

1 **Study of the Chlorfenvinphos pesticide removal under different anodic**  
2 **materials and different reactor configuration**

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13

14 **Abstract**

15

16 The present manuscript focuses on the study of the electrochemical oxidation of  
17 the insecticide Chlorfenvinphos (CVP). The assays were carried out under  
18 galvanostatic conditions using boron-doped diamond (BDD) and low-cost tin  
19 dioxide doped with antimony (Sb-doped SnO<sub>2</sub>) as anodes. The influence of the  
20 operating variables, such as applied current density, presence or absence of a  
21 cation-exchange membrane and concentration of supporting electrolyte, was  
22 discussed. The results revealed that the higher applied current density the higher  
23 degradation and mineralization of the insecticide for both anodes. The presence  
24 of the membrane and the highest concentration of Na<sub>2</sub>SO<sub>4</sub> studied (0.1 M) as a  
25 supporting electrolyte benefited the oxidation process of CVP using the BDD

26 electrode, while with the ceramic anode the elimination of CVP was lower under  
27 these experimental conditions. Although the BDD electrode showed the best  
28 performance, ceramic anodes appear as an interesting alternative as they were  
29 able to degrade CVP completely for the highest applied current density values.  
30 Toxicity tests revealed that the initial solution of CVP was more toxic than the  
31 samples treated with the ceramic electrode, while using the BDD electrode the  
32 toxicity of the sample increased.

33

34 *Keywords:* BDD anode, Chlorfenvinphos, electrochemical oxidation, Sb-doped  
35 SnO<sub>2</sub> ceramic anode.

36

## 37 **1. Introduction**

38 In the last century, the rapid increase in the world population has caused a  
39 growing demand for food. For this reason, chemical substances have been used  
40 in both agriculture and farming, among these chemicals organophosphate  
41 pesticides are found (Baken et al., 2018). The indiscriminate use of these  
42 compounds cause water pollution due to the lack of technologies capable of  
43 eliminating them (Oliveira et al., 2014).

44 Chlorfenvinphos (CVP), 2-chloro-1 vinyl diethyl phosphate, whose structure is  
45 shown in Figure 1 of the Supplementary Material, is used against pests of  
46 ectoparasitic insects, such as mosquitoes, sandflies, tsetse flies, blackflies,  
47 tabanids, etc. This pesticide is not only used in farming and agriculture but also  
48 to fight domestic pests (Dorsey and Kueberuwa, 1997). Consequently, CVP can  
49 be found in both domestic wastewater and natural water bodies (Barco-Bonilla et  
50 al., 2013).

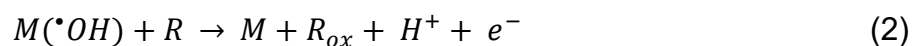
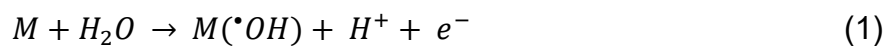
51 CVP is of artificial origin, that is, it is not generated naturally in the environment.  
52 Furthermore, this compound is hazardous for human health due to its  
53 neurotoxicity (Rickwood and Galloway, 2004). It acts as an inhibitor of the  
54 acetylcholinesterase enzyme, causing overstimulation of cholinergic  
55 neurotransmission, producing symptoms such as increased salivation, changes  
56 in blood pressure and heart rate, nausea, headache, muscle tremor, paralysis  
57 and even death (Acero et al., 2008). Due to its high toxicity, this compound has  
58 been banned in the European Union. It is also part of the list of 33 priority  
59 substances in the field of water policy approved in Decision 2455/2001/EC of the  
60 European Parliament and of the Council of 20 November 2001. In the United

61 States its use has been prohibited since 1991, as it was considered an extremely  
62 dangerous substance. On the other hand, in other countries such as Australia, it  
63 has been used until a few years ago (Szatkowska et al., 2012). In Kenya, a  
64 decade ago, CVP became the most widely used acaricide, which caused its  
65 presence even in cow's milk (Kituyi et al., 1997). Recent studies carried out in  
66 Spain confirmed CVP presence in honeybees, pollen and in their hive. In this last  
67 matrix, it was detected in 95% of the cases studied (Calatayud-Vernich et al.,  
68 2018). This insecticide causes the bees to become disoriented and unable to  
69 carry out pollination. This fact shows that CVP is still present in the environment  
70 despite its use was prohibited years ago. Therefore, it is necessary to develop an  
71 effective technique able to eliminate CVP presence in the environment.

72 Various authors have focused their research on the study of CVP degradation  
73 through techniques such as ozonation (Acero et al., 2008); adsorption (Rojas et  
74 al., 2015); Fenton and photo-Fenton (Gromboni et al., 2007; Oliveira et al., 2014;  
75 Ruíz-Delgado et al., 2019); and photoelectrocatalysis (Roselló-Márquez et al.,  
76 2019). This paper proposes the electrochemical advanced oxidation processes  
77 (EAOPs) for the elimination of this insecticide. This technique is very effective in  
78 removing emerging contaminants and refractory compounds from wastewater  
79 (Domínguez et al., 2012; Garcia-Segura et al., 2018; Martínez-Huitle et al., 2015),  
80 even for low concentrations. Moreover, EAOPs do not require the addition of  
81 chemicals and, generally, do not generate sludge either, so this method belongs  
82 to the category of clean technology (Forero et al., 2005).

83 EAOPs are based on the formation of hydroxyl radicals on the anodic surface  
84 through the oxidation of water (Equations 1 and 2).

85



86

87 where  $M$  is the anodic surface,  $M(\cdot OH)$  are the hydroxyl radicals adsorbed on the  
88 anodic surface,  $R$  and  $R_{ox}$  is the contaminant in its initial and oxidized form,  
89 respectively. Hydroxyl radicals are capable of oxidizing most organic compounds  
90 to carbon dioxide ( $CO_2$ ) and water (Moreira et al., 2017). The short life of these  
91 oxidants (Del Greco and Kaufman, 1962) explains why they are not present in  
92 the treated water.

93 EAOPs depend on the nature of the anode material. The complete mineralization  
94 of organic refractory compounds to  $CO_2$  is only achieved for anodes with high  
95 oxygen overvoltage because the generation of  $\cdot OH$  radicals destined for the  
96 oxidation of pollutants on the anodic surface is greater (Comninellis and Chen,  
97 2010; Hmani et al., 2009). One well known material is the BDD electrode widely  
98 used on a laboratory scale in EAOPs because this material presents a wide  
99 potential window, high chemical and mechanical stability and long life (Liu et al.,  
100 2009; Oturan et al., 2013), but its high cost and the need to find a suitable  
101 substrate do not make it viable for an industrial scale (Chaplin, 2014). Anodes  
102 based on  $SnO_2$  also poses a high oxygen overpotential (Comninellis and Chen,  
103 2010; Wang et al., 2016), however, they usually present low stability under anodic  
104 polarization (Lipp and Pletcher, 1997). This problem has been solved by  
105 developing  $SnO_2$  electrodes on a low-cost ceramic substrate (Droguett et al.,  
106 2020; Mora-Gómez et al., 2020), so these ceramic electrodes become very  
107 attractive for EAOPs. Additionally, these ceramic electrodes have shown  
108 acceptable degradation and mineralization results for other organic compounds,

109 becoming a suitable alternative to BDD anodes (Carrillo-Abad et al., 2020a,  
110 2020b; Droguett et al., 2020; Mora-Gómez et al., 2020, 2019, 2018).

111 The objective of this paper is to study the influence of different variables such as  
112 the anodic material (BDD or ceramic electrode based on SnO<sub>2</sub>), applied current  
113 density, reactor configuration (absence or presence of a cation-exchange  
114 membrane) and concentration of supporting electrolyte on the electro-oxidation  
115 of Chlorfenvinphos and on the toxicity of the treated solutions.

116

## 117 **2. Experimental**

### 118 *2.1 Electrochemical oxidation assays*

119 Electrolysis experiments were carried out galvanostatically in an undivided cell at  
120 applied current densities values (*i*) between 17 and 83 mA cm<sup>-2</sup> using a power  
121 supply (Peaktech® 1585) during 4 hours. The solution to be treated consisted of  
122 250 cm<sup>3</sup> of 60 ppm of CVP (Sigma-Aldrich) in 0.014 M of Na<sub>2</sub>SO<sub>4</sub> as supporting  
123 electrolyte. Two different materials were used as anodes: a microporous Sb-  
124 doped SnO<sub>2</sub> ceramic electrode, described in previous studies (Mora-Gómez et  
125 al., 2020, 2019, 2018), and a Boron-doped diamond (BDD) electrode (NeoCoat  
126 SA, Switzerland). The area of both anodes was 12 cm<sup>2</sup>. As cathode and reference  
127 electrodes were used an AISI 304 stainless steel sheet of 20 cm<sup>2</sup>, and an Ag/AgCl  
128 one, respectively.

129 Electro-oxidation tests were also performed in a divided reactor by a cation-  
130 exchange membrane (Nafion 117 from Dupont). In this reactor, the solution to be  
131 treated containing the insecticide (60 mg L<sup>-1</sup> of CVP and 0.014 M of Na<sub>2</sub>SO<sub>4</sub>) was

132 introduced in the anodic compartment and a solution with the same concentration  
133 of supporting electrolyte without CVP was put in the cathodic compartment.

134 The effect of the concentration of the supporting electrolyte was also studied  
135 under this reactor configuration. For this purpose, electrochemical tests were  
136 carried out with different concentrations of Na<sub>2</sub>SO<sub>4</sub>: 0.014, 0.05 and 0.1 M.

137

## 138 *2.2 Analytical methods*

### 139 *2.2.1 Analysis of Chlorfenvinphos degradation*

140 The evolution of CVP concentration was monitored by measuring its absorbance  
141 using a UV/Vis double beam spectrophotometer, model Unicam UV4-200 (Pye  
142 Unicam, Cambridge). The UV/VIS spectra of CVP presents two characteristic  
143 absorption bands, specifically at 205 and 244 nm. The band placed at 244 nm  
144 was the one selected to follow the evolution of the CVP concentration, since the  
145 first band presented a very low coefficient of linearity with the concentration  
146 (Acero et al., 2008). This second absorption band is related to the electronic  
147 transition  $\pi \rightarrow \pi^*$  of the aromatic ring (Fernández-Domene et al., 2019).

148 The measurement of Total Organic Carbon (TOC) was carried out through a  
149 Shimadzu TNM-L ROHS TOC analyser. The relationship between the partial and  
150 total mineralization of the compound is analysed by the extent of the  
151 electrochemical combustion parameter ( $\Phi$ ) defined in Equation 3.

152

$$\Phi(t) = \frac{\%[TOC(t)]_{removed}}{\%[CVP(t)]_{removed}} \quad (3)$$

153

154 The mineralization current efficiency (MCE) represents the fraction between the  
155 amount of organic matter removed and the amount of theoretical organic matter  
156 removed considering that the applied electrical charge is used only for the  
157 mineralization of the organic contaminant for a given instant of time. The MCE is  
158 calculated through Equation 4 (Özcan and Özcan, 2018):

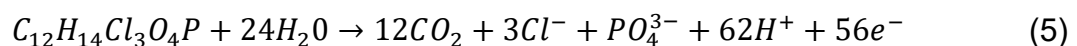
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$$MCE(\%) = \frac{nFV\Delta[TOC]_t}{7.2 \times 10^5 mIt} \times 100 \quad (4)$$

160

161 where  $\Delta[TOC]_t$  ( $\text{mg L}^{-1}$ ) is the TOC removal after a certain time,  $t$ (min),  $F$  is the  
162 Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $n$  is the number of exchanged electrons in the  
163 oxidation reaction of CVP (56 according to reaction 5),  $V$  is the volume of the  
164 electrolytic cell (L),  $m$  is the number of carbon atoms in the CVP molecule (12),  $I$   
165 the applied current (A) and  $7.2 \times 10^5$  is a conversion factor ( $60 \text{ s min}^{-1} \times 12000 \text{ mg}$   
166  $\text{mol}^{-1}$ ). Based on the molecular formula and the literature (Klamerth et al., 2009),  
167 the total mineralization reaction for CVP could be expressed as follows:

168



169

### 170 2.2.2 Determination of oxidizing species

171 During the electrochemical oxidation process, in addition to the  $\cdot\text{OH}$  radicals  
172 (Equation 1), the supporting electrolyte can also be oxidized and give rise to  
173 different oxidizing species depending on its composition. Furthermore,  $\text{H}_2\text{O}_2$  can  
174 also be formed from the decomposition of  $\cdot\text{OH}$  radicals. Considering that  $\text{Na}_2\text{SO}_4$



175 is the supporting electrolyte employed, the oxidation reactions involved are (de  
176 Araújo et al., 2018; Muruganathan et al., 2011; Zhang et al., 2015):

177



178

179 The determination of the  $S_2O_8^{2-}$  and  $H_2O_2$  species was carried out by iodometry  
180 and UV spectrophotometry (Mora-Gómez et al., 2020). The amount of  $\cdot OH$  and  
181  $SO_4^{\cdot -}$  radicals cannot be determined using these techniques due to their short  
182 lifetime (Del Greco and Kaufman, 1962; Olmez-Hanci and Arslan-Alaton, 2013;  
183 Roots and Okada, 1975).

184

### 185 2.2.3 Toxicity measurements

186 The oxidation processes of organic matter can lead to more toxic by-products  
187 than the initial compound (Heberle et al., 2017; Oturan et al., 2008). For this  
188 reason, ecotoxicity tests have been carried out using Microtox® bioassay. This  
189 method consisted of measuring the reduction in bioluminescence of the *Vibrio*  
190 *Fischeri* bacterium after 15 minutes of exposure. The bioluminescence study or  
191 Microtox® bioassay (standard method UNE-EN ISO 11348-3) was carried out  
192 with the Microtox M-500 equipment (Microbics, 1989).

193 The tests were carried out at 15°C, a salinity level of 2% NaCl and a pH in the 6  
194 to 8 range. Toxicity can be expressed as n-TU (toxicity units), where n is the

195 number of times that a sample has to be diluted in order to inhibit the  
196 luminescence of 50% of the luminescent microorganisms. This parameter is  
197 related to the  $EC_{50}$  one, which is defined as the effective nominal concentration  
198 of a toxicant ( $mg\ L^{-1}$ ) that reduces the intensity of light emission by 50%.

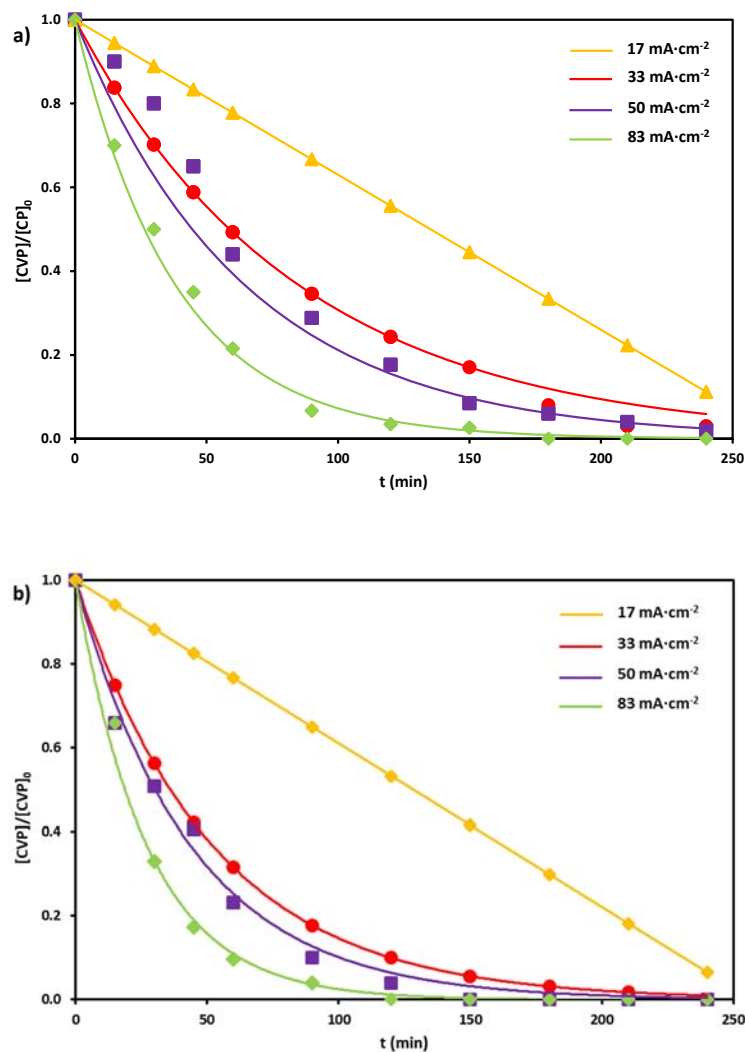
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### 200 **3. Results and discussion**

#### 201 *3.1 Effect of applied current density*

202 Figure 1 shows the variation of the CVP relative concentration as a function of  
203 time for the two electrodes under study. As can be seen, as the current density  
204 increased, the removal of the CVP was greater using both anodes. Regarding  
205 the anode material, less degradation of the CVP was achieved using the ceramic  
206 electrode with respect to the BDD one, and this difference was greater as the  
207 current density increased. This is due to the fact that the BDD electrode presents  
208 a higher overpotential for the formation of  $O_2$  than the ceramic electrode, as  
209 observed in a previous study (Mora-Gómez et al., 2018). Therefore, a greater  
210 amount of  $\cdot OH$  radicals are generated in the BDD electrode. In addition, the  
211 interaction of these radicals with the surface of the BDD electrode is weaker than  
212 with the ceramic electrode (Chen et al., 2005).

213



214 **Figure 1.** Effect of the applied current density on the decay of the  
 215 Chlorfenvinphos (CVP) relative concentration as a function of time for the ceramic  
 216 electrode (a) and BDD electrode (b).

217

218 In Figure 1 is also observed that when the applied current density is 17 mA cm<sup>-2</sup>,  
 219 the evolution of the relative concentration of CVP decreased linearly with time for  
 220 both anodes. This behaviour is typical of an electrochemical system controlled by  
 221 charge transfer (Li et al., 2008), that is, the velocity of <sup>•</sup>OH radicals generation on  
 222 the anodic surface is lower than the transport rate of the CVP molecules to the  
 223 anode, because the solution is fully stirred; and also than the chemical oxidation

224 reaction of CVP. Therefore, the rate of the degradation process is independent  
225 of the concentration of the compound to be oxidized (Equation 10)  
226 (Chatzisyneon et al., 2009).

227

$$r_{(R)} = V \frac{d[R]}{dt} = -V \frac{d[{}^{\bullet}OH]}{dt} = -\frac{I\theta}{nF} \quad (10)$$

228

229 where  $\theta$  represents the current efficiency related to the  ${}^{\bullet}OH$  radical generation.

230 In this case, for a constant current density, the system can be fitted to a pseudo-  
231 zero order kinetics (Equation 11), and the kinetic constant ( $k_0$ ) is calculated with  
232 Equation 12. The values obtained for  $k_0$  are 0.208 and 0.210 mg L<sup>-1</sup> for the  
233 ceramic and BDD electrodes, respectively. This indicates that for low current  
234 values, the CVP degradation rate is very similar using both anodes.

235

$$\frac{d[CVP]}{dt} = -\frac{I\theta}{nFV} = -k_0 \quad (11)$$

$$[CVP]_t = [CVP]_0 - k_0 \cdot t \quad (12)$$

236

237 However, from 33 to 83 mA·cm<sup>-2</sup>, the evolution of the relative concentration of  
238 CVP with time followed an exponential trend, as predicted by Equation (14).  
239 Assuming that the system was perfectly stirred, this trend indicates that the  
240 process was controlled by the oxidation reaction of CVP by  ${}^{\bullet}OH$  radicals, as  
241 observed in other studies (Mora-Gómez et al., 2020, 2019). In this case, the  
242 velocity of the CVP electro-oxidation reaction can be written according to  
243 Equation (13):

244

$$\frac{d[CVP]}{dt} = -k[CVP][\cdot OH] = -k_{app}[CVP] \quad (13)$$

245 where  $k$  is the kinetic constant. For a given current density, the concentration of  
246 hydroxyl radicals is constant, and an apparent pseudo-first order constant ( $k_{app}$ )  
247 can be defined. This parameter can be calculated by integrating the previous  
248 equation, Equation 14 (Mora-Gómez et al., 2020):

$$[CVP]_t = [CVP]_0 e^{-k_{app}t} \quad (14)$$

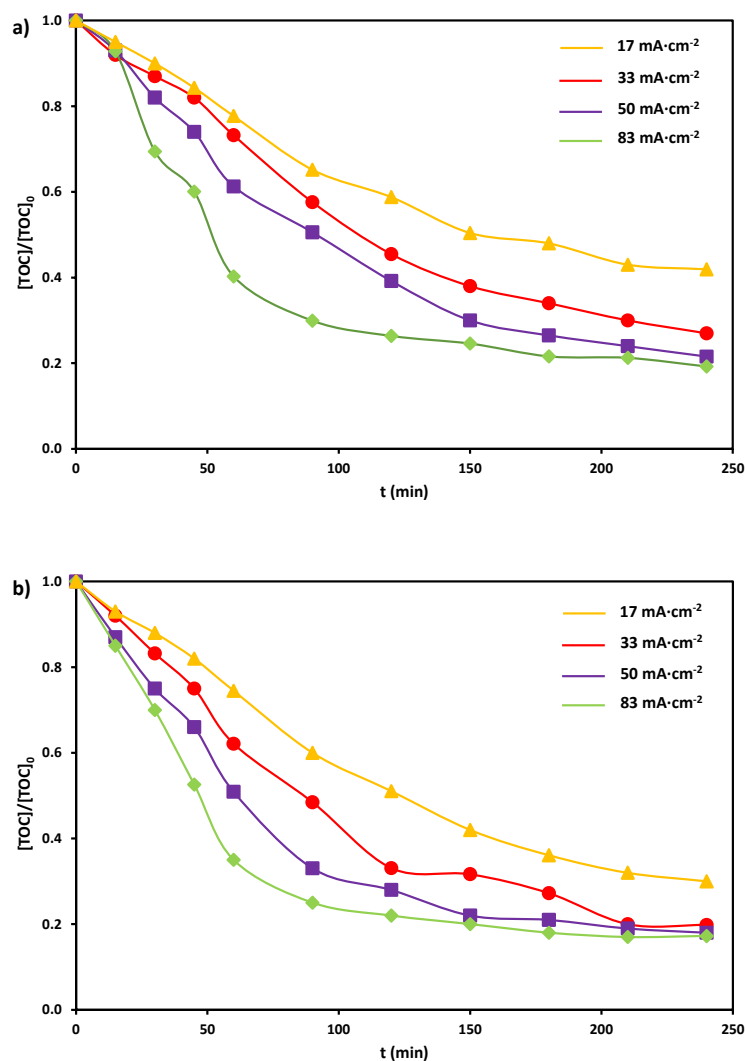
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250 The  $k_{app}$  values obtained for both anodes as a function of the current density are  
251 represented in Figure 2 of the Supplementary Material. The velocity of CVP  
252 removal with the BDD electrode was higher than that obtained with the ceramic  
253 one, since in the BDD electrode the formation of active radicals is greater, as  
254 already mentioned. Regarding the current density effect on the kinetics, when  $i$   
255 increased the  $k_{app}$  was also increased, and this increase is proportional to  $i$  for  
256 both electrodes. This can be explained by the proportional increase in the  
257 formation of active oxidant species, that react with CVP, as a function of the  
258 applied current.

259 The apparent kinetic constants calculated for both anode materials and for all the  
260 applied current values were used to calculate the theoretical decay of the CVP  
261 concentration predicted by Equation 14. In Figure 1a and 1b is also presented  
262 the comparison of the data (as dots) together with the theoretical values  
263 (continuous lines), where a good fitting is observed for all the conditions studied.

264 The evolution of the relative concentration of TOC with the electrolysis time for  
265 the previous conditions is shown in Figure 2. For an electrolysis time of 150 min,  
266 with the ceramic electrode, mineralization values of 49.6%, 62%, 70% and 75.4%  
267 were reached applying current densities of 17, 33, 50 and 83 mA cm<sup>-2</sup>,  
268 respectively. Under the same experimental conditions, the TOC decay obtained  
269 for the BDD one was of 58%, 68.3%, 78% and 80%. These results demonstrate  
270 the great oxidizing power of the BDD electrode to mineralize CVP and the rest of  
271 organic matter accumulated in solution to CO<sub>2</sub>. As was observed for CVP  
272 removal, increasing current density caused the increase in the mineralization  
273 rate. However, complete mineralization was not achieved for these experimental  
274 conditions, so organic matter continued present in solution even though CVP was  
275 completely degraded. This fact suggests the presence of short chain carboxylic  
276 acids, as also occurred in the mineralization of other organic contaminants  
277 (Coledam et al., 2016; Özcan et al., 2016). Klamerth et al., obtained similar  
278 results of TOC mineralization when studied the CVP degradation by a photo-  
279 fenton process, which was attributed to the presence of short-chain organic acids  
280 such as maleate, acetate and pyruvanate formed at the end of the process  
281 (Klamerth et al., 2009).

282



283 **Figure 2.** Effect of the applied current density on the decay of the relative total  
 284 organic carbon (TOC) concentration as a function of time for the ceramic  
 285 electrode (a) and BDD electrode (b).

286 Comparing the CVP degradation and its mineralization (Figures 1 and 2), it is  
 287 concluded that the degradation rate of this insecticide was greater than its  
 288 mineralization for both types of electrodes. This difference can be quantified by  
 289 the extent of electrochemical combustion ( $\phi$ ) defined in Equation 3.

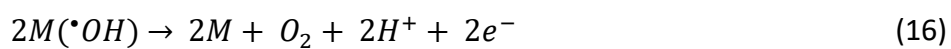
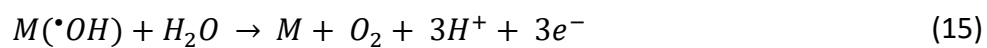
290 Figure 3a presents the  $\phi$  values obtained as a function of the electrolysis time.  
 291 As can be seen, when the system was limited by the charge transfer process (17

292 mA cm<sup>-2</sup>), initial values of  $\phi$  were equal to or close to unity, so the CVP removed  
293 was directly mineralized to CO<sub>2</sub>. Subsequently, the values of  $\phi$  decreased with  
294 the electrolysis time, being slightly higher with the BDD electrode. When the  
295 system was limited by the oxidation reaction of the CVP (50 mA cm<sup>-2</sup>), it can be  
296 observed that  $\phi$  was less than unity and it increased with the electrolysis time.  
297 This increase is related to the conversion of the organic by-products generated  
298 to CO<sub>2</sub> as the electrolysis progressed. This same trend was observed for 33 and  
299 83 mA·cm<sup>-2</sup> (not shown), actually, the curves for these three values of applied  
300 current and both anodic materials are almost overlapped. This behaviour is  
301 similar to that observed for other emerging contaminants under the same  
302 conditions (Mora-Gómez et al., 2020, 2019). On the other hand, for CVP, there  
303 was not a clear trend of  $\phi$  values regarding the type of anode.

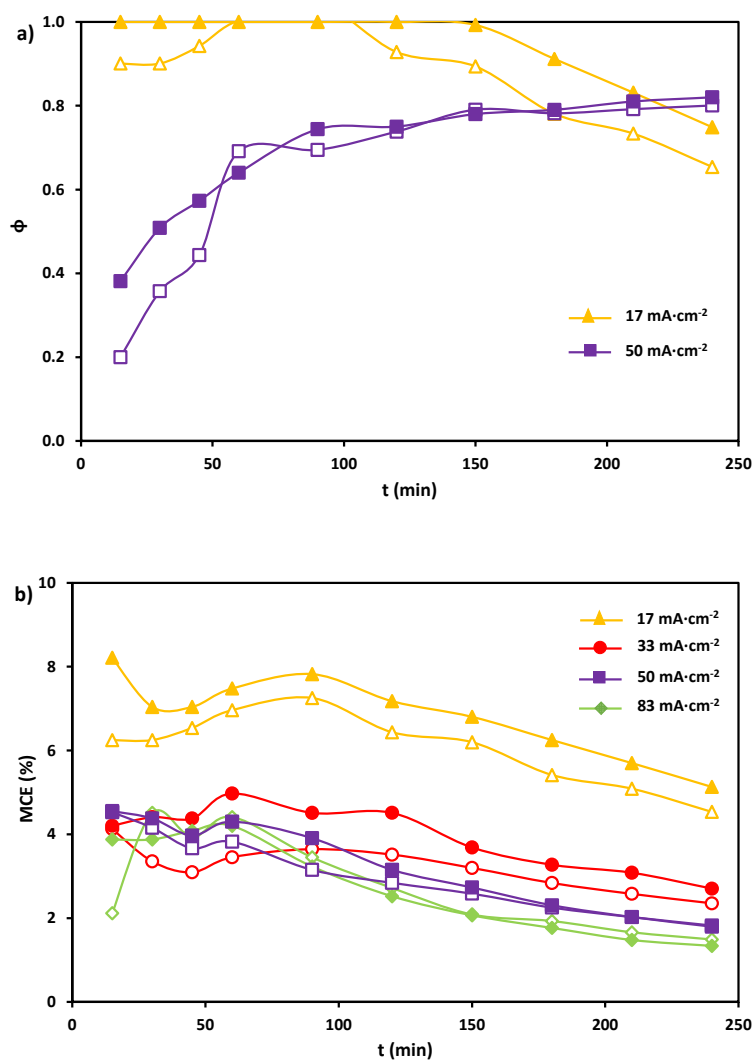
304 With respect to MCE, its evolution as a function of time for both electrodes is  
305 depicted in Figure 3b; this parameter decreased with time since the organic  
306 matter present in solution also decreased. Furthermore, this downward effect was  
307 more pronounced for the lowest current density. Using the ceramic electrode, the  
308 average MCE values reached were 6.1%, 3.22%, 3.1% and 2.83% for the current  
309 densities of 17, 33, 50, and 83 mA cm<sup>-2</sup>, respectively, while with the BDD  
310 electrode for the same assay conditions, average MCE values of 6.74%, 3.97%,  
311 3.31% and 2.84% were obtained. Therefore, this last electrode was slightly more  
312 efficient than the ceramic one due to its high capacity to generate active oxidants.  
313 The decrease of MCE as  $i$  increases observed for all the experimental conditions  
314 can be justified by the increase in the parasitic reactions (Equations 7 to 9, 15  
315 and 16).

316





317



318 **Figure 3.** Effect of the applied current density on  $\phi$  (a) and on MCE (b) as a  
 319 function of time. Solid points represent BDD electrode and empty points the  
 320 ceramic one.

321

### 322 3.2 Effect of the reactor configuration

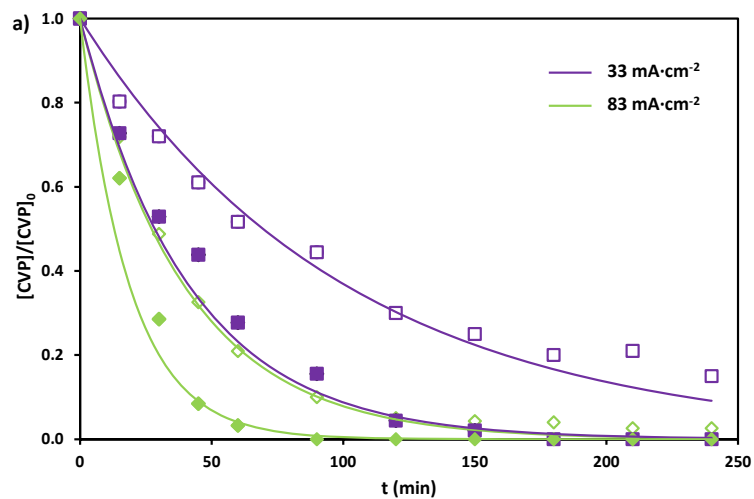
323 Figure 4 shows the evolution of the relative concentration of CVP (Figure 4a) and  
324 TOC (Figure 4b) as a function of time for both electrodes in the presence of a  
325 cation-exchange membrane. Regarding the CVP removed, for an electrolysis  
326 time of 150 minutes and at 33 and 83 mA cm<sup>-2</sup>, a CVP removal of 75% and  
327 95.69% was achieved using the ceramic electrode, and a 97.91% and 100% with  
328 the BDD one, respectively. Comparing these values with those obtained in the  
329 absence of membrane (82.97% and 97.38% for the ceramic electrode, and  
330 94.38% and 100% for the BDD), it is concluded that no improvements were  
331 observed due to the presence of the cation-exchange membrane, especially with  
332 respect to the ceramic electrode. This fact contrasts with the results observed for  
333 other studies carried out with this ceramic electrode (Mora-Gómez et al., 2020,  
334 2019).

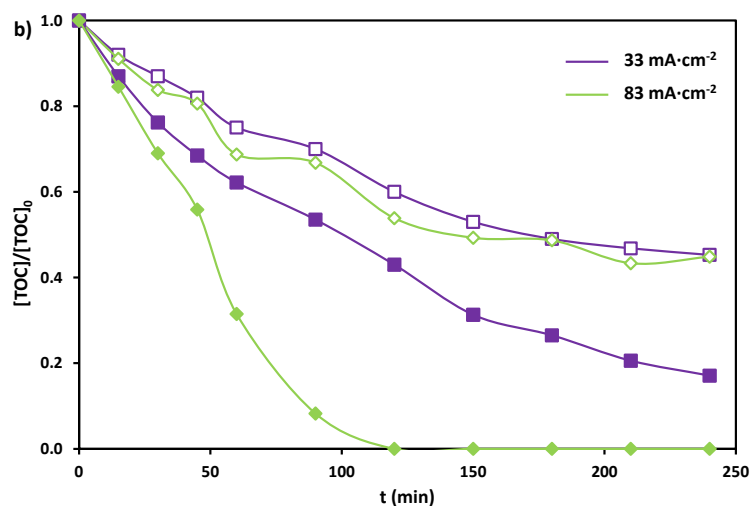
335 Regarding the mineralization of organic compounds (Figure 4b), after 150  
336 minutes of electrolysis, in the divided reactor the mineralization values of 47%  
337 and 50.73% were reached with the ceramic electrode and 68.7% and 100% with  
338 the BDD one at 33 and 83 mA cm<sup>-2</sup>, respectively, compared to 62% and 75.4%  
339 for the ceramic and 68.3% and 80% for the BDD electrode in the absence of a  
340 membrane, as previously mentioned. Hence, the use of the cation-exchange  
341 membrane worsened the mineralization of the organic matter for the ceramic  
342 electrode. This fact suggests that the intermediates formed from CVP in the  
343 membrane reactor were more persistent to the electrochemical degradation.  
344 Another explanation could be that CVP and its formed by-products with this  
345 anode in the undivided reactor could also be degraded by their reduction at the  
346 cathode, as it has previously been observed for other emerging pollutants

347 (Méndez-Martínez et al., 2012; Radjenović et al., 2012). On the contrary, with the  
348 BDD electrode, complete mineralization was achieved in the presence of the  
349 membrane at 83 mA cm<sup>-2</sup>.

350 To clarify the results obtained with the ceramic electrode, an experiment was  
351 carried out in the presence of the membrane at 83 mA cm<sup>-2</sup> but introducing the  
352 initial solution of CVP in the cathodic compartment. The results (Figure 3 of the  
353 Supplementary Material) showed that this insecticide was also degraded by its  
354 reduction during electrolysis as occurred with other compounds (Droguett et al.,  
355 2020; Méndez-Martínez et al., 2012; Radjenović et al., 2012). Therefore,  
356 improvements were observed in the undivided reactor with ceramic electrode. In  
357 the case of the BDD, since its oxidation power is greater, the effect of the  
358 reduction was not so evident.

359



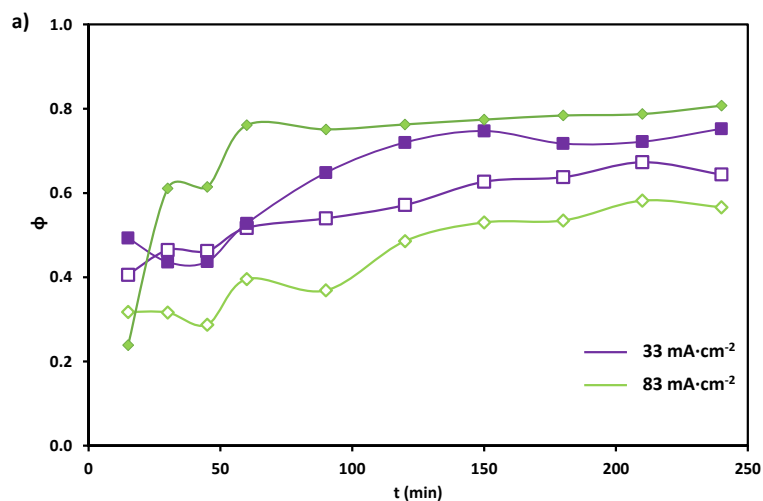


360 **Figure 4.** Effect of the applied current density on the decay of the relative CVP  
 361 (a) and TOC (b) concentration as a function of time for the divided reactor. Solid  
 362 points represent BDD electrode and empty points the ceramic electrode.

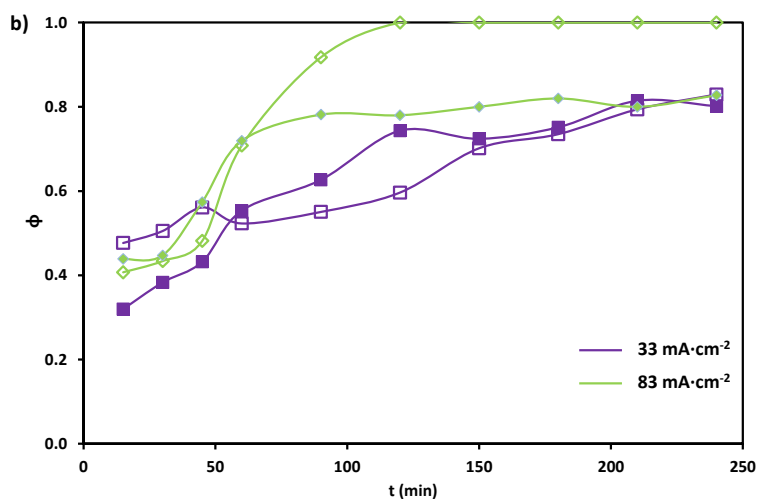
363

364 Regarding the electrochemical parameters of  $\phi$  and MCE, it was concluded that  
 365 the  $\phi$  value increased with the electrolysis time and, for this reactor configuration,  
 366 the obtained values of  $\phi$  were greater with the BDD electrode because the CVP  
 367 mineralization achieved was greater than with the ceramic one. However, in  
 368 presence of the membrane and using the BDD electrode at  $83 \text{ mA cm}^{-2}$ , after 120  
 369 minutes of electrolysis the extent of electrochemical combustion reached the  
 370 unity because all the initial CVP has been mineralized. Regarding the MCE  
 371 parameter, in the presence of the membrane, the average MCE values with the  
 372 ceramic electrode were 3.16% and 1.70%, and with the BDD anode were 4.94%  
 373 and 2.14% at 33 and  $83 \text{ mA cm}^{-2}$ , respectively. Therefore, it was verified that for  
 374 both reactor configurations an increase in the applied current density causes a  
 375 decrease in the MCE.

376 Figure 5 and 6 presents, respectively, the comparison of the electrochemical  
377 combustion parameter and the mineralization current efficiency, for both reactor  
378 configuration and both anodic materials at two different values of applied current.  
379 Comparing the reactor configuration, both the  $\phi$  and MCE values for the ceramic  
380 electrode were lower in the divided reactor (Figures 5a y 6a), while using the BDD  
381 anode, in the presence of a membrane the values obtained were higher since the  
382 mineralization achieved was also higher, specially at the highest applied current  
383 value. This fact can be attributed to the lower pH values reached in the anodic  
384 compartment since  $H^+$  ions were formed during the electrochemical process,  
385 which contribute to increase the standard redox potential of hydroxyl radicals and,  
386 consequently, to increase their oxidation power [27].  
387



388

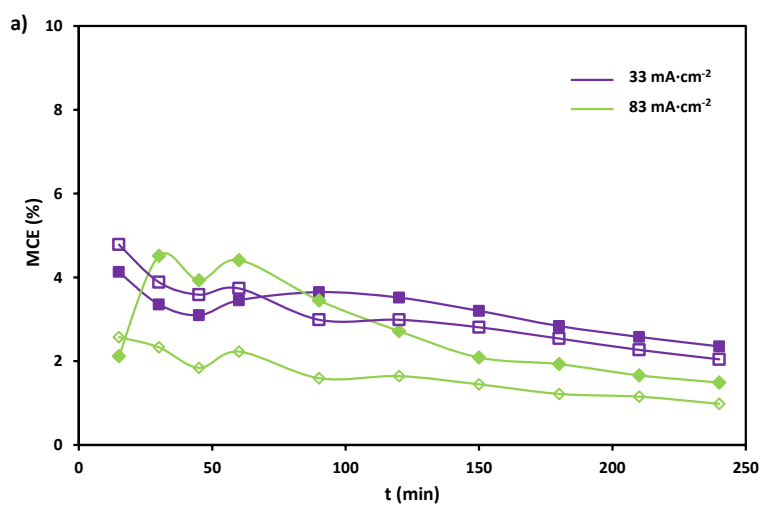


389

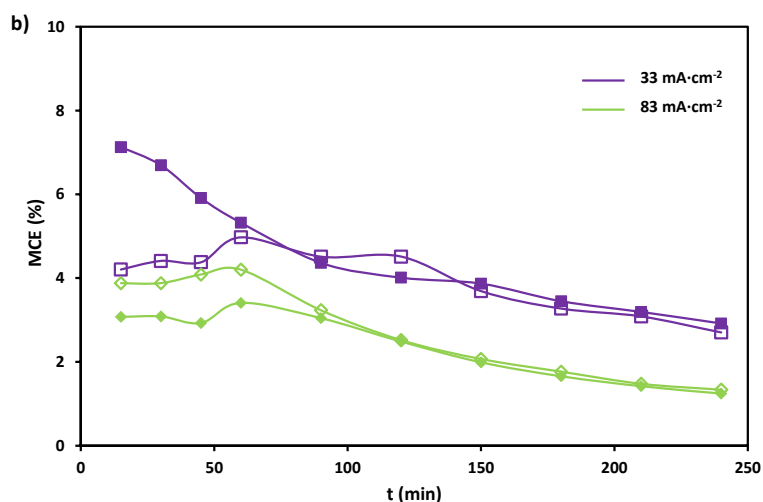
390

391 **Figure 5.** Evolution of  $\Phi$  as a function of time in the presence (empty points) and  
 392 absence (solid points) of the cation-exchange membrane for the ceramic  
 393 electrode (a) and the BDD electrode (b).

394



395



396

397 **Figure 6.** Evolution of MCE as a function of time in the presence (empty points)  
 398 and absence (solid points) of the cation-exchange membrane for the ceramic  
 399 electrode (a) and the BDD electrode (b).

400

401 Figure 4 presented in the Supplementary Material shows the evolution of the  
 402 UV/VIS spectra during the electrochemical degradation of CVP for both  
 403 electrodes and reactor configurations at 33 mA cm<sup>-2</sup>. In this figure, it is observed  
 404 that, generally, the UV/VIS spectrum decreased with time for the same assay.  
 405 For the BDD electrode in the divided reactor, it can be observed that for  
 406 intermediate times (between 30 and 90 minutes) in the UV/VIS spectrum a new  
 407 band appeared around a wavelength of 215 nm, indicating the formation of some  
 408 by-product of the CVP oxidation reaction that absorb at this wavelength. In  
 409 addition, it was also observed that for these conditions (BDD in the divided  
 410 reactor), from 150 minutes for wavelengths between 200 and 210 nm, the UV/VIS  
 411 spectrum increased with time, so it can be indicative of increased persulfate  
 412 formation, since these oxidant species absorb at a wavelength of 205 nm (An et  
 413 al., 2015), in addition to the formation of short-chain carboxylic acids (Coledam  
 414 et al., 2016; Özcan et al., 2016).

415

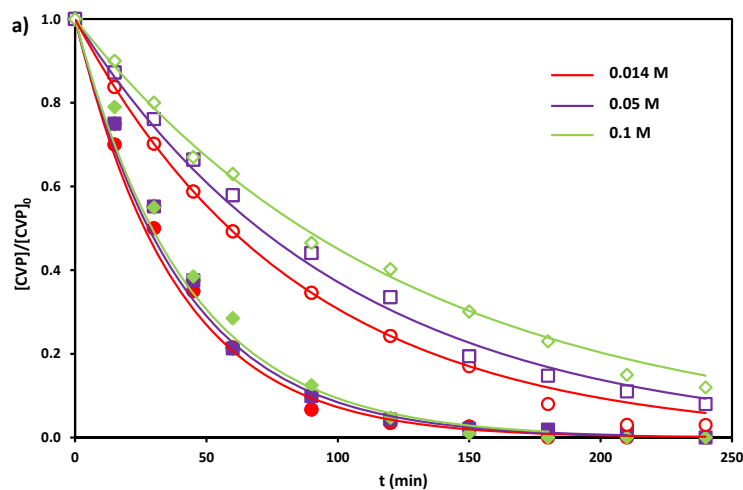
### 416 *3.3 Effect of sodium sulfate concentration*

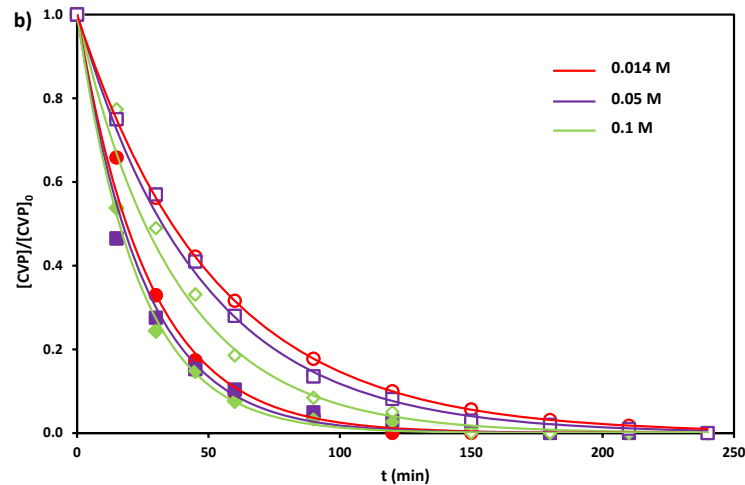
417 Figure 7 shows the evolution of CVP relative concentration with time as a function  
418 of the Na<sub>2</sub>SO<sub>4</sub> concentration for the applied current densities values of 33 and 83  
419 mA cm<sup>-2</sup>. In the case of the ceramic electrode (Figure 7a), the higher supporting  
420 electrolyte concentration the lower CVP degradation rate, this decrease being  
421 more notable at the lowest applied *i* (33 mA cm<sup>-2</sup>). As already observed by other  
422 authors (Zhang et al., 2015; Zhong et al., 2013), this fact may be associated to a  
423 larger amount of sulfate ions adsorbed on the anode surface minimizing active  
424 sites and, therefore, inhibiting the electro-generation of oxidizing species, mainly  
425 •OH radicals. For example, for Na<sub>2</sub>SO<sub>4</sub> concentrations of 0.014, 0.05 and 0.1 M  
426 at 45 minutes of electrolysis, applying a current density of 33 mA cm<sup>-2</sup>, a CVP  
427 removal of 41.2%, 33.6% and 32.9% was achieved, and at 83 mA·cm<sup>-2</sup>, a CVP  
428 degradation rate of 65.1%, 62.4% and 61.5%, respectively. At the highest *i* (83  
429 mA cm<sup>-2</sup>) with this electrode, after 180 minutes of electrolysis, the CVP was  
430 completely degraded for the three concentrations of supporting electrolyte.

431 Using the BDD electrode (Figure 7b), under the same current densities, the  
432 increase in the concentration of the supporting electrolyte implied an  
433 improvement in the degradation of the CVP specially at 33 mA cm<sup>-2</sup>. At the lowest  
434 *i*, after 45 minutes of assay, the CVP has been removed by 57.9%, 59.1% and  
435 66.9% for 0.014, 0.05 and 0.1 M of Na<sub>2</sub>SO<sub>4</sub> concentrations, respectively. On the  
436 other hand, for the highest *i*, the CVP removed was 82.6%, 84.7% and 85.15%,  
437 respectively. Generally, complete CVP degradation was reached at 120 minutes  
438 of electrolysis. This improvement with Na<sub>2</sub>SO<sub>4</sub> concentration was attributed to the



439 fact that the BDD electrode, in addition to  $\cdot\text{OH}$  radicals (Ma et al., 2018), it  
440 produces  $\text{S}_2\text{O}_8^{2-}$  and  $\text{SO}_4^{\cdot-}$  by oxidation of sulfates according to Equations 7 to 9.  
441 These species present a high oxidation power (2.07 V and 2.4 V vs SHE,  
442 respectively) (Huie et al., 1991; Liang et al., 2008), so they are capable of  
443 oxidizing organic compounds. This fact also coincides with the new absorption  
444 band observed in the UV/Vis spectra at 205 nm associated with a greater  
445 formation of persulfate ions (Figure 4b of the Supplementary material).  
446





447 **Figure 7.** Effect of  $\text{Na}_2\text{SO}_4$  concentration on the evolution of relative CVP  
 448 concentration as a function of time for the ceramic electrode (a) and the BDD  
 449 electrode (b). Empty points represent  $33 \text{ mA}\cdot\text{cm}^{-2}$  and solid points  $83 \text{ mA}\cdot\text{cm}^{-2}$ .

450

451 In Figure 7, it is also observed that the relative concentration of CVP follows an  
 452 exponential decay, and as the system was perfectly stirred, this is an indication  
 453 of that the system was limited by the oxidation reaction of CVP. Therefore, data  
 454 was fitted to a pseudo-first order system, Equation (14), and  $k_{app}$  values were  
 455 calculated. In Figure 5 of the Supplementary Material,  $k_{app}$  values are  
 456 represented as a function of the  $\text{Na}_2\text{SO}_4$  concentration for the two current  
 457 densities applied with both types of anodes. Using the ceramic electrode, it can  
 458 be verified that the CVP degradation velocity tended to decrease with the  
 459 concentration of the supporting electrolyte, as previously commented. On the  
 460 contrary, with the BDD electrode for both values of  $i$  applied, the CVP degradation  
 461 velocity increased with the concentration of  $\text{Na}_2\text{SO}_4$ . For both electrodes, and as  
 462 previously verified with this contaminant,  $k_{app}$  increased when the applied current

463 density, since the generation of oxidant species, especially  $\bullet\text{OH}$  radicals, was  
464 also greater.

465

466 Figure 6 of the Supplementary Material shows the influence of the  $\text{Na}_2\text{SO}_4$   
467 concentration on the mineralization of the CVP. The trend observed for each  
468 electrode similar to that described for the CVP degradation, that is, an increase  
469 in the concentration of  $\text{Na}_2\text{SO}_4$  caused a decrease in the velocity of the CVP  
470 mineralization process with the ceramic electrode and an increase with the BDD  
471 electrode. At the end of the electrolysis experiment, at  $33 \text{ mA cm}^{-2}$ , the CVP was  
472 mineralized by 73.0%, 67.1% and 61.9% using the ceramic electrode and by  
473 80.2%, 83.1 and 84.8% using the BDD for  $\text{Na}_2\text{SO}_4$  concentrations of 0.014, 0.05  
474 and 0.1 M, respectively. On the other hand, at the highest  $i$ , the percentage of  
475 mineralization was 80.7%, 78.9% and 75.0% with the ceramic electrode and  
476 82.8%, 90.0% and 92.5% with the BDD one, respectively.

477

#### 478 *3.4 Analysis of electrogenerated persulfates*

479 As mentioned previously, during the CVP electrochemical oxidation process, in  
480 addition to the  $\bullet\text{OH}$  radicals,  $\text{H}_2\text{O}_2$  can also be formed from the decomposition of  
481  $\bullet\text{OH}$  radicals, together with  $\text{S}_2\text{O}_8^{2-}$  and  $\text{SO}_4^{\bullet-}$  due to the supporting electrolyte  
482 oxidation. With the UV spectrophotometry method, the presence of hydrogen  
483 peroxide and  $\text{SO}_4^{\bullet-}$  was not detected during any of the assays carried out, so the  
484 number of total oxidants determined by iodometry was due to persulfates, since  
485 the supporting electrolyte only contained  $\text{Na}_2\text{SO}_4$ .

486

487 When the Na<sub>2</sub>SO<sub>4</sub> concentration was 0.014 M, with the ceramic electrode,  
488 persulfate formation was not detected in the single compartment reactor.  
489 Nevertheless, using the BDD electrode, the presence of these persulfate ions in  
490 solution was verified for all the experimental conditions, and their concentration  
491 was higher when *i* increased since the oxidation rate of the supporting electrolyte  
492 was higher. Regarding the reactor configuration, the membrane avoided the  
493 reduction at the cathode of these persulfate ions, therefore, the concentration of  
494 persulfate ions was higher in this reactor for both electrodes. With the BDD  
495 electrode, the use of the membrane caused an increase in the persulfate  
496 concentration in the anolyte of the order of 5 and 20 times with respect to the  
497 reactor in absence of membrane for both applied currents. However, the S<sub>2</sub>O<sub>8</sub><sup>2-</sup>  
498 ions present in solution using the ceramic electrode in the anodic compartment  
499 were 10 times lower. These results agree with the evolution of UV/VIS spectra  
500 (Figure 4 of the Supplementary Material) where the appearance of an  
501 absorbance band near to 200 nm observed was associated to the presence of  
502 S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions in presence of the membrane and using the BDD electrode.

503 Regarding the effect of the Na<sub>2</sub>SO<sub>4</sub> concentration, the higher the concentration  
504 of the supporting electrolyte, the greater the concentration of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions detected  
505 in solution for both anodes (Figure 7 of the Supplementary Material). Comparing  
506 both types of anodes, it is observed again that the BDD electrode produced more  
507 persulfate ions. In addition, the formation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions with the ceramic electrode  
508 only was observed for Na<sub>2</sub>SO<sub>4</sub> concentrations of 0.05 and 0.1 M.

509

510 *3.4 Analysis of toxicity with Vibrio Fischeri*

511 Finally, toxicity measurements were carried out for the CVP degradation tests  
512 using the *Vibrio Fischeri* method. The values of toxicity units (TU) of the initial  
513 CVP solutions at three different concentrations of Na<sub>2</sub>SO<sub>4</sub> (0.014, 0.05 and 0.1  
514 M) were 3, 2 and 3 TU, respectively.

515 Regarding the treated solutions, Table 1 of the Supplementary Material presents the  
516 different values of TU obtained as a function of the different experimental  
517 conditions. It was observed that with the ceramic electrode, generally, the TU  
518 values were null. Therefore, in addition to remove part of the contaminant and  
519 organic matter, the toxicity of the initial samples decreased. With the BDD  
520 electrode, in most of the treated samples, the TU values were non-zero and  
521 higher than TU values of initial solutions, mainly when i and the Na<sub>2</sub>SO<sub>4</sub>  
522 concentration increased, and in the presence of a membrane. Comparing this  
523 fact with the concentrations of electrogenerated persulfates, it is verified that  
524 these two measurements are related to each other, since the higher the  
525 concentration of persulfates the toxicity of the sample was greater. Another  
526 possibility was that phosphates and chlorides influenced in these toxicity  
527 measures. However, considering that the initial concentration of CVP was 60  
528 ppm, the maximum concentration of PO<sub>4</sub><sup>3-</sup> and Cl<sup>-</sup> that could be obtained from  
529 the complete oxidation of the CVP (reaction 5) was 15.85 and 5.91 ppm,  
530 respectively. However, in studies carried out using the Daphnia Magna method  
531 (48 h), the EC<sub>50</sub> of PO<sub>4</sub><sup>3-</sup> and Cl<sup>-</sup> were 1089 and 1000 ppm, respectively (Eur and  
532 Kгаа, 2007a, 2007b), which are concentrations much higher than those that may  
533 be present in the samples. This fact reinforces the theory that persulfates were  
534 responsible for the resulting toxicity of the sample, since its EC<sub>50</sub> was lower (133  
535 ppm) (Eur and Kгаа, 2007c), and as observed in Figure 7 of the Supplementary

536 Material, the persulfate concentration in solution is always higher than this value  
537 when using the BDD anode. Therefore, in terms of toxicity, the ceramic electrode  
538 is more suitable for the electrochemical oxidation of CVP than the BDD electrode.

539

#### 540 **4. Conclusions**

541 Recent studies have detected the presence in body waters of a neurotoxic  
542 insecticide, the Chlorfenvinphos (CVP). Traditional treatment methods are not  
543 adequate to treat these contaminated waters so in this work, the electrochemical  
544 advanced oxidation technique with two different anodic materials (BDD and Sb-  
545 doped SnO<sub>2</sub> ceramic) has been studied as an efficient method to remove this  
546 species.

547 This technique has been carried out in galvanostatic mode at current densities  
548 ranging from 17 to 83 mA·cm<sup>-2</sup>. For both anodes in the undivided reactor, at the  
549 lowest current density, the process is limited by charge transfer, that means, that  
550 the limiting step of the oxidation process is the velocity of generation of hydroxyl  
551 radicals (<sup>•</sup>OH). However, at higher current densities, the concentration of CVP  
552 decreases exponentially with electrolysis time since the process is limited by the  
553 chemical reaction oxidation of CVP by means of <sup>•</sup>OH radicals.

554 Furthermore, when *i* increases, both CVP degradation and mineralization  
555 degrees are greater for both anodic materials, due to a greater generation of  
556 oxidizing species, such as <sup>•</sup>OH radicals and persulfate ions. However, the  
557 process presents lower mineralization current efficiency (MCE).

558 The presence of the cation-exchange membrane benefited the oxidation process  
559 using the BDD electrode since the membrane prevented the reduction of the  
560 organic intermediates and oxidizing species formed. Nevertheless, with the  
561 ceramic electrode, the highest degrees of CVP and TOC removal were obtained  
562 in the undivided reactor, due to the contribution of the reduction reaction of CVP  
563 taking place in the absence of the membrane.

564 The  $\text{Na}_2\text{SO}_4$  concentration as supporting electrolyte also affects the  
565 electrochemical degradation process, since for the BDD electrode, a higher  
566 degree of mineralization is achieved at the highest  $\text{Na}_2\text{SO}_4$  concentration and, on  
567 the contrary, for the ceramic electrode, is achieved at the lowest one. This is due  
568 to the ability of each electrode to oxidize sulfate ions to persulfate and sulfate  
569 radicals.

570 Concerning the analysis of the oxidizing agents generated, it is proved that the  
571 sulfates ions of the supporting electrolyte are oxidized to persulfate ions,  
572 however, the  $\text{H}_2\text{O}_2$  presence was not detected. The formation of persulfate ions  
573 is favoured: using the BDD electrode, due to its wide electrochemical window;  
574 when the  $\text{Na}_2\text{SO}_4$  concentration is increased, at high working current densities  
575 and, in the presence of the cation exchange membrane, since it prevents the  
576 reduction of these species at the cathode.

577 Therefore, the results showed that ceramic electrodes can be used as effective  
578 anodes for the oxidation of CVP, since for high current densities it is possible to  
579 degrade a 100% of the CVP. However, the BDD electrode is the most efficient  
580 one since it generates more active oxidant species on its surface.

581 Finally, in terms of toxicity, it is shown that the samples treated with the ceramic  
582 electrode show less toxicity than the initial one. On the other hand, with the BDD  
583 electrode the toxicity is higher, since this parameter is attributed to the persulfate  
584 ions.

585

586

587



588

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590

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594

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