Improving biodegradability of clopyralid wastes by photoelectrolysis: the role of the anode material

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Abstract

In this work, the removal of the non-readily biodegradable herbicide clopyralid by electrochemical (EC) and photoelectrochemical (PhEC) oxidation with different anode materials were conducted looking to improve not only its oxidation but also its biodegradability. First, in order to find out optimal conditions, it was carried out EC and PhEC degradations in chloride medium, at current densities ranging from 30 to 100 mA cm⁻² during 1 h (0.8–2.7 A h L⁻¹), using as anodes MMO-RuO₂TiO₂, MMO-RuO₂IrO₂, MMO-IrO₂Ta₂O₅ and boron-doped diamond (BDD). Results show better efficiencies on clopyralid removal for MMO-RuO₂IrO₂ and BDD anodes at lower current densities. Then, the influence of all anodes on clopyralid transformation was evaluated, extending the electrolysis and photoelectrolysis for 8 h applying 30 mA cm⁻² (6.4 A h cm⁻³). At these conditions, better outcomes are observed for PhEC degradation, where complete pollutant removal is attained for BDD anode and 88.7 % for MMO-RuO₂IrO₂, while COD removal is 47.7 % for MMO and 43.1 % for BDD anode. Then, short-term biodegradability tests, conducted for EC and PhEC processes, pointed out that MMO-RuO₂TiO₂ is the most promising anode material, being capable of improving

biodegradability in 48.2 % and 53% for EC and PhEC degradation, respectively. The toxicity of treated solutions using MMO-RuO₂TiO₂ and BDD anodes in both EC and PhEC degradation were compared, employing the inhibitory effect in the bioluminescence of marine bacteria *Vibrio Fisheri*. Toxicity assessments show that toxicity significantly reduces by using the MMO-RuO₂TiO₂ in NaCl and Na₂SO₄ medium for both processes. Finally, this study demonstrates that photoelectrolysis with MMO anodes was the most effective strategy in order to increase biodegradability in chloride media, as well as to reduce the toxicity of the treated waste.

Keywords: Electrolysis; photoelectrolysis; clopyralid; BDD; MMO.

Highlights

- Clopyralid can be removed using electrolysis and photoelectrolysis
- Degradation is more efficient at low current densities using MMO-RuO₂TiO₂ anode
- Readily biodegradability could be doubled by photoelectrolysis with MMO-RuO₂TiO₂
- Treated solutions with MMO-RuO₂TiO₂ reduced their toxicity. Not the case of using BDD

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49 **1. Introduction**

50 Contamination of water associated with the use of pesticides and fertilizers is an issue of growing
51 concern because of the potential risk to both the environment and human health [1]. Clopyralid (3,6-
52 dichloro-2-pyridine-carboxylic acid) is an organochlorinated herbicide, persistent, and not readily
53 biodegradable [2, 3]. Due to its high solubility in water, clopyralid has been detected very frequently
54 in the environment and even in drinking water [4].

55 Nowadays, biological treatment is the most popular method to treat almost any type of wastewater,
56 possessing essential advantages as compared with other technologies and being cost-effective [5].
57 Unfortunately, biological methods are not always practical for treating wastewater polluted with
58 complex anthropogenic organic molecules (such as chlorinated organic compounds) [6, 7]. Therefore,
59 it is of great importance to search efficient treatments capable of removing this type of contaminants
60 from water resources [8]. In this context, electrochemical advanced oxidation processes (EAOPs) are
61 attracting attention because they are efficient to achieve the destruction of contaminants, and,
62 depending on the operational conditions, they can attain the complete mineralization [9-11]. As it is
63 well-known, anode material plays a vital role in EAOPs: non-active anodes comprise materials with
64 high oxygen evolution overpotentials that favor the total oxidation of organics to CO₂; active anodes
65 include materials with low oxygen evolution overpotential, that permit mainly the transformation of
66 organics into other more oxidized organic metabolites [12, 13]. The mixed metal oxides (MMOs)
67 anodes belong to this latter category. They are made of a mixture of metallic oxides supported on less
68 expensive materials such as titanium and can be produced by diverse techniques [14-17]. Opposite,
69 BDD is a well-known non-active anode that exhibits weak surface interactions with hydroxyl radicals
70 [18], favoring mineralization of organics.

71 Another important point to be addressed is the oxidants that can be formed depending on the salts
72 that are present in the electrolytic solution. In particular, the occurrence of chloride is significant.
73 This anion can be found in most water and wastewater sources, exhibiting a pivotal role in the
74 electrolysis of actual wastes. In the electrolysis of wastewater containing chloride, chlorine and

hypo-chlorite are expected to be produced. However, the main problems associated with the chloride ions are the formation of organochlorinated species and the production of chlorates and perchlorates. Because of this occurrence, toxicity is also an important parameter and must be accompanied in order to ensure safe treated solutions [4, 9, 19].

The main drawback of the electrochemical-based process is the energy required [20], which motivates research towards improvements in this approach in order to be more energy-efficient and cost-effective [21, 22]. Thus, the proposal of a coupled process to be applied as a pre-treatment step prior to the usually cheaper biological treatment has been a topic of great interest [5, 23, 24].

Hence, in this work, the degradation of clopyralid wastes by the electrochemical and photoelectrochemical processes was investigated. The influence of the different types of anodes materials (i.e., distinct MMOs and BDD) on the biodegradability and toxicity of the final treated wastes was studied. In both processes, we focused on the transformation of the contaminant into more readily biodegradable compounds, and not on the total mineralization.

2. Materials and Methods

2.1 Chemicals

Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) (Sigma Aldrich), sodium chloride (Panreac), anhydrous sodium sulfate (Panreac), sodium hydroxide (Sigma Aldrich) and sulfuric acid (Sigma Aldrich) were of analytical grade and used as received. These reagents were used to make the synthetic wastewater and for pH adjustment. Both methanol HPLC grade and formic acid (Sigma-Aldrich) were used in the mobile phase. All solutions were prepared using high-purity water (Millipore Milli-Q system, resistivity: 18.2 M Ω cm at 25 °C).

2.2 Preparation of the electrodes

The Ti/RuO₂-TiO₂ and Ti/RuO₂-IrO₂ anodes were prepared by the thermal decomposition of polymeric precursors (or Pechini method), using CO₂ laser and microwave heating, respectively. To

101 obtain the precursor solutions, ruthenium chloride (III) hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, 99.99%), iridium
102 chloride (III) hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, 99.0 %), titanium (IV) butoxide (97.0 %) and ethylene glycol (EG)
103 (99.8 %), were purchased from Sigma Aldrich[®], and anhydrous citric acid (CA) (99.5 %), from
104 Vetec[®]. First, Ti plates, with a geometric area of 4 cm^2 , were polished, and then rinsed with ultrapure
105 water. After that, they were immersed into boiling hydrochloric acid (HCl, 38.0% from Neon[®])
106 solution (20 % v/v) for 15 min, followed by immersion into boiling oxalic acid (99.5%, from Vetec[®])
107 solution (10 % v/v), and then finally rinsed with ultrapure water. In order to obtain the precursor
108 solutions, the ruthenium chloride and titanium butoxide were weighed in the molar ratio of 0.3/0.7
109 (Ru/Ti); whereas the ruthenium and iridium chloride were weighed in the molar ratio of 0.5/0.5
110 (Ru/Ir), to be subsequently dissolved in the EG:CA solution (10:3).

111 The solutions were spread over the Ti surface by brushing. For the laser heating employed to
112 obtain the Ti/RuO₂-TiO₂ anode, the strategy was to increase the temperature almost instantaneously
113 to reach 400 °C for 40 s and then cooled immediately to room temperature [16]. For the Ti/RuO₂-
114 IrO₂ anodes, the heating consisted of a hybrid process [25] where the electrodes were placed at 45
115 degrees inside the SiC (used as susceptor due to its high dielectric loss) in order to be irradiated for
116 23 min until reaching 350 °C. After that, the irradiation was stopped, and the electrodes were cooled.
117 The Ti supports were coated with successive layers of the oxides until they reached a mass density of
118 1.2 mg cm^{-2} , as determined by weight difference.

119

120 **2.3 Experimental set-up**

121 The electrochemical (EC) and photoelectrochemical oxidation (PhEC) experiments were conducted
122 in a one-compartment electrochemical cell. The capacity of the cell was 0.15 L containing 100 mg
123 L^{-1} of clopyralid at natural pH (3.4). Aqueous sodium chloride (3.7 g L^{-1}) was used as the supporting
124 electrolyte. Some experiments using Na_2SO_4 (3.0 g L^{-1}) at the same ionic strength were performed.
125 The working electrodes were the different MMO anodes, namely MMO-RuO₂TiO₂ (laser-prepared),
126 MMO-RuO₂IrO₂ (microwave-prepared), an MMO-IrO₂Ta₂O₅ (supplied by Tiaano[®]) and a BDD

(supplied by Adamant technologies). The MMOs consist of metallic support of titanium, where the coatings proportions are 70:30 for RuO_2TiO_2 , 50:50 for $\text{MMO-RuO}_2\text{IrO}_2$, and 70:30 for the commercial $\text{MMO-IrO}_2\text{Ta}_2\text{O}_5$. BDD anode was a thin-film deposited on p-Si with 8000 ppm of boron doping (sp^3/sp^2 : 80). All anodes had a geometric exposed area of 4.0 cm^2 . The cathode was a platinum wire, and the reference electrode was AgCl .

The applied current density ranged from 30 to 100 mA cm^{-2} provided by potentiostat/galvanostat 302N. For the photoelectrochemical (PhEC) oxidation, a 9 W UV-C lamp (254 nm) was directly immersed into the electrochemical cell. All solutions were stirred with a magnetic agitator during experiments. Aliquots were taken during each experiment at different time intervals and then filtered through $0.45 \mu\text{m}$ filters for posterior analysis.

137

138 2.4 Analytical Methods

The clopyralid removal was monitored using HPLC (Agilent 1260, ZORBAX Eclipse C18 analytical column). The mobile phase consisted of 30% methanol/70% water with 0.1 % of formic acid (flow rate: $1.0 \text{ cm}^3 \text{ min}^{-1}$). The DAD detection wavelength was 280 nm, the temperature was maintained at 25°C , and the injection volume was $20 \mu\text{L}$. Acids were identified by an HPLC equipped with a Zorbax SB-Aq, column ($4.6\text{mm} \times 150\text{mm}$). The mobile phase consisted of $4 \text{ mM H}_2\text{SO}_4$. The detection wavelength was fixed at 210 nm. The intermediates were identified by comparison of their retention times with standard solutions. The measurements of cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were performed by a potentiostat/galvanostat model PGTAT 302 N. CVs were recorded at the potential interval from 0.0 to 1.3 V for the MMO and 0.0 to 3.0 in the case of BDD, while the LSVs were performed in the potential interval of 0.0 to 1.4 V for MMOs and 0.0 to 2.2 for BDD anode, at a scan rate of 0.01 mV s^{-1} .

The instantaneous current efficiency (ICE) for the electrochemical oxidation was calculated from Eq. (1), where $(\text{COD})_t$ and $(\text{COD})_{t + \Delta t}$ are the chemical oxygen demands at times t and $t + \Delta t$ (in $\text{g O}_2 \text{ L}^{-1}$), respectively, I is the current (in A), F is the Faraday constant (96487 C mol^{-1}), and V is the

153 solution volume (L) [26, 27]. The specific energy consumption (SEC) was calculated according to
 154 Eq (2), and volumetric energy consumption (VEC) according to Eq (3), where E_{cell} is the average cell
 155 voltage (V).

$$156 \quad ICE (\%) = F V \frac{(COD)_t - (COD)_{t+\Delta t}}{8 I \times \Delta t} \times 100 \quad (1)$$

$$157 \quad SEC (kW h g^{-1} COD) = \frac{E_{cell} I t}{V (COD)_t - (COD)_0} \quad (2)$$

$$158 \quad VEC (kW h L^{-1}) = \frac{E_{cell} I t}{V} \quad (3)$$

159

160 **2.5 Biodegradability tests**

161 For short-term biodegradability (BOD_{st}), unacclimated activated sludge, taken from a local
 162 conventional wastewater treatment plant (WTTP) (Ciudad Real, Spain), was used in the
 163 biodegradability test. The sludge was maintained with sodium acetate (100 mg L^{-1}) as carbon sources
 164 in the bioreactor at $21 \pm 3 \text{ }^{\circ}\text{C}$. The assays were conducted in a 100 mL beaker filled with 95 mL of
 165 activated sludge under continuous stirrer by magnetic bars. The dissolved oxygen (DO) concentration
 166 decay was measured with oximetry (WWR-OX4100H). Before biodegradability and toxicity
 167 analysis, pH values were adjusted to 7.0. Chemical oxygen demand (COD) analyses were conducted
 168 by using Spectroquant[®] test kits from Merck.

169

170 **2.6 Toxicity towards *Vibrio fischeri***

171 The acute toxicity of initial and treated clopyralid synthetic solutions was measured with Microtox[®]
 172 by inhibition of bioluminescence of marine bacteria *Vibrio fischeri* according to the protocol indicated
 173 by the manufacturer. The osmotic control of the samples was adjusted prior to tests. The emitted bio-
 174 luminescence was recorded for 5 and 15 min of exposure and compared to that of the blank sample.

175

176 **3. Results and Discussion**

177 **3.1 Electrochemical characterization**

178 Anode materials are of great importance in electrochemical oxidation, and anodes with different

179 coatings are known to exhibit different electrocatalytic properties. Then, to further understand the
180 electrochemical behavior of the anodes here studied, voltammetric curves of the MMO-RuO₂TiO₂,
181 MMO-IrO₂RuO₂, MMO-IrO₂Ta₂O₅, and BDD anodes were recorded at a scan rate of 50 mV s⁻¹ and
182 LSV curves were recorded at 10 mV s⁻¹ in 3.7 mg L⁻¹ NaCl solutions (**Figure 1**).

183 The voltammetric charge, q^* , obtained by the integration of the CVs between the oxygen and
184 hydrogen evolution reactions, can be considered as a relative measurement of the electrochemically
185 active surface area (EASA) of the anodes, and its values are collected in **Table 1**. The EASA reduces
186 in the following order: RuO₂TiO₂ > RuO₂IrO₂ > IrO₂Ta₂O₅ > BDD.

187 Note from LSV data (**Figure 1e**) that the oxygen evolution potential (OEP) increases according to
188 the sequence BDD > IrO₂Ta₂O₅ > RuO₂TiO₂ $\approx$ RuO₂IrO₂.

189 It is worth to point out that the LSV experiments were performed in a diluted chloride
190 solution; then, the oxygen evolution is expected to occur concomitantly with the generation of
191 chlorine gas [28]. The much higher OEP value for the BDD anodes, regardless of the electrolyte
192 media, is well-known in the literature due to the “non-active” nature of this material, which favors
193 the generation of large amounts of physisorbed hydroxyl radicals. However, considering that the
194 MMO anodes are suitable catalysts for chlorine evolution, in the presence of Cl⁻ ions, the use of these
195 anodes for the generation of active chlorine is of interest in the sense of mediated oxidation. Thus, in
196 order to enhance the active chlorine, these materials should mitigate the oxygen evolution reaction.
197 At this point, note that although it is impossible to estimate the number of chlorine species produced
198 with the voltammetry experiment, it is evident that the lower is the potential, the higher is the catalytic
199 activity at a fixed current density.

200

Figure 1. Cyclic voltammograms recorded at 50 mV s⁻¹ of MMO-RuO₂TiO₂ (a), MMO-RuO₂IrO₂ (b) MMO-IrO₂Ta₂O₅ (c) BDD (d) in NaCl 3.7 g L⁻¹ electrolyte and linear sweep voltammetry curves of the different anode materials recorded in at 10 mV s⁻¹.

208

209 **Table 1.** Voltammetric charge (q^*) and the OEP values found for different anodes studied.

Anode	$q^* / \text{mC cm}^{-2}$	OEP / V vs. Ag/AgCl
MMO-RuO ₂ TiO ₂	77.13	1.13
MMO-RuO ₂ IrO ₂	72.80	1.07
MMO-IrO ₂ Ta ₂ O ₅	57.40	1.32
BDD	-	2.45

210

211 **3.2 Electrochemical degradation of clopyralid**

212 It is well-known that EC results are dependent on the applied current density [29]. Thus, the
 213 simultaneous selection of the anode material and the current density operating conditions is of great
 214 importance in order to select the best option capable of transforming the herbicide into more
 215 biodegradable molecules. The comparison of anodes helps to select the most suitable material and
 216 condition envisaging a combination with biological treatment.

217 **Figure 2** shows the clopyralid removal in chloride medium by electrochemical oxidation at
 218 MMO-RuO₂TiO₂, MMO-RuO₂IrO₂, MMO-IrO₂Ta₂O, and BDD anodes at current densities of 30 mA
 219 cm⁻² (**Figure 2a**), 50 mA cm⁻² (**Figure 2b**) and 100 mA cm⁻² (**Figure 2c**) for 1 h in NaCl 3.7 g L⁻¹.
 220 It is important to point out that any of the experimental conditions tested result in the complete
 221 removal of clopyralid, as expected, because of the low applied electric charge per unit volume
 222 (ranging from 0.8 to 2.7 A h L⁻¹). However, these experiments help to clarify the most suitable current
 223 densities, as well as the behavior of different anodes employed. **Figure 2** shows that the increase in
 224 the current density does not significantly improve the clopyralid removal, which can be due to side
 225 reactions, such as oxygen evolution occurring at the anode surface (Eq. 4).

226

228

Plotting the clopyralid removal as a function of applied electric charge per unit volume, Q (Ah L^{-1}) (**Figure S1**) for all the anodes studied, it can be seen that for the same electric charge passed, the oxidation reached is not the same. A clear improvement occurs by lowering the current density, which indicates that the process is under mass-transport control, confirming that secondary reactions (such as oxygen evolution) are involved, then decreasing the process efficiency as already pointed out in previous works [30-32].

Regarding the influence of the different anode materials tested on the removal performance at different current densities, it is observed that the MMO-RuO₂TiO₂ is as efficient as the BDD. Thus, 30 mA cm⁻² (0.8 A h L⁻¹), seems to be the most suitable current density found, showing a clopyralid removal of 17.1 % of 16.6 %, for MMO and BDD respectively.

Further analysis from instantaneous current efficiency (ICE) and volumetric energy consumption (VEC) data obtained for the electrochemical oxidation using the different anodes materials tested (**Figure S2**) confirm that the application of lower current density results in higher ICE and lower VEC.

The values found for clopyralid removal for MMO-RuO₂TiO₂ can be explained in terms of different mechanisms involving the formation of reactive chlorine species. Chlorine can be generated on the anode surface (Eq. 5) and can be transformed in bulk into hypochlorous acid/hypochlorite. (Eqs. 6–7).

On the other hand, when BDD anodes are used, large quantities of hydroxyl radicals which are formed in co-existence with chlorine species, successively oxidize Cl⁻ to different oxochlorinated compounds by different reactions shown in Eqs. (8–12), which leads to the formation of non-useful and hazardous chlorate and perchlorate.

260

261 Results from COD removal show slight removals for all anodes at these conditions (i.e., low applied
 262 electric charge ranging from 0.8 to 2.7 A h L⁻¹), which indicates that more extended experiments are
 263 necessary to attain a higher degree of contaminant transformation.

264

265

266

Figure 2. Clopyralid removal by electrochemical oxidation applying a fixed current density of a) 30 mA cm⁻², b) 50 mA cm⁻² (c), and 100 mA cm⁻² in NaCl medium 3.7 g L⁻¹ for the four anodes tested during 1h.

3.3 Photoelectrochemical degradation

The system was irradiated with 9 W UV-C light (254 nm), looking for reaching higher efficiencies in the clopyralid removal. **Figure 3** shows the clopyralid removal in the photoelectrochemical (PhEC) degradation at current densities ranging from 30 to 100 mA cm⁻² in NaCl 3.7 g L⁻¹ for MMO-RuO₂TiO₂ and BDD anodes. Regarding current density, the same trend previously seen in the EC degradation is observed for the PhEC with MMO-RuO₂TiO₂, i.e., the higher is the current density applied, the lower is the process efficiency. On the other hand, for PhEC-BDD, the trend is opposite to the previously observed for EC, where the higher is the applied current, the higher is the removal, and under irradiation with 9 W UV-C light at higher current densities, the efficiency of the process decreases.

The plot of clopyralid removal as a function of the applied electric charge per unit volume for the different anodes materials tested at different current densities (**Figure S1**) clearly shows that for the same applied electric charge, there is no improvement by increasing the current. On the other hand,

PhEC process with MMO-RuO₂TiO₂ resulted in a significative increase in clopyralid transformation from 17.1 % (from EC degradation) to 54.9 % (PhEC degradation), while for the BDD anode the improvement was even more significant (from 16.6 % for EC to 88.3 % for PhEC degradation). These improvements can be a result of the contribution of mediated oxidation in the bulk solution. Then, when UV-C light irradiates the solution, chlorine and hydroxyl radicals can be formed by a homolytic homogeneous reaction (Eq. 13) in the bulk solution [33, 34]. Also, it is worthy of mentioning that the irradiation of photoactive materials, such as TiO₂ (present in the anode surface) can affect the efficiency of clopyralid removal through the formation of Cl[•] radicals (Eq. 14) [35].

293

296

297

Figure 3. Clopyralid removal in PhEC degradation at 30 mA cm⁻² (●,○), 50 mA cm⁻² (▲,Δ) and 100 mA cm⁻² (■, □) in NaCl 3.7 g L⁻¹ for MMO-RuO₂TiO₂ (Full symbols) and BDD (empty symbols) anodes.

301

Once clarified the role of anodes on the electrochemical oxidation process in the removal of clopyralid, and that lowering current density increases the efficiency of the process, extensive EC and PhEC were carried out for a longer period of 8 h (6.4 A h L^{-1}) for a higher degree of clopyralid transformation.

Figure 4 shows clopyralid removal during 8 h of EC (**Figure 4a**) and PhEC degradation (**Figure 4b**) at a fixed current density of 30 mA cm^{-2} in $\text{NaCl } 3.7 \text{ g L}^{-1}$ for all anodes. $\text{MMO-RuO}_2\text{TiO}_2$ and BDD presented better efficiencies in both systems.

Figure 4. Clopyralid removal in electrochemical (EC) (a) and photoelectrochemical (PhEC) (b) at a fixed current density of 30 mA cm^{-2} in $\text{NaCl } (3.7 \text{ g L}^{-1})$ for all anodes.

313

314 At this point, we point out that, due to the relevance of Na₂SO₄ (3.0 g L⁻¹) as a supporting
 315 electrolyte, we also carried out EC and PhEC degradation experiments at 30 mA cm⁻² in order to
 316 compare the behavior of the MMO-RuO₂TiO₂ and BDD anodes during clopyralid removal in both
 317 processes. As can be observed in **Figure S4**, BDD was much more effective than MMO in this
 318 medium, regardless of the process employed. It is an expected result, considering that BDD is known
 319 to generate large amounts of hydroxyl radicals, whereas much lower amounts of reactive •OH are
 320 formed on the surface of the MMO anodes. In comparing the EC with PEC results, significant
 321 differences in the efficiencies can be observed. Note that for the MMO, the use of UV-C improved
 322 the clopyralid removal by almost 30%. By contrast, when UV-C light is coupled to electrochemical
 323 degradation with BDD, worse results were observed.

324 To explain this unexpected antagonistic behavior, it must be considered that when using BDD,
 325 a large amount of •OH, instead of attacking organic species, may combine and form less reactive
 326 species according to reactions 15-19 [36].

332 These reactions compete with the oxidation of pollutants, which points out that the nature of
 333 the pollutant may play an essential role in the efficiency of the combined process. The uncertainty in
 334 the positive synergism or antagonisms of coupling UV-C irradiation to BDD has already been
 335 reported [36, 37]. However, for some pollutants, this behavior is not well understood in the literature.
 336 Further studies should be performed focusing on the effect of the nature of the pollutant on the
 337 efficiency of photoelectrochemical degradation with BDD.

338 The quantification of specific energy consumption (SEC) is of a great relevance to evaluate
 339 the possible application of an electrochemical-based technology and it is shown in **Figure 5**. As seen,
 340 the SEC increases for PhEC-BDD in both electrolytes, which indicates that from the energy point of
 341 view the integration of technologies is not showing a clear advantage. In addition, the higher reactivity
 342 in supporting electrolytes containing chlorides help to explain the lower energy consumption
 343 observed.
 344

345
 346 **Figure 5.** Specific energy consumption for the electrochemical (EC) and photoelectrochemical
 347 (PhEC) processes carried out at 30 mA cm⁻² in NaCl (3.7 g L⁻¹) or Na₂SO₄ (3.0 g L⁻¹) by using
 348 MMO-RuO₂TiO₂ and BDD anodes.

349

350 3.4 Biodegradability evaluation

351 From this point, EC and PhEC degradation at MMO-RuO₂TiO₂ and BDD anodes will be denoted as
352 EC-MMO, PhEC-MMO, EC-BDD, and PhEC-BDD, as only these technologies are going to be
353 compared. Short-term biodegradability tests were carried through the measurements of the dissolved
354 oxygen uptake of non-acclimated activated sludge when in contact with treated samples (**Figure S5**).
355 The biodegradability of wastewater is commonly evaluated in terms of the BOD to COD ratio. Thus,
356 the biodegradability of untreated and treated clopyralid solutions was evaluated to show the feasibility
357 of the biological process as post-treatment. The short-term biodegradability of the untreated solution
358 was found to be as low as 8.3%. **Figure 6** shows the effect of electrochemical (EC) and
359 photoelectrochemical (PhEC) degradation on COD removal after 8 h of treatment in NaCl (3.7 g L⁻¹)
360 (**Figure 6a**) and on the biodegradability (**Figure 6b**) at a current density of 30 mA cm⁻². COD
361 removals (**Figure 6a**) show that EC-BDD was capable of removing COD more efficiently, followed
362 by PhEC-MMO. The PhEC-BDD and EC-MMO were less efficient conditions. However,
363 biodegradability was improved differently according to anode material in both EC and PhEC
364 treatments. Thus, **Figure 6b** notably shows that PhEC-MMO was capable of transforming clopyralid
365 into more biodegradable by-products, such as short-chain carboxylic acids (**Table 2**), leading to a
366 sample with higher biodegradability. Notably, the formation of carboxylic acids increased after the
367 photoelectrochemical degradation process, being more pronounced in chloride media. It means that
368 clopyralid is converted into more biodegradable compounds in the mediated process, as previously
369 stated, due to the action of Cl[•] and [•]OH in the bulk solution.

Figure 6. Effect of electrochemical (EC) and photoelectrochemical (PhEC) degradation on a) COD removal after 8 h of treatment and b) biodegradability. Conditions: pH: 3.4; Clopyralid₀: 100 mg L⁻¹; current density: 30 mA cm⁻²; electrolyte: NaCl (3.7 mg L⁻¹). The dashed line indicates BOD_{st}/COD of the untreated solution.

Figure 7 shows the effect of electrochemical (EC) and photoelectrochemical (PhEC) degradation on COD removal after 8 h of treatment in Na₂SO₄ (3.0 g L⁻¹) (**Figure 7a**) and on the biodegradability (**Figure 7b**) at a current density of 30 mA cm⁻².

Figure 7. Effect of electrochemical (EC) and photoelectrochemical (PhEC) degradation on COD removal after 8 h of treatment in a) Na_2SO_4 (3.0 g L^{-1}) and b) biodegradability. Conditions: pH: 3.4; Clopyralid₀: 100 mg L^{-1} ; current density: 30 mA cm^{-2} . The dashed line indicates BOD_{st}/COD of the untreated solution.

A higher percentage of biodegradability of 23.3 % (**Figure 7b**) is observed for EC-BDD. However, when UV-C is irradiated, the biodegradability decreases to 13.5 %. It may indicate that more refractory by-products should be formed during PhEC degradation. Regarding the MMO anode, a slight from 15.2 %, for the EC degradation, to 14.9 % of biodegradability after PhEC degradation

indicates that for Na₂SO₄ medium, the MMO is not efficient to improve the biodegradability of the final waste.

393

Table 2. Obtained values for COD, total carboxylic acids, short term biodegradability for the samples after 8 h EC, and PhEC degradations. COD₀ = 130 mg O₂ L⁻¹.

Process	Supporting electrolyte	Total carboxylic acids (HPLC area)	BOD _{st}	COD (mg O ₂ L ⁻¹)	Biodegradability (BOD _{st} /COD)
EC-MMO	Cl ⁻	1724.2	0.5	89	11.2
EC-BDD		843.2	0.4	49	16.3
PhEC-MMO		4444.3	0.5	67	17.9
PhEC-BDD		4987.1	0.5	74	13.5
EC-MMO	SO ₄ ²⁻	121.0	0.8	105.3	15.2
EC-BDD		2015.0	0.7	60	23.3
PhEC-MMO		197.3	0.5	67	14.9
PhEC-BDD		982.8	0.5	74	13.5

396

3.5 Toxicity Assessment

Figure 8 presents the effect of electrochemical (EC) and photoelectrochemical (PhEC) process on toxicity of treated clopyralid solutions at 30 mA cm⁻² in NaCl (3.7 g L⁻¹) (**Figure 8a**) and Na₂SO₄ (3.0 g L⁻¹) (**Figure 8b**) by using MMO-RuO₂TiO₂ and BDD anodes using the bioluminescent marine bacteria *Vibrio fischeri*. **Part a** shows that at the initial stage of the degradation (0.8 A h L⁻¹) in NaCl medium, the toxicity is still high. However, extending the treatments for 8 h (6.4 A h L⁻¹), the bacteria inhibition is significantly reduced to 29.1% after EC-MMO and 34.2% for PhEC-MMO, after 8 h of treatment just in the case of MMO-RuO₂TiO₂. It means that the toxicity of the treated solutions can be quite different depending on the anode material. On the contrary, EC-BDD and PhEC-BDD

406 resulted in total inhibition even at lower dilution values. It suggests that by-products formed during
407 EC and PhEC at BDD at these conditions possibly favor the formation of by-products as toxic as the
408 initial clopyralid solution.

409 For comparison purposes, the experiments were also conducted in Na_2SO_4 (3.0 g L^{-1}) (**Figure**
410 **8b**) as supporting electrolyte to investigate the behavior of both anodes during clopyralid
411 transformation. In the presence of Na_2SO_4 , the electrochemical oxidation at BDD anode presents the
412 lower inhibition effect of 26.8%, while a higher inhibition of 87.5% is obtained for the PhEC process.
413 As compared to the results obtained in NaCl media, EC-BDD in Na_2SO_4 shows better outcomes in
414 terms of efficiency and COD removal, as seen in **Figure 7**. Thus, the higher degree of COD removal
415 in Na_2SO_4 seems to favor a reduction in the toxicity. For MMO- RuO_2TiO_2 anode, 35.2% of inhibition
416 is obtained after 8 h of EC-MMO treatment, while 64.2% is the inhibition measured for PhEC-MMO.
417 These data point out that when coupling UV-C light irradiating Na_2SO_4 solution containing 100 mg
418 L^{-1} clopyralid, oxidants are activated in a distinct way than those in chloride medium.

419 In order to better understand the electrolyte effect, experiments were performed to evaluate
420 the contribution of the oxidative species electrogenerated to the toxicity, putting under electrolysis
421 the NaCl and Na_2SO_4 solutions in the absence of the contaminant. NaCl and Na_2SO_4 electrolyte
422 solutions (in the absence of the contaminant) prior electrolysis does not generate significant inhibitory
423 effects being non-toxic to the organism. However, after 8 h electrolysis in NaCl media (6.4 A h L^{-1}),
424 the inhibition value is 100% for EC-MMO. This outcome comes from the electrogenerated active
425 chlorine (such as hypochlorite/hypochlorous) that was continuously accumulated in the solution
426 during the 8 h of electrolysis in the MMO- RuO_2TiO_2 case. For BDD anode, at the same condition,
427 23.5% of inhibition is seen. Small amounts of hypochlorite/hypochlorous are expected.

428 In contrast, chlorate and perchlorate species are the species mainly reported after electrolysis
429 of NaCl using a BDD anode. For the Na_2SO_4 solution, the inhibitory effect was only 20.7% for MMO-
430 RuO_2TiO_2 and 46.1% for BDD. These results point out that electrolyte solution may influence the
431 inhibitory effect after treatments. Remarkably, the final treated solutions containing NaCl with

MMO-RuO₂TiO₂ presented reduced toxicity, which suggests that hypochlorite concentration substantially decreases at the end of treatment due to the reaction with the clopyralid molecule.

Considering that the formation of chlorates and perchlorates may be different in the presence of clopyralid, these species were quantified after the electrochemical oxidation with and without clopyralid. After the electrolysis of a chloride solution using the BDD, the chlorates and perchlorates were found at the concentrations of 1582.2 ppm and 233.35 ppm, respectively. Meanwhile for MMO electrolysis, this value was 62.3 ppm for chlorates, while no perchlorate was detected. In the presence of clopyralid, the values found for chlorates and perchlorates increased to 2346.7 ppm and 345.4 ppm, respectively. The same trend was observed using the MMO anode with chlorates concentration of 217.1 ppm, and again without perchlorate. The significant increase in the amount of chlorates and perchlorates in the treated solutions with BDD has to be explained by the high reactivity of the electrogenerated •OH radicals with chloride ions. In the treatment of solutions containing clopyralid, besides chlorides contained in the electrolyte, more chlorides can come after their release from the clopyralid molecule during degradation. Taking this into account, the increase in the hazardous chlorates and perchlorates for EC/PhEC-BDD may play an essential role in the inhibitory effect observed in **Figure 8a**.

448

Figure 8. Effect of electrochemical (EC) and photoelectrochemical (PhEC) process on the toxicity of treated clopyralid solutions at 30 mA cm^{-2} in NaCl (3.7 g L^{-1}) a) and Na_2SO_4 (3.0 g L^{-1}) b) by using $\text{MMO-RuO}_2\text{TiO}_2$ and BDD anodes using the bioluminescent marine bacteria *Vibrio fischeri*. Conditions: Clopyralid₀: 100 mg L^{-1} ; current density: 30 mA cm^{-2} .

The results here obtained are quite impressive, considering a matrix containing chlorides. The reduced toxicity and improved biodegradability for EC-MMO and PhEC-MMO degradation highlight the use of $\text{MMO-RuO}_2\text{TiO}_2$ as anode material capable of transforming clopyralid into by-products more biodegradable and less toxic for a post-treatment by conventional biological treatment.

Conclusions

Based on the results obtained from this research, the following conclusions are drawn:

- Results from the electrochemical characterization of anodes materials revealed that $\text{MMO-RuO}_2\text{IrO}_2$ presented higher voltammetric charges while possesses low OEP. Meanwhile, BDD and $\text{MMO-IrO}_2\text{Ta}_2\text{O}_5$ presented the highest overpotential for OEP, which affects the electrochemical degradation systems directly.
- The optimal current density of 30 mA cm^{-2} was found for both electrochemical and photoelectrochemical degradation regardless of the anode material.

- Photoelectrochemical degradation was the most efficient at low applied electric charges (6.4 A h L⁻¹) only when MMO-RuO₂TiO₂ anode is used, which can be explained in terms of the different mechanism of formation of hydroxyl radicals through a homolytic homogenous reaction in bulk, resulting in the improvement of biodegradability of the final sample.
- Toxicity assays pointed out significant differences. For both processes using MMO-RuO₂TiO₂, lower toxicity was found when compared to BDD anode. Finally, the MMO-RuO₂TiO₂ showed to be suitable for electrochemical and photoelectrochemical degradation of clopyralid in solutions containing chlorides being competitive with a BDD anode as a pre-treatment before biological treatment.

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