Biodegradability improvement of clopyralid wastes through electrolysis
using different diamond anodes

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Abstract

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

Keywords

Biodegradability; electrolysis; diamond anodes; combined process; clopyralid
1. Introduction

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

\[
BDD (H_{2}O) \rightarrow BDD(\cdot OH) + H^{+} + e^{-} \tag{1}
\]

Moreover, if sulfates and chlorides salts are contained in the wastewater (which is a common situation in real wastes), these species can be oxidized either by direct electron-transfer on the surface of the electrode or by the electrogenerated \( \cdot OH \), forming more stable oxidants, which can act in the bulk solution during the treatment [22, 24]. This production of
oxidants helps to minimize the problems associated with mass transport limitations, typically
found during the electrochemical treatment of lowly concentrated wastewater. As it is known,
the principal mediator species for chloride and sulfate-containing solutions are hypochlorite
and peroxosulfate, respectively [25-28]. These stable oxidants and other less stable species
derived from them (such as the chlorine and the sulfate radicals) are expected to be formed
when these salts are present in the waste, and they may affect the electrochemical oxidation
of clopyralid differently. Besides, the efficiency of this process may also depend on the
electrode properties, such as the boron doping level, substrate resistivity, and thickness of the
diamond layer [29, 30].

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

Considering this background, the goal of this work is to determine the role of boron-
doped diamond anodes with distinct characteristics on the capability of enhancement of the
biodegradability of synthetic wastes polluted with clopyralid, used as a model organochlorine
pollutant. For this, electrochemical oxidation of clopyralid in the two most common
supporting electrolytes (containing sulfate or chloride ions) was carried out. No real waters
were used because the aim of the study is prospective, trying to determine conditions for a
further successful application of the combined technology, and this goal requires a good
understanding of the composition of the waste. The performance of the anodes in the degradation of organochlorines was analyzed through High-Performance Liquid Chromatography (HPLC), chemical oxygen demand (COD), total organic carbon (TOC), ion chromatography and novel rapid biodegradability assays, trying to shed light on the mechanisms and electrode characteristics that promote a successful technology combination.

2. Experimental

2.1 Chemicals

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

2.2 Electrodes

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

The characterization of conductive-diamond lots was carried out by Adamant Technologies and information about boron contents, sp³/sp² ratio, the thickness of the diamond layer, the roughness of the p-Si substrate and resistivity of the p-Si substrate were provided in a report. From this report, the main characteristics of these anodes are summarized in Table 1.
Table 1. Characteristics of different BDD anodes used in this work (provided from Adamant Technologies).

<table>
<thead>
<tr>
<th>Anode</th>
<th>Boron content / ppm</th>
<th>Ratio sp³/sp²</th>
<th>Thickness of the BDD layer / μm</th>
<th>Si-resistivity / Ohm</th>
<th>Roughness, Si-Surfinra / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD8000</td>
<td>8000</td>
<td>80</td>
<td>1.05</td>
<td>10</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>BDD2500</td>
<td>2500</td>
<td>43</td>
<td>1.13</td>
<td>10</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>BDD1300</td>
<td>1300</td>
<td>77</td>
<td>2.27</td>
<td>10</td>
<td>0.3 – 0.5</td>
</tr>
<tr>
<td>BDD200</td>
<td>200</td>
<td>75</td>
<td>1.14</td>
<td>100</td>
<td>0.3 – 0.5</td>
</tr>
<tr>
<td>BDD100</td>
<td>100</td>
<td>89</td>
<td>1.03</td>
<td>10</td>
<td>0.3 – 0.5</td>
</tr>
</tbody>
</table>

2.2 Electrochemical measurements

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

2.3 Analytical techniques

The evolution of the concentration of clopyralid and its aromatic intermediates was monitored by high-performance liquid chromatography (HPLC). An Agilent 1100, equipped
with an Eclipse Plus C-18 column (4.6 mm × 100 mm; 3.5 μm) was used. The mobile phase was a mixture of 30% methanol and 70% formic acid (0.1%) at a flow rate of 1 mL min⁻¹, with the detection at 280 nm. The injection volume was 20.0 μL, the column temperature was set to 20°C, and the retention time was around 2.7 min for clopyralid. Acids were identified by an HPLC equipped with a Zorbax SB-Aq column (4.6 mm × 150 mm), the mobile phase consists of 4 mM H₂SO₄ with detection at 210 nm. The retention time comparison identified the intermediates with standard solutions. Inorganic ions (nitrite, nitrate, ammonium, chlorate, and perchlorate) concentrations were measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Chemical oxygen demand (COD) analyses were conducted by using a Spectroquant® test CSB from Merck.

2.4 Biodegradability tests

Unacclimated activated sludge, was taken from a local municipal wastewater treatment plant (WTTP), located in Ciudad Real, Spain, and was used for short-term biodegradability assessment. Prior to the tests, the collected sludge was aerated for more than one night in the absence of external substrate addition. Changes in the oxygen concentration were measured with an oximetry WWR-OX4100H. For the tests, a volume of waste (5 mL) was added to 100 ml bioreactor filled (95 mL) of activated sludge under continuous stirrer by magnetic bars. The short-term biodegradability is then estimated taking into account the primary decay related to the concentration of dissolved oxygen (DO) associated with endogenous consumption and variation from linear to exponential decay when these external compounds are added provoking an increased consumption rate associated with the consumption of the organics contained. Then, the primary decay is reestablished (at the new sludge
concentration), and a linear decay rate is kept related to the initial one. Thus, the oxygen consumption associated with the substrate contained in the samples is calculated by mass balance added. The obtained value correspondent to the short-term biological oxygen demand (BOD₅), and when related to the COD, the ratio indicates the biodegradability of the sample. Before the biodegradability analysis, pH values were adjusted to 7.0.

3. Results and discussion

Figure 1 shows the linear sweep voltammetry curves of the BDD anodes taken in a 0.5 mol L⁻¹ H₂SO₄ solution. These measurements are essential to confirm that the electrochemical anodic potential interval of the diamond electrodes decreases with the increase in the boron doping level. This trend is pointed out in several works employing BDD anodes with distinct doping levels [29, 32, 33].

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

Figure 1. Linear sweep voltammetric curves performed at 10 mV s⁻¹ in 0.5 mol L⁻¹ H₂SO₄.

Figure 2 shows the clopyralid removal with different BDD anodes as a function of the current charge passed for electrolysis carried out in 3.0 g L⁻¹ Na₂SO₄ at a fixed current density of 30 mA cm⁻². Note that clopyralid is incompletely removed during 8 h for all anodes, which confirms the stability of this molecule. The highest removal percentage of clopyralid is 88.6%, obtained using the BDD200 anode, suggesting the generation of higher concentration of oxidants onto the surface of this anode that, in turn, can react with sulfate species to form more stable oxidants in the bulk solution. On the other hand, for the rest of the anodes, the percentage of removal remained between 72.2% and 83.0% after 8 h of treatment. Inset in Figure 2 shows the exponential decay of the clopyralid concentration, suggesting that the clopyralid removal obeys a pseudo-first-order kinetic. This result indicates that the mass transport of reactants towards the anodes limited the process, which is an expected response for electrochemical diffusion-controlled systems.
Figure 2. Clopyralid removal on different BDD anodes in Na$_2$SO$_4$ (3 g L$^{-1}$) at a fixed current density: 30 mA cm$^{-2}$. Conditions: pH: 3.6; Clopyralid$_0$: 100 mg L$^{-1}$. Inset: Kinetic for clopyralid removal.

Figure 3 shows the total dissolved organic carbon (DOC) removal on the different BDD anodes. The use of different types of diamonds results in different DOC removals after the same charge passed (6.4 A h dm$^{-3}$). In Na$_2$SO$_4$ media, the BDD200 leads to higher DOC removal of 88.7%. The inset shows the logarithmic plot, which also fits well with a pseudo-first-order kinetic model. The values of k$_{DOC}$ and R$^2$ are in Table 2. The fastest DOC kinetics decay is observed for BDD200.
Figure 3. DOC removal on different BDD anodes in Na$_2$SO$_4$ (3.0 g L$^{-1}$) at a fixed current density of 30 mA cm$^{-2}$. Conditions: pH: 3.6; Clopyralid$_0$: 100 mg L$^{-1}$. Inset: Kinetic for DOC removal.

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

<table>
<thead>
<tr>
<th>Anode</th>
<th>Na$_2$SO$_4$</th>
<th>$k_{\text{Clop}}$/min$^{-1}$</th>
<th>$R^2$</th>
<th>%</th>
<th>Na$_2$SO$_4$</th>
<th>$R^2$</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDD8000</td>
<td></td>
<td>0.202</td>
<td>90.7</td>
<td>81.8</td>
<td>0.174</td>
<td>99.7</td>
<td>76.0</td>
</tr>
<tr>
<td>BDD2500</td>
<td></td>
<td>0.207</td>
<td>99.1</td>
<td>83.0</td>
<td>0.161</td>
<td>94.2</td>
<td>78.2</td>
</tr>
<tr>
<td>BDD1300</td>
<td></td>
<td>0.138</td>
<td>99.8</td>
<td>72.2</td>
<td>0.128</td>
<td>99.2</td>
<td>67.7</td>
</tr>
<tr>
<td>BDD200</td>
<td></td>
<td>0.255</td>
<td>99.3</td>
<td>88.6</td>
<td>0.227</td>
<td>99.3</td>
<td>85.0</td>
</tr>
<tr>
<td>BDD100</td>
<td></td>
<td>0.150</td>
<td>99.2</td>
<td>72.2</td>
<td>0.154</td>
<td>99.5</td>
<td>69.0</td>
</tr>
</tbody>
</table>

To evaluate the influence of the salts contained in the waste, Figure 4 shows the removal of clopyralid with different BDD anodes, as a function of current charge passed for
electrolysis carried out in an electrolyte containing 3.7 g L\(^{-1}\) NaCl at a fixed current density of 30 mA cm\(^{-2}\). The inset of Figure 4 displays the semilogarithmic plot, made for easy kinetic analysis. Note that BDD200 removed 71.1% of clopyralid, while other anodes removed the herbicide in percentages that range from 55.6% to 62.0%. This outcome agrees with the observed in sulfate media, which indicates that mediated oxidation is playing an essential role in the clopyralid removal.

The removal of the total dissolved organic carbon (DOC) (Figure 5) seen for sulfate media, shows that the mineralization process obeys pseudo-first-order kinetics (as indicated by straight lines seen in the inset of Figure 5). Table 3 summarizes the values of \(k_{\text{DOC}}\) and \(R^2\). The highest constant rate is observed for the BDD200 anode, also pointing out that this anode is more efficient in producing hydroxyl radicals as well as other reactive oxidative species.
Figure 5. DOC removal on different BDD anodes in NaCl (3.7 g L\(^{-1}\)) at a fixed current density of 30 mA cm\(^{-2}\). Conditions: pH: 3.6; Clopyralid\(_{0}\): 100 mg L\(^{-1}\). Inset: Kinetic for DOC removal.

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

<table>
<thead>
<tr>
<th>Anode</th>
<th>NaCl</th>
<th>R(^2)</th>
<th>% clopyralid</th>
<th>NaCl</th>
<th>R(^2)</th>
<th>% DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k(_{\text{clop}}) / min(^{-1})</td>
<td>k(_{\text{DOC}}) / min(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BDD8000</td>
<td>0.1027</td>
<td>99.9</td>
<td>55.6</td>
<td>0.041</td>
<td>99.6</td>
<td>25.6</td>
</tr>
<tr>
<td>BDD2500</td>
<td>0.1214</td>
<td>98.1</td>
<td>62.0</td>
<td>0.094</td>
<td>94.3</td>
<td>42.8</td>
</tr>
<tr>
<td>BDD1300</td>
<td>0.1112</td>
<td>99.2</td>
<td>56.7</td>
<td>0.061</td>
<td>99.3</td>
<td>38.1</td>
</tr>
<tr>
<td>BDD200</td>
<td>0.1504</td>
<td>98.4</td>
<td>71.1</td>
<td>0.126</td>
<td>98.8</td>
<td>67.6</td>
</tr>
<tr>
<td>BDD100</td>
<td>0.1032</td>
<td>99.1</td>
<td>56.4</td>
<td>0.074</td>
<td>98.8</td>
<td>52.4</td>
</tr>
</tbody>
</table>

Hence, in chloride and sulfate media, the resistivity of the substrate influences the results, which agrees with the voltammetric observations (Figure 1). Regarding the boron...
doping, the influence is not as evident, indicating that this parameter is not as important in the oxidation of the model herbicide tested, although in comparing the extreme values, more critical oxidation in the case of the low-doped anodes can be suggested.

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

Again, as a general trend, and regardless of the supporting electrolyte, the anodes with high boron doping level favor the concentration of these dehalogenated intermediates, suggesting the more difficult oxidation of these cathodically formed intermediates with those anodes. It helps to explain the more limited mineralization rate observed for these anodes. In turn, anodes with low doping levels, do not favor the accumulation of intermediates, indicating that they are oxidized to carboxylic acids.
Figure 6. Evolution of byproducts concentration during the electrochemical oxidation of clopyralid on different BDD anodes in Na$_2$SO$_4$ (a and b) and NaCl (c and d) at a fixed current density: 30 mA cm$^{-2}$. Conditions: pH: 3.6; Clopyralid$_0$: 100 mg L$^{-1}$.

Figure 7 and Figure 8 show, respectively, the evolution of the formation of short-chain carboxylic acids and inorganic ions. Oxalic acid and oxamic acid were detected in sulfate media (Figure 7a and 7b), while only oxalic acid was detected in chloride media (Figure 7c). Typically, the concentration of these intermediates (except for the oxalic acid with the BDD8000 anode) increases as the boron doping decreases, suggesting more effective oxidation of the aromatic intermediates, but the more considerable difficulties in the oxidation of these acid intermediates formed. Accumulation of carboxylic acids is positive from the viewpoint of a further combination of technologies because, typically, these species are readily biodegradable.
Figure 7. Evolution of main carboxylic acid concentration during the electrochemical oxidation of clopyralid on different BDD anodes in Na₂SO₄ (a and b) and NaCl (c) at a fixed current density: 30 mA cm⁻². Conditions: pH: 3.6; Clopyralid₀: 100 mg L⁻¹.

Concerning inorganic species, ion chromatography indicates the formation of ammonium, chlorides, and nitrate ions (Figure 8). In sulfate media, it can be easily seen the
formation rate of chloride ions, reaching a maximum for the BDD200 anode and a minimum for the BDD8000 anode (Figure 8a). The same trend is observed regarding the ammonium and nitrate ions released in sulfate media, which is consistent with previously discussed regarding the reduction of total dissolved organic carbon (DOC). Nevertheless, for chloride media, it is difficult to find differences in chloride ions, since a large amount of this salt in the electrolyte makes it difficult to get any conclusion in this media. On the other hand, for ammonium and nitrate, it is possible to note interesting differences among anodes. The main difference observed, again, for the BDD200 anode, which was responsible for the formation of higher quantities of nitrate and almost no detected ammonium.
Figure 8. Evolution of inorganic ions formed during the electrochemical oxidation of clopyralid on different BDD anodes in Na₂SO₄ (a, c and e) and NaCl (b, d, and f) at a fixed current density: 30 mA cm⁻². Conditions: pH: 3.6; Clopyralid₀: 100 mg L⁻¹.

Samples obtained before and after the different electrolysis underwent respirometric tests, consisting of monitoring the oxygen consumption evolution in an activated sludge sample before and after the addition of a volume of waste. Figure 9 shows that before the addition of the waste, the sludge, obtained from the biological reactor of a municipal WWTP and previously aerated for more than one night in the absence of external substrate addition, presents a linear decay in the concentration of oxygen. It is associated with endogenous consumption, which is the consuming of dead microorganisms by the living microorganisms, which value depends on the concentration of the sludge. It means that when diluted, the oxygen consumption rate decreases linearly with the dilution rate. Then, by adding an increased volume of waste, the decay rate reduces (because of the dilution of the concentration of the microorganisms), but increases the rate associated with the consumption of the organics contained. Changes in the oxygen concentration vary from linear to exponential decay. After consumption of these external compounds, the endogenous rate (at the new sludge concentration) is again the primary decay, and a linear decay rate is kept (whose slope is related to the initial one taking into account the dilution undergone). By mass
balance, the oxygen consumption associated with the substrate contained in the samples added to the sludge can be easily calculated. This value corresponds to the short-term biological oxygen demand, and when related to the COD, the ratio indicates the biodegradability of the sample.

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:
BDD200 anode; pH: 3.6; Clopyralid: 100 mg L\(^{-1}\); current density: 30 mA cm\(^{-2}\); NaCl: 3.7 g L\(^{-1}\).

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

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

<table>
<thead>
<tr>
<th>Anode</th>
<th>Supporting electrolyte</th>
<th>COD a</th>
<th>aromatics HPLC area</th>
<th>Total carboxylic acids HPLC area</th>
<th>DBOst</th>
<th>Biodegradability (DBOst/COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD8000</td>
<td>Na(_2)SO(_4) ((3.0 \text{ g L}^{-1}))</td>
<td>60.0</td>
<td>592.0</td>
<td>2015.0</td>
<td>0.4</td>
<td>13.3</td>
</tr>
<tr>
<td>BDD2500</td>
<td></td>
<td>87.9</td>
<td>602.1</td>
<td>529.0</td>
<td>0.9</td>
<td>20.4</td>
</tr>
<tr>
<td>BDD1300</td>
<td></td>
<td>36.0</td>
<td>516.9</td>
<td>986.7</td>
<td>0.5</td>
<td>27.7</td>
</tr>
<tr>
<td>BDD200</td>
<td></td>
<td>28.2</td>
<td>393.3</td>
<td>2254.9</td>
<td>0.8</td>
<td>57.0</td>
</tr>
<tr>
<td>BDD100</td>
<td></td>
<td>19.7</td>
<td>107.4</td>
<td>1774.1</td>
<td>0.6</td>
<td>60.8</td>
</tr>
<tr>
<td>BDD8000</td>
<td>NaCl ((3.7 \text{ g L}^{-1}))</td>
<td>90.0</td>
<td>252.1</td>
<td>843.2</td>
<td>0.5</td>
<td>11.1</td>
</tr>
<tr>
<td>BDD2500</td>
<td></td>
<td>70.1</td>
<td>305.0</td>
<td>4485.9</td>
<td>0.8</td>
<td>22.8</td>
</tr>
<tr>
<td>BDD1300</td>
<td></td>
<td>80.8</td>
<td>205.7</td>
<td>3195.9</td>
<td>0.8</td>
<td>19.8</td>
</tr>
<tr>
<td>BDD200</td>
<td></td>
<td>62.6</td>
<td>31.50</td>
<td>3966.7</td>
<td>0.8</td>
<td>25.5</td>
</tr>
<tr>
<td>BDD100</td>
<td></td>
<td>51.4</td>
<td>133.5</td>
<td>3641.6</td>
<td>0.9</td>
<td>35.0</td>
</tr>
</tbody>
</table>
Figure 10 shows significant differences among anodes studied that strongly depend on the doping level. For both electrolytes studied, the BDD100 and BDD200 anodes provided better responses in terms of improved biodegradability, which is more than 4.5 times better than that obtained by the diamond doped with 8000 ppm of boron. Comparing the biodegradability of the treated wastes and the initial wastes, we see that it improved significantly, as biodegradability of the initial waste was found to be as low as 8.3%. In general, in sulfate media, the biodegradability is higher than in chloride media. It can be explained in terms of the negative effect of the electrochemically generated chlorine on the microorganisms. Although peroxosulfates can also affect negatively to microorganisms, chlorine, and derivatives lead to a more negative effect.
The results obtained confirm that electrolysis with diamond anodes can be a good pre-treatment for a later biological stage, although, in order to improve this combination, electrodes with low boron doping have to be used, because these electrodes, besides, to attain higher mineralization, lead to effluents with a higher biodegradability.

**Conclusions**

The electrochemical oxidation using boron-doped diamonds with different characteristics contributes differently to the improvement of biodegradability of the poorly biodegradable herbicide, clopyralid. Distinct boron-doped diamonds provide different efficiencies in terms of clopyralid removal and mineralization. These efficiencies, in turn, depend on the composition of the supporting electrolyte. For both supporting electrolytes (chloride or sulfate) evaluated, the anode of 200 ppm content in boron (BDD200) was the most efficient in removing and to transform clopyralid into more biodegradable compounds. The resistivity
of the diamond substrate seems to be a significant parameter in order to explain the results of electrolysis. On the other hand, BDD with a high doping level favors the formation of intermediates, while low doping levels only favor a small accumulation of intermediates, which favors mineralization rate. Regardless of the electrolyte media, lower doping levels enhanced 1.8–4.5-times, for BDD100 and BDD200, respectively, the solution biodegradability for the model contaminant here studied. Finally, these findings point out that lower doping levels are preferable for improving biodegradability in order to make the sequenced process using electrolysis before biodegradation with activated sludge, economically attractive.

Conflicts of interest
There are no conflicts to declare.

Acknowledgments
Financial support from the Agencia Estatal de Investigación through project CTM2016-76197-R (AEI/FEDER, UE) is gratefully acknowledged. The authors also acknowledge the financial support from the Brazilian agencies CNPq (305438/2018-2 and 310282/2013-6), CAPES (88882.365552/2018-01 and 88881.187890/2018-01) and FAPITEC/SE.

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