

1 **Biodegradability improvement of clopyralid wastes through electrolysis**
2 **using different diamond anodes**

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26

27 **Abstract**

28 The use of boron-doped (BDDs) anodes for efficient removal of complex organic molecules,
29 such as organochlorine compounds, is well stated in the literature. However, the role of the
30 different characteristics of this anode on the transformation of these type of contaminants into
31 more biodegradable molecules is a topic of interest that need to be clarified when aimed an
32 efficient combination of an electrochemical system as a previous step to biological treatment.
33 In this work, improvement in the biodegradability of synthetic wastes polluted with
34 clopyralid, as an organochlorine model compound, is studied after electrolysis with different
35 BDDs in the presence of the two most common supporting electrolytes (containing sulfate or
36 chloride ions). For that, clopyralid removal, mineralization, aromatics intermediates, short-
37 chain carboxylic acids, and inorganic ions were monitored. Improved results were found in
38 sulfate media for BDD with 200 ppm, capable of removing 88.7 % of contaminants and 85 %
39 of TOC, resulting in an improvement in biodegradability of almost 7-fold compared to the
40 initial sample. These findings point out that lower doping levels are preferable when coupling
41 studied technologies.

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46 **Keywords**

47 Biodegradability; electrolysis; diamond anodes; combined process; clopyralid

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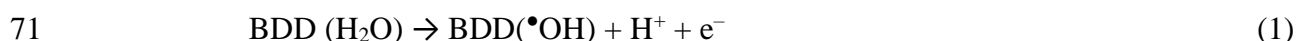
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52 1. Introduction

53 Mainly because of the massive amount of pesticides used in agriculture, the contamination of
54 water by organochlorine compounds generated from industrial and agricultural activities is
55 currently a matter of great concern [1]. These contaminants are typically highly toxic and
56 non-biodegradable [2-4]. Therefore, it is essential to find effective ways to remove them from
57 water [5-8] to protect the environment. The herbicide clopyralid (3,6-dichloro-2-pyridine-
58 carboxylic acid) is a widely used organochlorinated hydrocarbon applied for the removal of
59 broadleaf weed in crops [9-12]. Due to its high solubility in water, clopyralid has been
60 frequently detected in the environment. As many other persistent organic pollutants, its
61 resistance to biodegradation makes this contaminant hard to be removed by conventional
62 technologies [12-14]. Because of that, electrochemical oxidation with boron-doped diamond
63 (BDD) anodes appears as one of the most promising treatment alternatives [14-16], in
64 particular when taking into account the unique properties of BDD, which have allowed,
65 during the last two decades, its efficient application in the electrochemical oxidation of
66 wastes polluted with many different types of complex organic molecules [17-21]. This
67 technology is known to generate high amounts of highly reactive and non-selective hydroxyl
68 radicals (Eq. 1) capable of attaining the complete mineralization of contaminants, that is, to
69 transform them into carbon dioxide, water and inorganics molecules [7, 22, 23].

70



72

73 Moreover, if sulfates and chlorides salts are contained in the wastewater (which is a
74 common situation in real wastes), these species can be oxidized either by direct electron-
75 transfer on the surface of the electrode or by the electrogenerated $\bullet\text{OH}$, forming more stable
76 oxidants, which can act in the bulk solution during the treatment [22, 24]. This production of

77 oxidants helps to minimize the problems associated with mass transport limitations, typically
78 found during the electrochemical treatment of lowly concentrated wastewater. As it is known,
79 the principal mediator species for chloride and sulfate-containing solutions are hypochlorite
80 and peroxosulfate, respectively [25-28]. These stable oxidants and other less stable species
81 derived from them (such as the chlorine and the sulfate radicals) are expected to be formed
82 when these salts are present in the waste, and they may affect the electrochemical oxidation
83 of clopyralid differently. Besides, the efficiency of this process may also depend on the
84 electrode properties, such as the boron doping level, substrate resistivity, and thickness of the
85 diamond layer [29, 30].

86 Regardless of the variability associated with the different characteristics of diamond
87 or the composition of the salts in the waste, the efficiency of the electrolysis with diamond
88 electrodes is typically very high. However, the harsh oxidation conditions produced in bulk
89 during the treatment are associated with large consumption of electricity, which, in turn, leads
90 to high-energy costs. The combination of electrochemical technology with cheaper biological
91 treatments is a challenge, which can help to reduce the operation cost importantly [31]. Thus,
92 the pre-treatment of wastes containing a hardly-to-degrade anthropogenic pollutant to break
93 its molecules into easier to degrade shorter molecules (mainly carboxylic acids) is one of the
94 most critical challenges faced nowadays by the environmental electrochemical technology.

95 Considering this background, the goal of this work is to determine the role of boron-
96 doped diamond anodes with distinct characteristics on the capability of enhancement of the
97 biodegradability of synthetic wastes polluted with clopyralid, used as a model organochlorine
98 pollutant. For this, electrochemical oxidation of clopyralid in the two most common
99 supporting electrolytes (containing sulfate or chloride ions) was carried out. No real waters
100 were used because the aim of the study is prospective, trying to determine conditions for a
101 further successful application of the combined technology, and this goal requires a good

102 understanding of the composition of the waste. The performance of the anodes in the
103 degradation of organochlorines was analyzed through High-Performance Liquid
104 Chromatography (HPLC), chemical oxygen demand (COD), total organic carbon (TOC), ion
105 chromatography and novel rapid biodegradability assays, trying to shed light on the
106 mechanisms and electrode characteristics that promote a successful technology combination.

107

108 **2. Experimental**

109 ***2.1 Chemicals***

110 Clopyralid was of analytical grade (99%), purchased from Sigma Aldrich. Sodium chloride
111 and anhydrous sodium sulfate used as supporting electrolytes were of analytical grade and
112 purchased from Panreac. Methanol and formic acid used for the mobile phase of HPLC were
113 purchased from Sigma-Aldrich. All aqueous solutions were prepared using high-purity water
114 (Millipore Milli-Q system, resistivity > 18 MΩ). All reactants were used as received.

115

116 ***2.2 Electrodes***

117 The experiments were performed in an electrochemical cell using different compositions of
118 BDD supplied by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the
119 hot filament chemical vapor deposition (CVD-HF) on monocrystalline substrate p-type Si (1
120 0 0) wafers (Siltronix).

121 The characterization of conductive-diamond lots was carried out by Adamant
122 Technologies and information about boron contents, sp^3/sp^2 ratio, the thickness of the
123 diamond layer, the roughness of the p-Si substrate and resistivity of the p-Si substrate were
124 provided in a report. From this report, the main characteristics of these anodes are
125 summarized in Table 1.

126

127 **Table 1.** Characteristics of different BDD anodes used in this work (provided from Adamant
128 Technologies).

Anode	Boron content /ppm	Ratio sp^3/sp^2	Thickness of the BDD layer / μm	Si-resistivity / Ohm	Roughness, Si-Surfinra / μm
BDD8000	8000	80	1.05	10	< 0.1
BDD2500	2500	43	1.13	10	< 0.1
BDD1300	1300	77	2.27	10	0.3 – 0.5
BDD200	200	75	1.14	100	0.3 – 0.5
BDD100	100	89	1.03	10	0.3 – 0.5

129

130 **2.2 Electrochemical measurements**

131 The electrochemical measurements were performed in a conventional three-electrode cell
132 connected to a computer connect with an Autolab potentiostat/galvanostat model PGCTAT
133 302N. The cell used an Ag/AgCl (3 M KCl) as the reference electrode and a platinum wire
134 (Pt) as the counter electrode. The working electrodes used were BDD anodes with a
135 geometric surface area of 4 cm². All electrolysis of clopyralid wastes were performed in the
136 three-electrode cell using 150 mL of the electrolyte solution (synthetic wastewater) that was
137 kept in a double-jacket cell at a constant temperature of 25 °C. Electrolyzes were performed
138 in galvanostatic mode at a fixed current density of 30 mA cm². During the process, no pH
139 control was performed.

140

141 **2.3 Analytical techniques**

142 The evolution of the concentration of clopyralid and its aromatic intermediates was
143 monitored by high-performance liquid chromatography (HPLC). An Agilent 1100, equipped

144 with an Eclipse Plus C-18 column (4.6 mm × 100 mm; 3.5 μm) was used. The mobile phase
145 was a mixture of 30% methanol and 70% formic acid (0.1%) at a flow rate of 1 mL min⁻¹,
146 with the detection at 280 nm. The injection volume was 20.0 μL, the column temperature was
147 set to 20°C, and the retention time was around 2.7 min for clopyralid. Acids were identified
148 by an HPLC equipped with a Zorbax SB-Aq, column (4.6 mm × 150 mm), the mobile phase
149 consists of 4 mM H₂SO₄ with detection at 210 nm. The retention time comparison identified
150 the intermediates with standard solutions. Inorganic ions (nitrite, nitrate, ammonium,
151 chlorate, and perchlorate) concentrations were measured by ion chromatography using a
152 Metrohm 930 Compact IC Flex coupled to a conductivity detector. The total organic carbon
153 (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.
154 Chemical oxygen demand (COD) analyses were conducted by using a Spectroquant[®] test
155 CSB from Merck.

156

157 **2.4 Biodegradability tests**

158 Unacclimated activated sludge, was taken from a local municipal wastewater treatment plant
159 (WTP), located in Ciudad Real, Spain, and was used for short-term biodegradability
160 assessment. Prior to the tests, the collected sludge was aerated for more than one night in the
161 absence of external substrate addition. Changes in the oxygen concentration were measured
162 with an oximetry WWR-OX4100H. For the tests, a volume of waste (5 mL) was added to 100
163 ml bioreactor filled (95 mL) of activated sludge under continuous stirrer by magnetic bars.
164 The short-term biodegradability is then estimated taking into account the primary decay
165 related to the concentration of dissolved oxygen (DO) associated with endogenous
166 consumption and variation from linear to exponential decay when these external compounds
167 are added provoking an increased consumption rate associated with the consumption of the
168 organics contained. Then, the primary decay is reestablished (at the new sludge

169 concentration), and a linear decay rate is kept related to the initial one. Thus, the oxygen
170 consumption associated with the substrate contained in the samples is calculated by mass
171 balance added. The obtained value correspondent to the short-term biological oxygen demand
172 (BOD_{st}), and when related to the COD, the ratio indicates the biodegradability of the sample.
173 Before the biodegradability analysis, pH values were adjusted to 7.0.

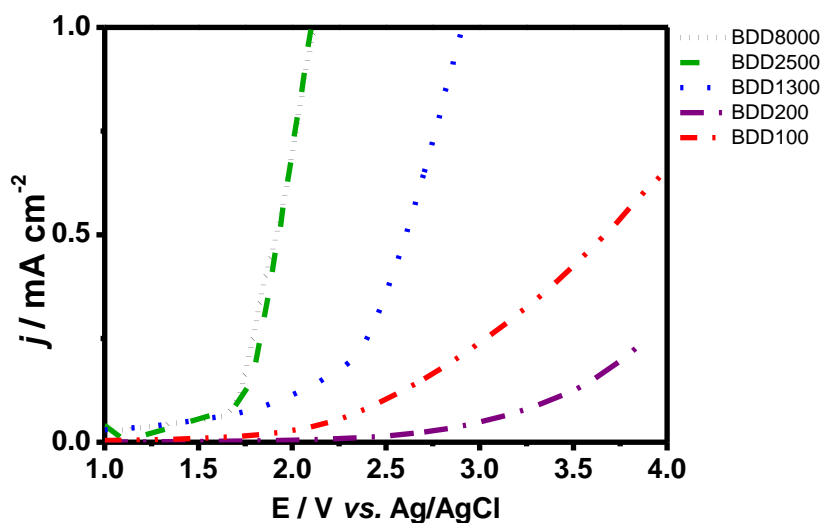
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175 **3. Results and discussion**

176 **Figure 1** shows the linear sweep voltammetry curves of the BDD anodes taken in a 0.5 mol
177 L^{-1} H_2SO_4 solution. These measurements are essential to confirm that the electrochemical
178 anodic potential interval of the diamond electrodes decreases with the increase in the boron
179 doping level. This trend is pointed out in several works employing BDD anodes with distinct
180 doping levels [29, 32, 33].

181 As can be seen, the oxygen evolution reaction (OER) occurs at the same potential at
182 highly-doped anodes (BDD8000 and BDD2500), which means that this property does not
183 influence the potential window at this range of boron doping. On the contrary, OER
184 overpotential shifts more significantly to values that are more positive when boron doping
185 decreases from 1300 ppm to 100 ppm. The BDD200 anode presented a larger potential
186 window than BDD100. This behavior can be explained in terms of the influence of the silicon
187 substrate that is 10-folds more resistive than for the BDD100 anode. This observation is in
188 agreement with findings reported by Moraleda *et al.* [23] that recently showed that the use of
189 different substrates during the diamond deposition influences the formation of hydroxyl
190 radicals. The significant difference observed points out that the resistance of the silicon
191 substrate is a more meaningful input than the boron content, at least within the range of low
192 boron doping levels studied. It is essential to consider that the broadest potential window is
193 desirable when working with BDD anodes, because it is related to the more critical

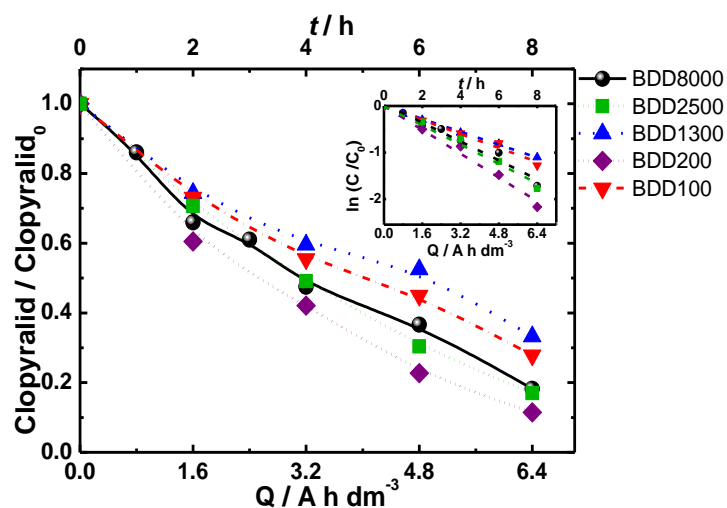
194 production of oxidants and, hence, it is expected to influence the oxidation behavior at these
195 anodes.
196



197
198 **Figure 1.** Linear sweep voltammetric curves performed at 10 mV s^{-1} in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

199
200 **Figure 2** shows the clopyralid removal with different BDD anodes as a function of the
201 current charge passed for electrolysis carried out in $3.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ at a fixed current
202 density of 30 mA cm^{-2} . Note that clopyralid is incompletely removed during 8 h for all
203 anodes, which confirms the stability of this molecule. The highest removal percentage of
204 clopyralid is 88.6%, obtained using the BDD200 anode, suggesting the generation of higher
205 concentration of oxidants onto the surface of this anode that, in turn, can react with sulfate
206 species to form more stable oxidants in the bulk solution. On the other hand, for the rest of
207 the anodes, the percentage of removal remained between 72.2% and 83.0% after 8 h of
208 treatment. Inset in Figure 2 shows the exponential decay of the clopyralid concentration,
209 suggesting that the clopyralid removal obeys a pseudo-first-order kinetic. This result indicates
210 that the mass transport of reactants towards the anodes limited the process, which is an
211 expected response for electrochemical diffusion-controlled systems.

212



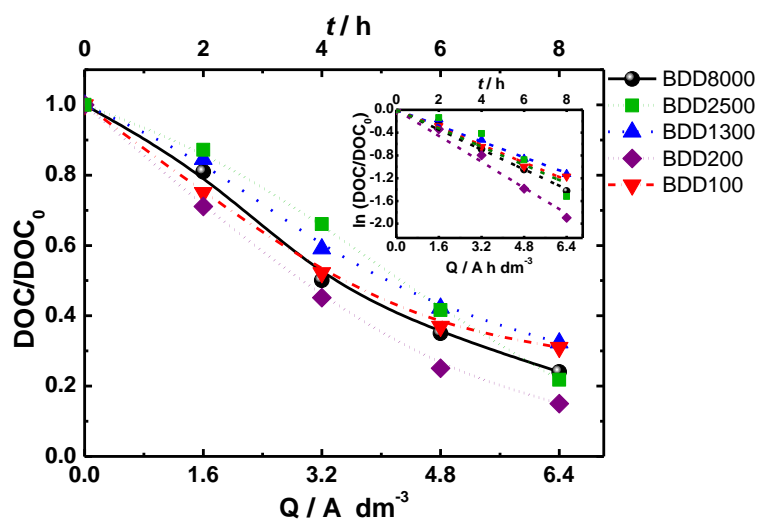
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214 **Figure 2.** Clopyralid removal on different BDD anodes in Na_2SO_4 (3 g L^{-1}) at a fixed current
 215 density: 30 mA cm^{-2} . Conditions: pH: 3.6; Clopyralid₀: 100 mg L^{-1} . Inset: Kinetic for
 216 clopyralid removal.

217

218 **Figure 3** shows the total dissolved organic carbon (DOC) removal on the different
 219 BDD anodes. The use of different types of diamonds results in different DOC removals after
 220 the same charge passed (6.4 A h dm^{-3}). In Na_2SO_4 media, the BDD200 leads to higher DOC
 221 removal of 88.7%. The inset shows the logarithmic plot, which also fits well with a pseudo-
 222 first-order kinetic model. The values of k_{DOC} and R^2 are in **Table 2**. The fastest DOC kinetics
 223 decay is observed for BDD200.

224



225

226 **Figure 3.** DOC removal on different BDD anodes in Na_2SO_4 (3.0 g L^{-1}) at a fixed current
 227 density of 30 mA cm^{-2} . Conditions: pH: 3.6; Clopyralid₀: 100 mg L^{-1} . Inset: Kinetic for DOC
 228 removal.

229

230 **Table 2.** Pseudo-first-order kinetics constants calculated for clopyralid and DOC removal and
 231 the percentage of clopyralid and DOC removal.

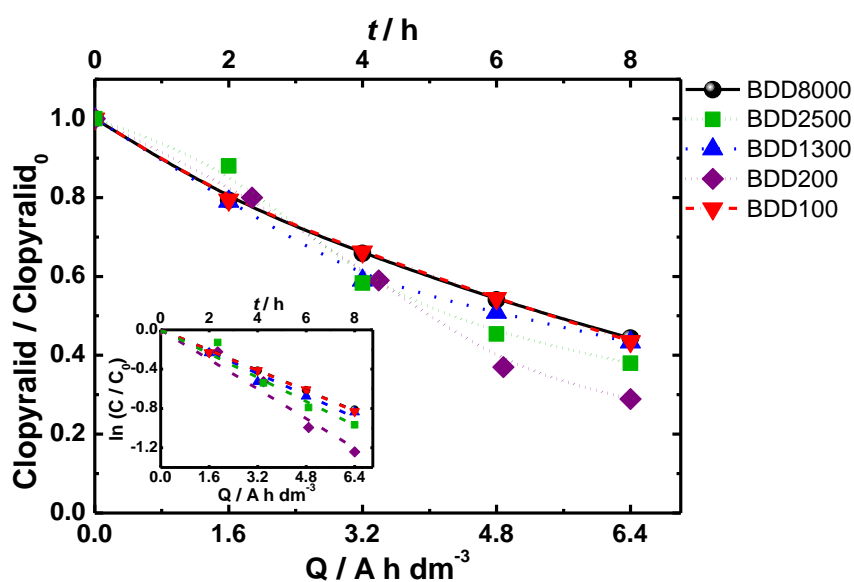
Anode	Na_2SO_4	R^2	%	Na_2SO_4	R^2	%
	$k_{\text{Cllop}} / \text{min}^{-1}$			clopyralid		
BDD8000	0.202	90.7	81.8	0.174	99.7	76.0
BDD2500	0.207	99.1	83.0	0.161	94.2	78.2
BDD1300	0.138	99.8	72.2	0.128	99.2	67.7
BDD200	0.255	99.3	88.6	0.227	99.3	85.0
BDD100	0.150	99.2	72.2	0.154	99.5	69.0

232

233 To evaluate the influence of the salts contained in the waste, **Figure 4** shows the
 234 removal of clopyralid with different BDD anodes, as a function of current charge passed for

235 electrolysis carried out in an electrolyte containing 3.7 g L^{-1} NaCl at a fixed current density
 236 of 30 mA cm^{-2} . The inset of Figure 4 displays the semilogarithmic plot, made for easy kinetic
 237 analysis. Note that BDD200 removed 71.1% of clopyralid, while other anodes removed the
 238 herbicide in percentages that range from 55.6% to 62.0%. This outcome agrees with the
 239 observed in sulfate media, which indicates that mediated oxidation is playing an essential role
 240 in the clopyralid removal.

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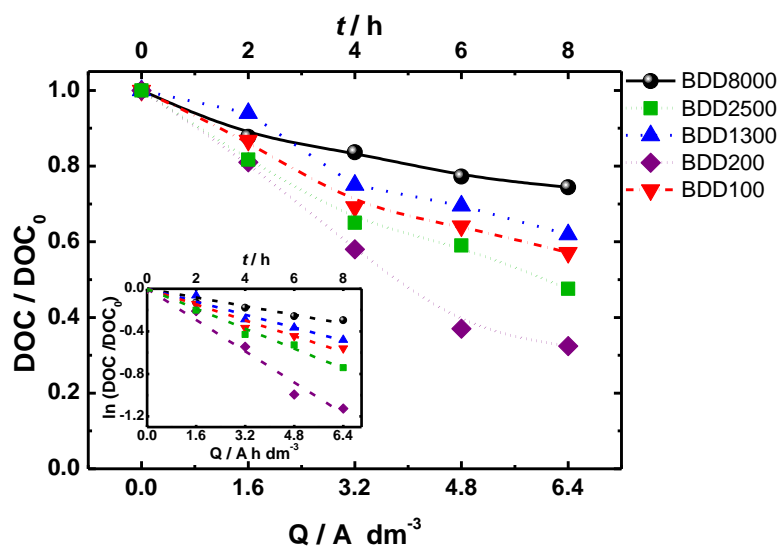
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243 **Figure 4.** Clopyralid degradation as a function of time and current charge passed for
 244 electrolysis carried out in NaCl 3.7 g L^{-1} at a fixed current of 30 mA cm^{-2} .

245

246 The removal of the total dissolved organic carbon (DOC) (**Figure 5**) seen for sulfate
 247 media, shows that the mineralization process obeys pseudo-first-order kinetics (as indicated
 248 by straight lines seen in the inset of Figure 5). **Table 3** summarizes the values of k_{DOC} and
 249 R^2 . The highest constant rate is observed for the BDD200 anode, also pointing out that this
 250 anode is more efficient in producing hydroxyl radicals as well as other reactive oxidative
 251 species.

252



253

254 **Figure 5.** DOC removal on different BDD anodes in NaCl (3.7 g L^{-1}) at a fixed current
 255 density of 30 mA cm^{-2} . Conditions: pH: 3.6; Clopyralid₀: 100 mg L^{-1} . Inset: Kinetic for DOC
 256 removal.

257

258 **Table 3.** Pseudo-first-order kinetics constants calculated for clopyralid and DOC removal and
 259 the percentage of clopyralid and DOC removal.

Anode	NaCl	R^2	% clopyralid	NaCl	R^2	% DOC
	$k_{\text{clon}} / \text{min}^{-1}$			$k_{\text{DOC}} / \text{min}^{-1}$		
BDD8000	0.1027	99.9	55.6	0.041	99.6	25.6
BDD2500	0.1214	98.1	62.0	0.094	94.3	42.8
BDD1300	0.1112	99.2	56.7	0.061	99.3	38.1
BDD200	0.1504	98.4	71.1	0.126	98.8	67.6
BDD100	0.1032	99.1	56.4	0.074	98.8	52.4

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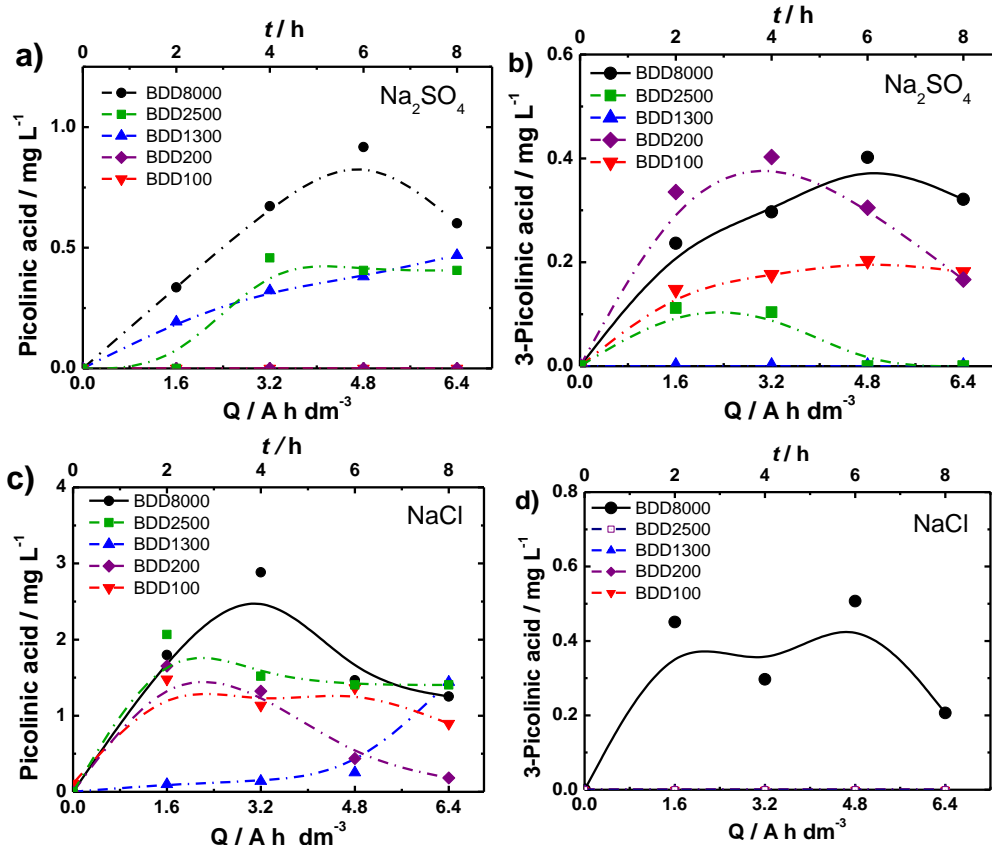
261 Hence, in chloride and sulfate media, the resistivity of the substrate influences the
 262 results, which agrees with the voltammetric observations (**Figure 1**). Regarding the boron

263 doping, the influence is not as evident, indicating that this parameter is not as important in the
264 oxidation of the model herbicide tested, although in comparing the extreme values, more
265 critical oxidation in the case of the low-doped anodes can be suggested.

266 HPLC analysis of the treated solution of clopyralid showed the formation of two
267 primary by-products: picolinic acid and 3-picolinic acid, corresponding to the dehalogenation
268 of clopyralid, which may be developed on the cathode of the electrochemical cell and not on
269 the anode (cathodic hydrodehalogenation process). **Figure 6** presents the evolution of these
270 reaction intermediates during the different electrolytic tests. The absence of other peaks
271 indicates that oxidation does not form stable aromatic intermediates in significant
272 concentrations, that is, that oxidation intermediates formed are rapidly oxidized.
273 Consequently, only carboxylic acids are going to be found as intermediates coming from the
274 oxidation process in the cell.

275 Again, as a general trend, and regardless of the supporting electrolyte, the anodes with
276 high boron doping level favor the concentration of these dehalogenated intermediates,
277 suggesting the more difficult oxidation of these cathodically formed intermediates with those
278 anodes. It helps to explain the more limited mineralization rate observed for these anodes. In
279 turn, anodes with low doping levels, do not favor the accumulation of intermediates,
280 indicating that they are oxidized to carboxylic acids.

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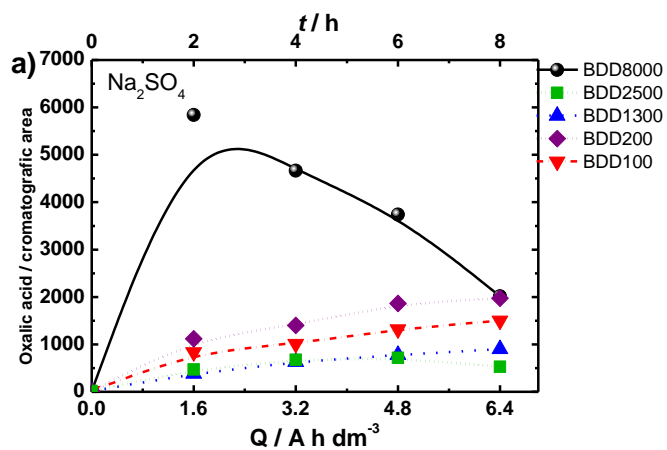
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284 **Figure 6.** Evolution of byproducts concentration during the electrochemical oxidation of
 285 clopyralid on different BDD anodes in Na₂SO₄ (a and b) and NaCl (c and d) at a fixed current
 286 density: 30 mA cm⁻². Conditions: pH: 3.6; Clopyralid₀: 100 mg L⁻¹.

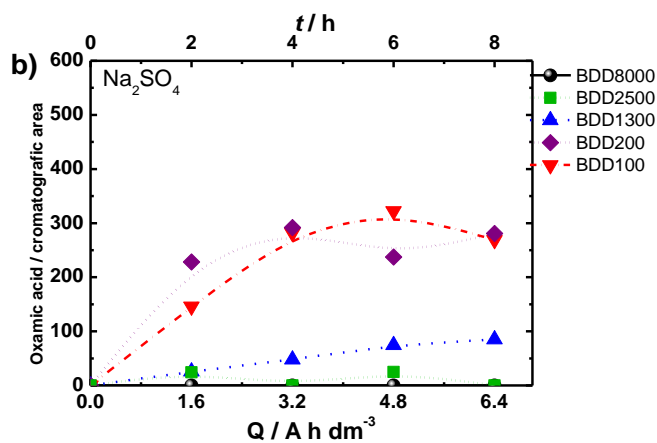
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288 **Figure 7** and **Figure 8** show, respectively, the evolution of the formation of short-
 289 chain carboxylic acids and inorganic ions. Oxalic acid and oxamic acid were detected in
 290 sulfate media (**Figure 7a and 7b**), while only oxalic acid was detected in chloride media
 291 (**Figure 7c**). Typically, the concentration of these intermediates (except for the oxalic acid
 292 with the BDD8000 anode) increases as the boron doping decreases, suggesting more effective
 293 oxidation of the aromatic intermediates, but the more considerable difficulties in the
 294 oxidation of these acid intermediates formed. Accumulation of carboxylic acids is positive
 295 from the viewpoint of a further combination of technologies because, typically, these species
 296 are readily biodegradable.

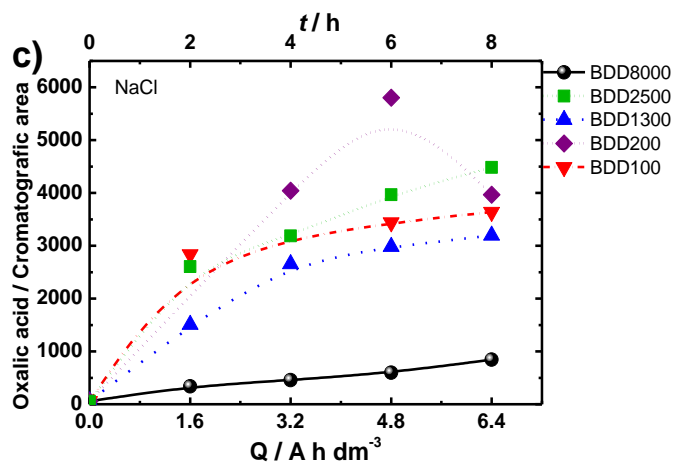
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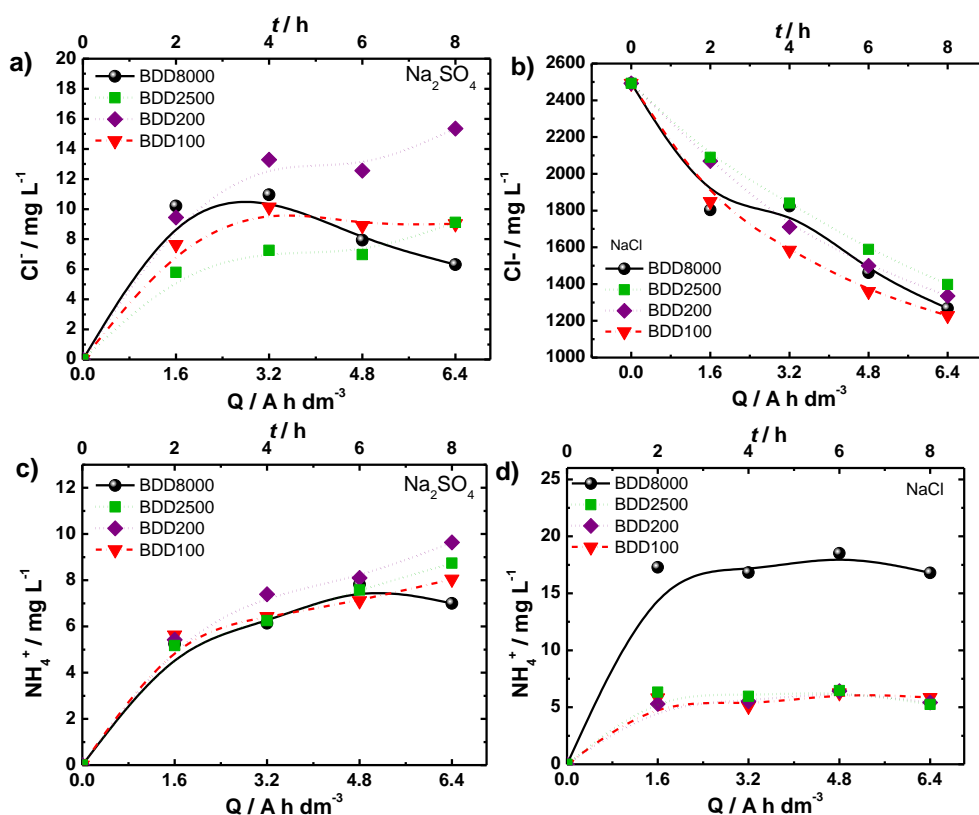
300 **Figure 7.** Evolution of main carboxylic acid concentration during the electrochemical
301 oxidation of clopyralid on different BDD anodes in Na₂SO₄ (a and b) and NaCl (c) at a fixed
302 current density: 30 mA cm⁻². Conditions: pH: 3.6; Clopyralid₀: 100 mg L⁻¹.

303

304 Concerning inorganic species, ion chromatography indicates the formation of
305 ammonium, chlorides, and nitrate ions (**Figure 8**). In sulfate media, it can be easily seen the

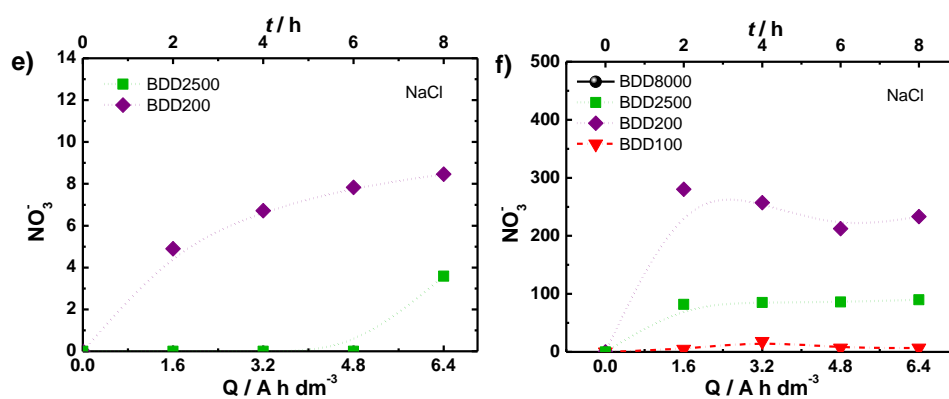
306 formation rate of chloride ions, reaching a maximum for the BDD200 anode and a minimum
 307 for the BDD8000 anode (**Figure 8a**). The same trend is observed regarding the ammonium
 308 and nitrate ions released in sulfate media, which is consistent with previously discussed
 309 regarding the reduction of total dissolved organic carbon (DOC). Nevertheless, for chloride
 310 media, it is difficult to find differences in chloride ions, since a large amount of this salt in the
 311 electrolyte makes it difficult to get any conclusion in this media. On the other hand, for
 312 ammonium and nitrate, it is possible to note interesting differences among anodes. The main
 313 difference observed, again, for the BDD200 anode, which was responsible for the formation
 314 of higher quantities of nitrate and almost no detected ammonium.

315



316

317



318

319 **Figure 8.** Evolution of inorganic ions formed during the electrochemical oxidation of
 320 clopyralid on different BDD anodes in Na_2SO_4 (a, c and e) and NaCl (b, d, and f) at a fixed
 321 current density: 30 mA cm^{-2} . Conditions: pH: 3.6; Clopyralid₀: 100 mg L^{-1} .

322

323 Samples obtained before and after the different electrolysis underwent respirometric
 324 tests, consisting of monitoring the oxygen consumption evolution in an activated sludge
 325 sample before and after the addition of a volume of waste. **Figure 9** shows that before the
 326 addition of the waste, the sludge, obtained from the biological reactor of a municipal WWTP
 327 and previously aerated for more than one night in the absence of external substrate addition,
 328 presents a linear decay in the concentration of oxygen. It is associated with endogenous
 329 consumption, which is the consuming of dead microorganisms by the living microorganisms,
 330 which value depends on the concentration of the sludge. It means that when diluted, the
 331 oxygen consumption rate decreases linearly with the dilution rate. Then, by adding an
 332 increased volume of waste, the decay rate reduces (because of the dilution of the
 333 concentration of the microorganisms), but increases the rate associated with the consumption
 334 of the organics contained. Changes in the oxygen concentration vary from linear to
 335 exponential decay. After consumption of these external compounds, the endogenous rate (at
 336 the new sludge concentration) is again the primary decay, and a linear decay rate is kept
 337 (whose slope is related to the initial one taking into account the dilution undergone). By mass

338 balance, the oxygen consumption associated with the substrate contained in the samples
339 added to the sludge can be easily calculated. This value corresponds to the short-term
340 biological oxygen demand, and when related to the COD, the ratio indicates the
341 biodegradability of the sample.
342

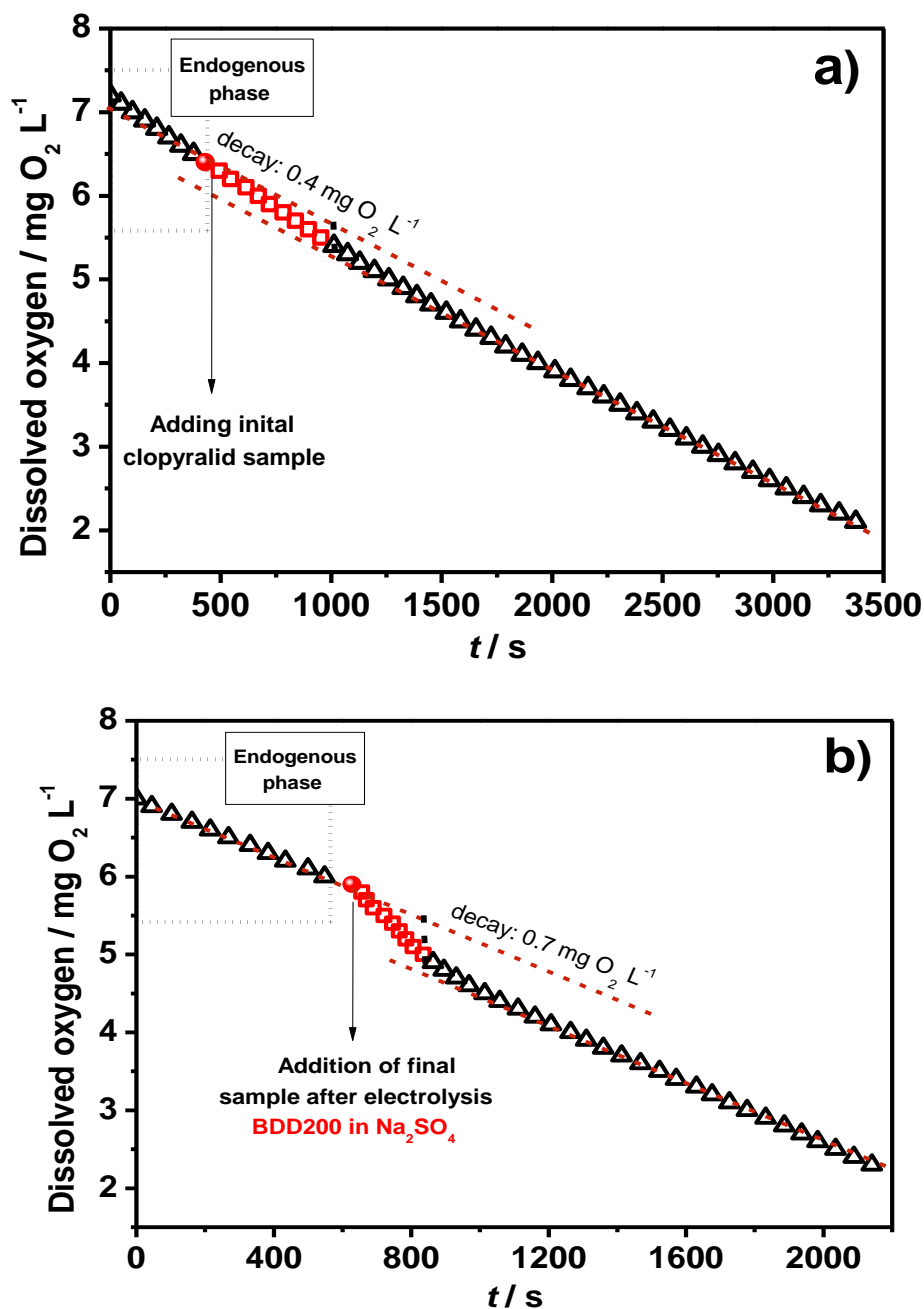


Figure 9. Dissolved oxygen *versus* time graphs used to calculate biodegradability of the samples obtained before (a) and after electrolysis (b) for a representative sample. Conditions:

347 BDD200 anode; pH: 3.6; Clopyralid₀: 100 mg L⁻¹; current density: 30 mA cm⁻²; NaCl: 3.7 g
 348 L⁻¹.

349

350 **Table 4** shows the calculated short-term oxygen demand, the COD of the samples,
 351 and the biodegradability. It also shows the total aromatic and aliphatic chromatographic area
 352 of intermediates.

353

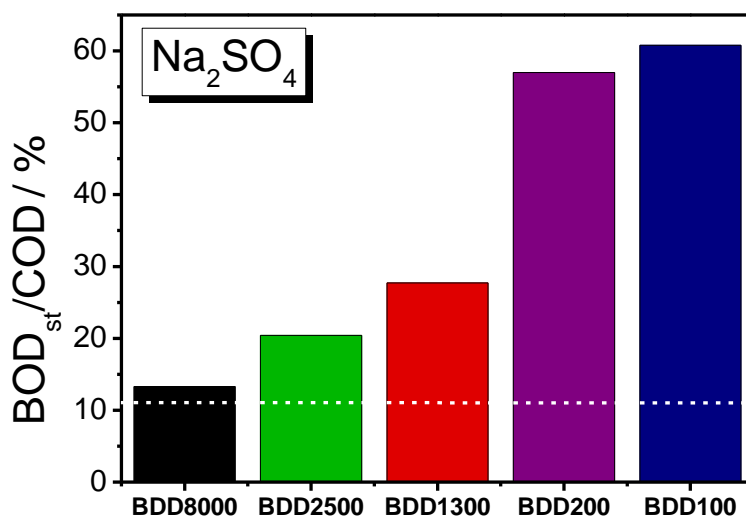
354 **Table 4.** Obtained values for COD of the samples, the total aromatic and aliphatic
 355 chromatographic area of intermediates, short-term oxygen demand, and the biodegradability.

Anode	Supporting electrolyte	COD	Total	Total	DBOst	Biodegradability (DBOst/COD)
			aromatics HPLC area	carboxylic acids HPLC area		
BDD8000	Na ₂ SO ₄	60.0	592.0	2015.0	0.4	13.3
BDD2500	(3.0 g L ⁻¹)	87.9	602.1	529.0	0.9	20.4
BDD1300		36.0	516.9	986.7	0.5	27.7
BDD200		28.2	393.3	2254.9	0.8	57.0
BDD100		19.7	107.4	1774.1	0.6	60.8
BDD8000		NaCl	90.0	252.1	843.2	0.5
BDD2500	(3.7 g L ⁻¹)	70.1	305.0	4485.9	0.8	22.8
BDD1300		80.8	205.7	3195.9	0.8	19.8
BDD200		62.6	31.50	3966.7	0.8	25.5
BDD100		51.4	133.5	3641.6	0.9	35.0

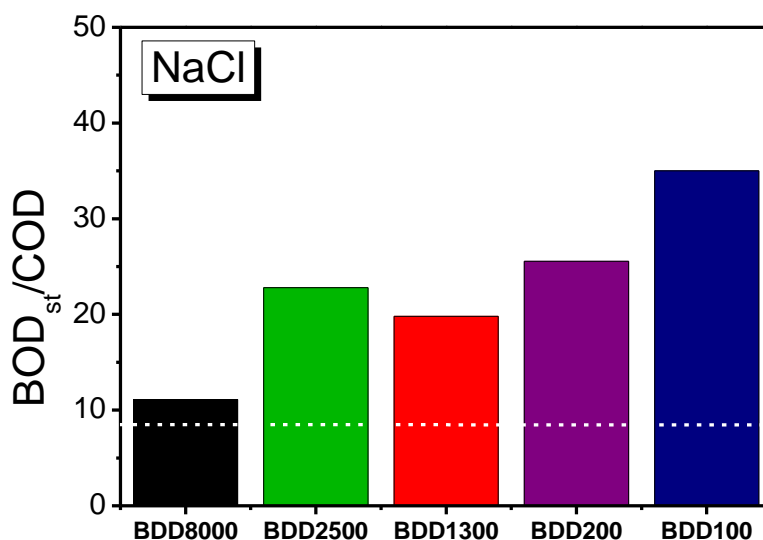
356

357 **Figure 10** shows significant differences among anodes studied that strongly depend
358 on the doping level. For both electrolytes studied, the BDD100 and BDD200 anodes provided
359 better responses in terms of improved biodegradability, which is more than 4.5 times better
360 than that obtained by the diamond doped with 8000 ppm of boron. Comparing the
361 biodegradability of the treated wastes and the initial wastes, we see that it improved
362 significantly, as biodegradability of the initial waste was found to be as low as 8.3 %. In
363 general, in sulfate media, the biodegradability is higher than in chloride media. It can be
364 explained in terms of the negative effect of the electrochemically generated chlorine on the
365 microorganisms. Although peroxosulfates can also affect negatively to microorganisms,
366 chlorine, and derivatives lead to a more negative effect.

367



368



369

370 **Figure 10.** Biodegradability tests after treatment in Na₂SO₄ (3.0 g L⁻¹) (a) and NaCl (3.7 g L⁻¹) (b). Conditions: pH: 3.6; Clopyralid₀: 100 mg L⁻¹; current density: 30 mA cm⁻². White
 371
 372 discontinuous line: ratio before degradation tests

373

374 The results obtained confirm that electrolysis with diamond anodes can be a good pre-
 375 treatment for a later biological stage, although, in order to improve this combination,
 376 electrodes with low boron doping have to be used, because these electrodes, besides, to attain
 377 higher mineralization, lead to effluents with a higher biodegradability.

378

379 **Conclusions**

380 The electrochemical oxidation using boron-doped diamonds with different characteristics
 381 contributes differently to the improvement of biodegradability of the poorly biodegradable
 382 herbicide, clopyralid. Distinct boron-doped diamonds provide different efficiencies in terms
 383 of clopyralid removal and mineralization. These efficiencies, in turn, depend on the
 384 composition of the supporting electrolyte. For both supporting electrolytes (chloride or
 385 sulfate) evaluated, the anode of 200 ppm content in boron (BDD200) was the most efficient
 386 in removing and to transform clopyralid into more biodegradable compounds. The resistivity

387 of the diamond substrate seems to be a significant parameter in order to explain the results of
388 electrolysis. On the other hand, BDD with a high doping level favors the formation of
389 intermediates, while low doping levels only favor a small accumulation of intermediates,
390 which favors mineralization rate. Regardless of the electrolyte media, lower doping levels
391 enhanced 1.8–4.5-times, for BDD100 and BDD200, respectively, the solution
392 biodegradability for the model contaminant here studied. Finally, these findings point out that
393 lower doping levels are preferable for improving biodegradability in order to make the
394 sequenced process using electrolysis before biodegradation with activated sludge,
395 economically attractive.

396

397 **Conflicts of interest**

398 There are no conflicts to declare.

399

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