 W ultrasonic power was put into to a 1000 mL cylindrical cell. More experimental details  
117 of the flow cell reactor and a schematic representation of the ultrasound-assisted system  
118 can be found elsewhere [16] .

119

120

### 121 **2.3 Analysis procedures and methods**

122 Electrolysis was performed using 1.2 dm<sup>3</sup> of a solution containing 100 mg dm<sup>-3</sup> 2,4-D at  
123 natural pH (3.5) and 3 g L<sup>-1</sup> NaCl as the supporting electrolyte. Tests were performed  
124 galvanostatically (the external current intensity applied was 10 A) and in discontinuous  
125 mode. Water was recirculated between the cell and an auxiliary tank at a constant flow  
126 rate (26.4 dm<sup>3</sup> h<sup>-1</sup>) to favor mixing conditions, gas stripping and temperature regulation.  
127 A heat exchanger coupled with a controlled thermostatic bath was used to maintain the  
128 temperature at 25 °C.

129 All samples taken from electrolyzed solutions were filtered with 0.45 µm nylon filters  
130 from Whatman before analysis. Measurements of pH were performed with an InoLab  
131 WTW pH-meter. The decay of herbicide and the evolution of aromatic products were  
132 followed using reversed-phase chromatography, Total Organic Carbon (TOC) and  
133 Chemical Oxygen Demand (COD). The chromatography system was an Agilent 1100  
134 series coupled to a UV detector. A Phenomenex Gemini 5 µm C18 analytical column was  
135 used. The mobile phase consisted of 60 % acetonitrile /40 % water with 2 % acetic acid  
136 (flow rate = 0.4 cm<sup>3</sup> min<sup>-1</sup>). The UV detection wavelength was 280 nm, the temperature  
137 was kept at 25 °C, and the volume injection was 20 µL. A calibration graph was

138 constructed in the range of 0.1 to 150 mg dm<sup>-3</sup>, and regression analysis showed a linear  
139 relationship with a correlation coefficient  $r = 0.998$ . The detection limit was 0.018 mg  
140 dm<sup>-3</sup>.

141 The Total Organic Carbon concentration was monitored using a Multi N/C 3100 Analytik  
142 Jena analyzer. TOC reproducibility showed a standard error below 2%. Chemical Oxygen  
143 Demand (COD) was monitored using standard kits from Merck. Solutions were oxidized  
144 by digestion for 2 h at 150 °C in a block ECO 25 Thermoreactor (Velp Scientifica). Then,  
145 after the ambient temperature was reached, the absorbance of the samples was read at 600  
146 nm in a spectrophotometer (Hach DR 2000). Samples containing chloride concentrations  
147 above 2 g dm<sup>-3</sup> were diluted as recommended.

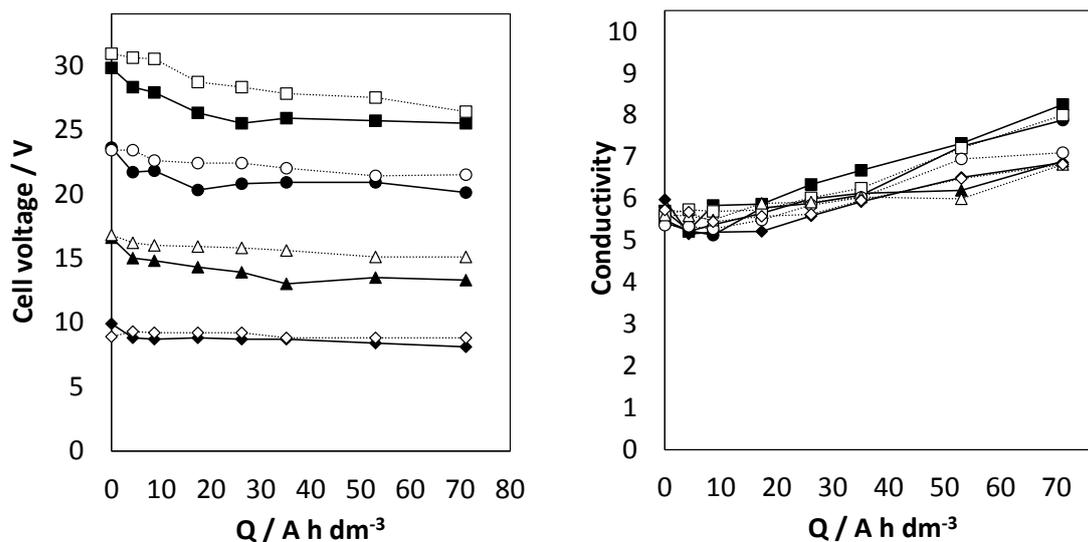
148 Chloride anions (Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) were determined using ion chromatography with a  
149 Shimadzu LC-20A equipped with a Shodex IC I-524A column: mobile phase, 2.5 mM  
150 phthalic acid at pH 4.0; flow rate,  $1 \times 10^{-3}$  dm<sup>3</sup> min<sup>-1</sup>. Hypochlorite (HClO<sup>-</sup>) was  
151 determined by titration with 0.001 M As<sub>2</sub>O<sub>3</sub> in 2.0 M NaOH. Pretreatment of the samples  
152 was performed by adding  $2 \times 10^{-3}$  dm<sup>3</sup> of 2.0 M NaOH to increase the pH. Peroxosulfate  
153 was determinate iodometrically according to Kolthoff & Carr (1953) [40].

154

## 155 **Results and discussion**

156 Figure 1 shows the changes in the cell potential during electrolysis and sono-electrolysis  
157 of synthetic wastewater containing the herbicide 2,4-D as the organic pollutant and  
158 sodium chloride as the salt.

159



160

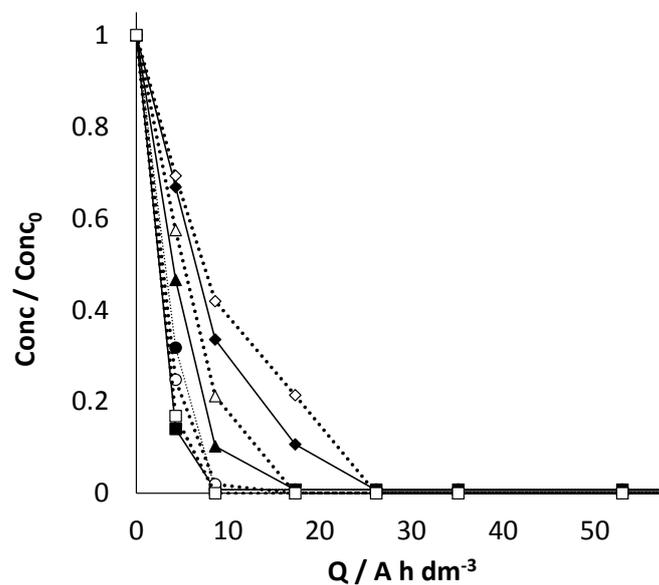
161 **Figure 1.** Changes in the cell voltage and conductivity during the sono-electrochemical  
 162 (solid symbols) and silent electrochemical (open symbols) oxidation of synthetic  
 163 wastewater using a DIACELL 401 equipped with (■, □) 3 compartments; (●, ○) 2  
 164 compartments; (◆, ◇) 1 compartment; (▲, Δ) no compartments.

165

166 In all tests, the cell voltage decreased slightly during the electrolytic and sono-electrolytic  
 167 treatments down to a constant value. This behavior is typical of most electrochemical  
 168 remediation tests and can be related to the change in the conductivity of the electrolyte  
 169 (and hence with the resulting ohmic drop), as seen in Figure 1b. These changes can be  
 170 related to the electrolysis of water (which occurs on the surface of both electrodes) and to  
 171 a lesser extent the formation of intermediates and final products from the electrolysis of  
 172 2,4-D and chloride. Changes are highly significant and within the 5.6-19.9% range, with  
 173 higher observed in the case of the coupled US irradiation technology. The lower cell  
 174 voltage value in the sono-electrolytic cell, which is 2.9-9.6 %, is lower than in the  
 175 corresponding silent electrolytic test (using only the electrochemical process). Cell  
 176 voltage is directly related to the energy cost in a cell in galvanostatic operation mode, and

177 this decrease reflects a decrease in the energy cost associated with electricity. In addition,  
 178 the changes in the cell potential are higher in the sono-electrolytic cell, although there is  
 179 no direct correspondence with the increase in electrolyte conductivity. Lower cell  
 180 voltages in the application of US irradiation could partially reduce the energy demand of  
 181 this irradiation technology.

182 Figure 2 shows the changes in the concentration of 2,4-D during test treatments. US  
 183 irradiation has a very positive effect on the oxidation of 2,4-D and favors faster oxidation  
 184 of the herbicide.



185

186 **Figure 2.** Relative 2,4-D decay as a function of the applied charge per unit volume of  
 187 electrolyzed solution ( $Q_{ap}$ ) during the sono-electrochemical (solid symbols) and silent  
 188 electrochemical (open symbols) oxidation using a DIACELL 401 equipped with (■, □) 3  
 189 compartments; (●, ○) 2 compartments; (◆, ◇) 1 compartment; (▲, △) no compartments.

190

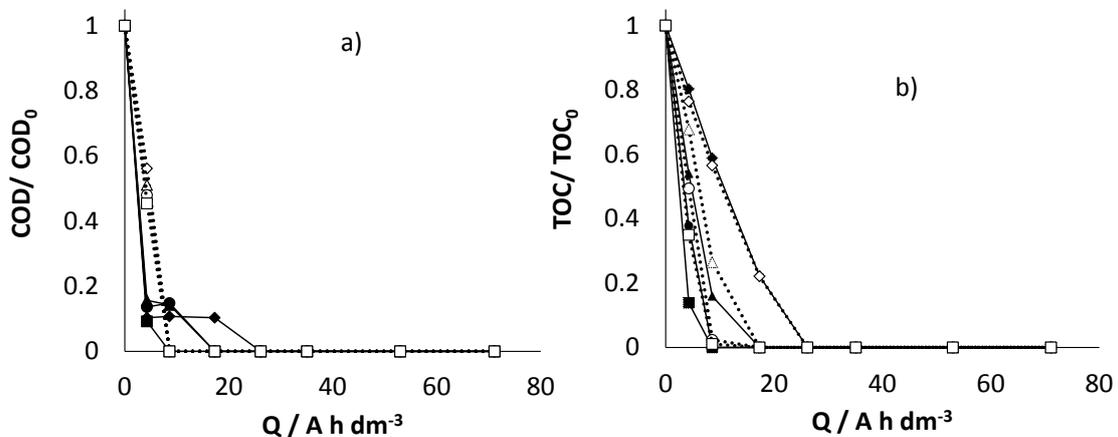
191 The external current charge passed required for the complete oxidation of 2,4-D decreases  
 192 with the number of bipolar electrodes; the cell with three bipolar electrodes required 2.5

193 times lower current charge. These observations can be easily explained by taking into  
194 account the internal electric charge supplied by the bipolar electrodes, transferring  
195 electrons from one face of the electrode to the other, without passing through an external  
196 circuit. The difference between the silent electrolysis and the sono-electrolysis decreased  
197 when the number of bipolar electrodes increased; however, this decrease only indicates  
198 that the raw herbicide is oxidized but it does not mean that the organic pollutant is  
199 depleted or that the treated water is less hazardous.

200

201 Both pollutant depletion and hazards are assessed using COD and TOC. Figure 3 shows  
202 the changes in COD. Due to the presence of chlorides and the formation of a high  
203 concentration of chlorinated oxidants, this parameter changes very rapidly and total  
204 depletion is obtained at very low current. Likewise, the TOC is very efficiently removed,  
205 and the effect of US irradiation on depletion is highly significant and the opposite of what  
206 was observed for the removal of the raw pollutant; i.e., it is much more pronounced for  
207 systems with many bipolar electrodes. The combined process thus works better in systems  
208 with a higher area of bipolar electrodes.

209



210

211 **Figure 3.** Relative *COD and TOC* decay as a function of the applied charge per unit  
 212 volume of electrolyzed solution ( $Q_{ap}$ ) during the sono-electrochemical (solid symbols)  
 213 and electrochemical silent (open symbols) oxidation using a DIACELL 401 equipped  
 214 with (■, □) 3 compartments; (●, ○) 2 compartments; (◆, ◇) 1 compartment; (▲, Δ) no  
 215 compartments.

216 Another important parameter to be considered in this system is the energy consumption.  
 217 In a batch system, the energy consumption in an electrolytic treatment can be estimated  
 218 from Eq. 1, where  $Q$  is the specific charge applied,  $I$  is the cell intensity,  $V$  is the  
 219 electrolyte volume,  $t$  is the treatment time and  $E$  is the cell voltage. Likewise, energy  
 220 consumption by a sonolytic treatment (assuming 100 % efficiency) can be calculated from  
 221 Eq. 2, where  $w$  is the US power irradiated (200 W).

$$222 \quad W_{electrolysis} (kWhm^{-3}) = Q(kAhm^{-3}) \cdot E(V) = \frac{I(A) \cdot t(h) \cdot E(V)}{V(m^{-3})} \quad \text{Eq. (1)}$$

$$223 \quad W_{sonolysis} (kWhm^{-3}) = \frac{w(kW) \cdot t(h)}{V(m^{-3})} \quad \text{Eq. (2)}$$

224

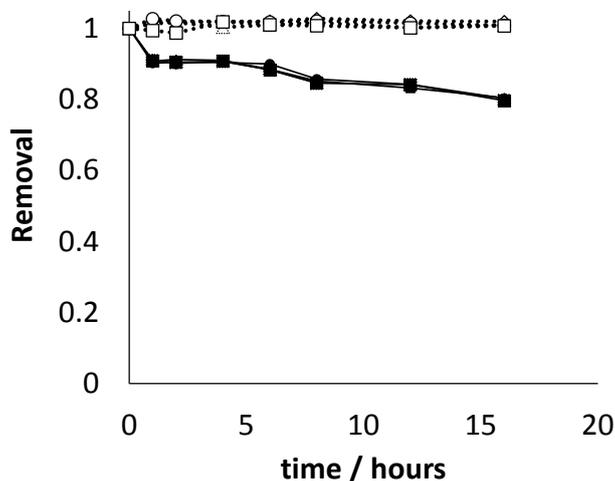
225 In the silent electrolytic process, the power consumption increases with the number of  
 226 bipolar electrodes from 227.4 kWh m<sup>-3</sup> to 455.4 kWh m<sup>-3</sup>. In contrast, in the sono-  
 227 electrochemistry process, the power consumption decreases from 325.4 kWh m<sup>-3</sup> to 302.3  
 228 kWh m<sup>-3</sup>. US irradiation in electrochemical waste treatment therefore makes the most  
 229 sense in electrochemical cells with multiple electrodes.

230

231 Figure 4 focuses on the removal of 2,4-D using a single sono-chemical process in the  
 232 same experimental setup. The results are highly reproducible, as the four experiments  
 233 overlie each other, and it is clearly seen that no mineralization but just oxidation of the  
 234 herbicide is obtained with the US irradiation; hence, the combination of technologies

235 enhances oxidation because it speeds up removal in the electrolytic process and leads to  
236 the mineralization of the herbicide.

237



238

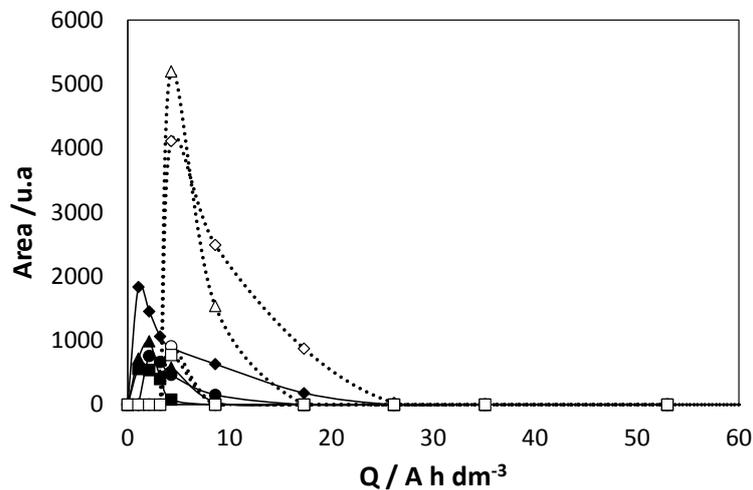
239 **Figure 4.** Relative concentration (solid symbols) and TOC decay (open symbols) as a  
240 function of the reaction time during the sono-chemical process using a DIACELL  
241 equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (◆, ◇) 1 compartment; (▲,  
242 Δ) no compartments.

243

244 Regarding the formation of intermediates during the process, Figure 5 shows the changes  
245 in the total chromatographic area of the peaks of intermediates detected during the silent  
246 electrolytic and sono-electrolytic tests (calculated by single addition of the areas obtained  
247 at each sampling time and used as an indicator of the presence of intermediates). Sono-  
248 electrolysis led to harsher oxidation conditions compared with electrolysis alone, yielding  
249 faster removal of intermediates and a lower maximum concentration. In addition, the  
250 maximum was present for a shorter amount of time (half of the time required in the sono-  
251 electrolysis experiment).

252 US irradiation significantly improves the mass transfer coefficient and thus the amount  
 253 of pollutant that near the electrode surface. In addition, US irradiation leads to the  
 254 formation of hydroxyl radicals from water hydrolysis, which also help explain the  
 255 observed improvements. Hydroxyl radicals generated via this non-electrochemical  
 256 mechanism are produced in the bulk solution, and hence, their action is not limited to the  
 257 oxidation of pollutants at the diamond electrode surface but is extended to the whole  
 258 electrolyte. This oxidation mechanism helps to explain the improvement in electrolysis  
 259 with the addition of ultrasound [23, 25, 35].

260



261

262 **Figure 5.** Changes in the aromatic intermediates as a function of the applied charge per  
 263 unit volume of electrolyzed solution ( $Q_{ap}$ ) during the sono-electrochemical (solid  
 264 symbols) and silent electrochemical (open symbols) processes using a DIACELL 401  
 265 equipped with (■, □) 3 compartments; (●, ○) 2 compartments; (◆, ◇) 1 compartment; (▲,  
 266 Δ) no compartments.

267

268 The main intermediates detected were 4-chlororesorcinol, 2-chlorophenol,  
 269 2,4-dichlorophenol, hydroquinone and benzoquinone. Their maximum concentrations are  
 270 shown in Table 1.

271 **Table 1.** Maximum concentration (mg dm<sup>-3</sup>) detected for aromatic intermediates.

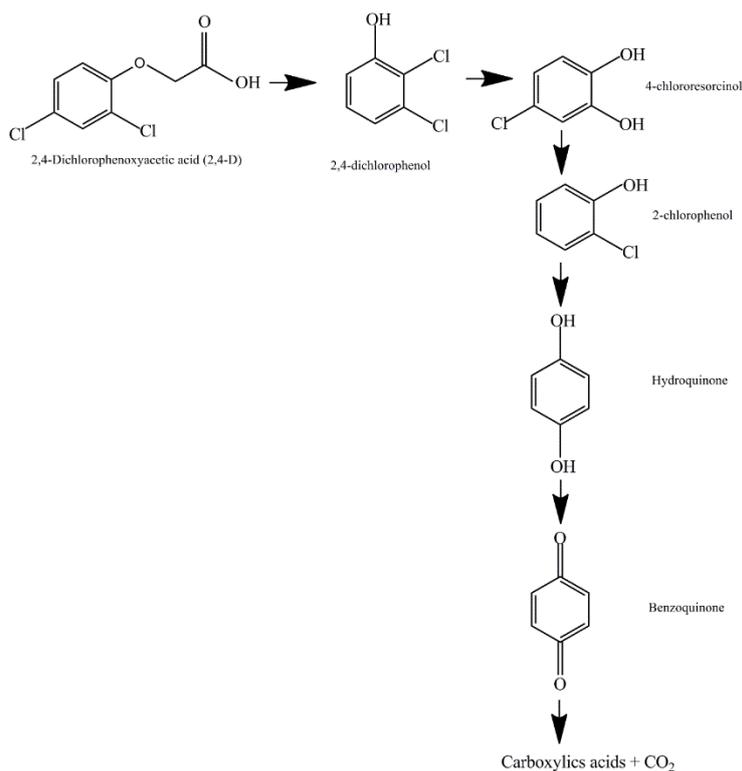
Intermediate	Electrochemical process				Sono-electrochemical process			
	3 bipolar	2 bipolar	1 bipolar	No bipolar	3 bipolar	2 bipolar	1 bipolar	no bipolar
4-Chlororesorcinol	3.63	2.90	4.61	3.70	3.56	0	6.63	3.26
2-Chlorophenol	45.12	57.63	63.46	49.94	0	6.34	8.44	24.88
2,4-Dichlorophenol	8.41	18.95	30.18	26.23	0	0	0	13.84
Hydroquinone	0	0	1.97	2.23	12.44	11.33	11.31	3.75
Benzoquinone	0	0	11.55	9.28	0	13.22	11.15	0

272

273

274 US irradiation does not influence the nature of the intermediates formed but only their  
 275 concentration, indicating that mechanism by which 2,4-D is removed is the same in the  
 276 silent electrolytic and sono-electrolytic technologies. It can thus be assumed that the  
 277 degradation of 2,4-D follows the oxidation pathway shown in Figure 7 based on the rapid  
 278 cleavage of the 2,4-D molecule to form 2,4-dichlorophenol, which is further oxidized to  
 279 4-chlororesorcinol. After that, dehalogenation and hydroxylation of the aromatic ring lead  
 280 to the formation of chlorinated compounds. Once in chloride medium, due to the high  
 281 production of the active chlorine atoms, organo chlorine species, such as 4-  
 282 chlororesorcinol and 2-chlorophenol, form. These species are then oxidized to  
 283 hydroquinone followed by benzoquinone. This mechanism is in agreement with  
 284 mechanisms previously proposed for other Advanced Oxidation Processes [42-44].

285

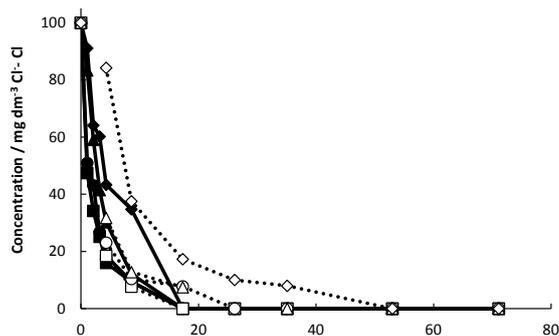


286

287 **Figure 7.** Proposed mechanism for the silent electrolytic and sono-electrolytic oxidation  
 288 of 2,4-D.

289

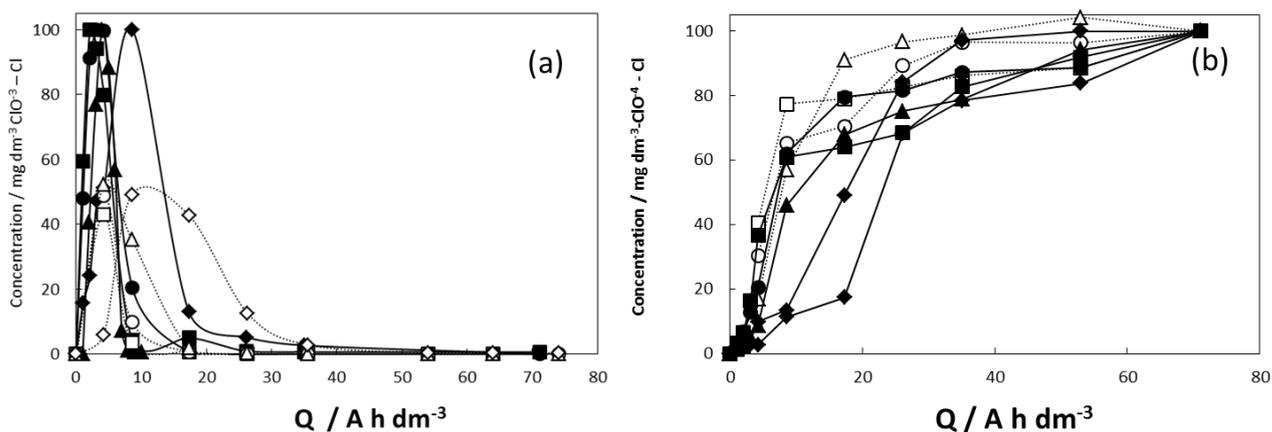
290 Figures 8 and 9 focus on chloride oxidation and the resulting chlorine speciation. As  
 291 described in the introduction, this paper focuses not only on the removal of a herbicide  
 292 but also on the influence of bipolar electrodes and ultrasound in the production of  
 293 oxidants. The oxidation of chlorides may be used as an indicator of this process because  
 294 these species are oxidized to gaseous chlorine/hypochlorite and oxidation does not stop  
 295 at this point but continues to chlorate and perchlorate, which despite having a high  
 296 reduction potential, are very soft oxidants at room temperature and atmospheric pressure  
 297 and have no influence on the oxidation process. Chloride is oxidized faster with the same  
 298 current density using sono-electrolysis (Fig. 8).



299

300 **Figure 8.** Changes in the chloride concentration as a function of the applied charge per  
 301 unit volume of electrolyzed solution ( $Q_{ap}$ ) during the sono-electrochemical (solid  
 302 symbols) and electrochemical (open symbols) processes with an external current intensity  
 303 of 10 A using a DIACELL<sup>®</sup> equipped with (■, □) 3 compartments; (●, ○) 2 compartments;  
 304 (◆, ◇) 1 compartment; (▲, Δ) no compartments.

305 This increased oxidation rate reflects the faster production of chlorate, which is produced  
 306 in at much higher concentrations in the sono-electrolysis compared with single  
 307 electrolysis (Fig. 9a). This species is not the final product but is further oxidized to  
 308 perchlorate (Fig. 9b), which is the final product in the oxidation of chloride both in the  
 309 electrolysis alone and the US-irradiated technology.



310

311 **Figure 9.** Changes in the chlorate (a) and perchlorate (b) concentrations as a function of  
 312 the applied charge per unit volume of electrolyzed solution ( $Q_{ap}$ ) during the sono-  
 313 electrochemical (solid symbols) and silent electrochemical (open symbols) processes

314 with an external current intensity of 10 A using a DIACELL<sup>®</sup> 401 equipped with: (■, □)  
315 3 compartments; (●, ○) 2 compartments; (◆, ◇) 1 compartment; (▲, Δ) no compartments.

316

317 Formation of perchlorate is disfavored in sono-electrolysis compared to silent  
318 electrolysis, which is reflected by the higher concentration of chlorates and in the longer  
319 time required in the sono-electrolysis for the complete oxidation of chloride to  
320 perchlorate. There are thus significant differences in the way in which oxidants are  
321 produced and behave under the US irradiation, which may influence the results of the  
322 electrolysis of organic pollutants if the oxidants are needed for the reaction; hence,  
323 oxidant production should be taken into account. Oxidation of chlorate to perchlorate is  
324 partially prevented by US irradiation, which could be due to the lack of hydroxyl radicals  
325 to catalyze this reaction and the increase in mass transfer, which allows chlorate to escape  
326 from the hydroxyl radical cage generated around the diamond electrode surface.  
327 Obviously, perchlorate should be avoided in any remediation technology, and in this  
328 study, it was only used to increase knowledge about the production of oxidants while  
329 simultaneously depleting the herbicide.

330

### 331 **Conclusions**

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

333

- 334 - 2,4-D can be efficiently depleted from synthetic wastewater obtaining complete  
335 mineralization regardless of the number of bipolar electrodes used. Ultrasound  
336 irradiation improves results obtained using a single electrolytic processes.

- 337 - For the same external current applied, the higher the number of bipolar electrodes  
338 connected, the faster and more efficient the removal and the clearer the differences  
339 between the silent and the US irradiated processes.
- 340 - Lower cell voltages result from the application of US irradiation, which could  
341 compensate for the energy demand of this irradiation.
- 342 - 4-Chlororesorcinol, 2-chlorophenol, 2,4-dichlorophenol, hydroquinone and  
343 benzoquinone are the main intermediates found in both technologies. Their  
344 concentrations are much lower under US irradiation.
- 345 - US irradiation influences the formation of oxidants in the reaction media. Under  
346 US irradiation, production of chlorates is promoted compared with the formation  
347 of perchlorates.

348

349

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356

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