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Combined electrochemical treatment/biological process for the removal of a commercial herbicide solution, U46D

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24 **Abstract**

25 The removal of a commercial solution of 2,4-D, U46D[®], was carried out by coupling an
26 electrochemical oxidation and a biological process involving activated sludge.

27 The similar electrochemical behavior of 2,4-D and U46D[®] highlighted their oxidation around
28 1.6 V/SCE and the feasibility of an electrochemical pretreatment. It was based on a home-
29 made flow cell involving bare graphite felt electrode. To propose a consistent mechanism for
30 2,4-D oxidation, the indirect determination of •OH has been performed and the absence of
31 radicals formation during 2,4-D electrolysis was confirmed. Consequently, the proposed
32 pretreatment can be considered as a 'direct' electrochemical process instead of an advanced
33 electrochemical oxidation process.

34 The impact of the flow rate on the pretreatment showed that 3 mL min⁻¹ was a good
35 compromise between the pretreatment time and the electrolysis efficiency, since it led to an
36 almost total degradation of the pollutant while its mineralization remained limited. At this
37 flow rate and for 500 mg L⁻¹ of 2,4-D, the energy cost was estimated at 5 kWh m⁻³. The
38 biodegradability of U46D[®] solution was not significantly modified after electrolysis, most
39 likely due to the presence of dimethylamine salt in U46D[®]. Owing to the significant
40 BOD₅/COD ratio measured, a biological treatment of the commercial U46D[®] solution was
41 however considered.

42 The electrochemical pretreatment shortened the duration of the biodegradation. For non-
43 pretreated U46D[®] (100 mg L⁻¹ 2,4-D), mineralization remained limited until 6 days of culture
44 (33.7% DOC removal), and total removal of the DOC was observed after 8 days. For
45 pretreated U46D[®], 63.7% decrease until the fifth day of culture was observed but total
46 mineralization was not reached at the end of culture (72.1%). An overall mineralization yield
47 during the coupled process of 82.1% was therefore reached. The presence of refractory

48 compounds generated during the electrochemical pretreatment in small concentration was
49 therefore shown.

50

51 **Key-words.** Commercial pesticide U46D[®]; Combined process; Electrochemical process;
52 Biological treatment; Activated sludge.

53

54 **1. Introduction**

55 Electrochemical processes for pesticides removal have been mainly investigated from the
56 nineties. The adaptability and applicability to different volumes, media and pollutants as well
57 as the possibility and ease of automation (current intensity or electrode potential are easy to
58 control) constitute obvious advantages of electrochemical processes [1-3]. Moreover, these
59 processes can be applied to flow systems [4].

60 Concerning pesticides removal, three main processes are studied: electro-coagulation, electro-
61 oxidation and electro-Fenton.

62 Electro-coagulation is based on the soluble anodes principle. When current intensity or
63 potential is generated between two electrodes (in general iron or aluminum electrodes), the
64 corresponding ions are produced which entails the generation of coagulants in solution and
65 then the coagulation-flocculation of pollutants [5]. For example, when a sacrificial iron anode
66 is implemented, the produced ferrous ions are oxidized to ferric ions which precipitate into
67 $\text{Fe}(\text{OH})_3$. The metallic hydroxide is produced in order to reach a sufficient concentration to
68 initiate polymerization or condensation reactions [6, 7]. Fine hydrogen and oxygen bubbles
69 produced at the cathode and anode surfaces, respectively drag particles in suspension to
70 solution surface by electroflotation. This process is effective in mild conditions (of
71 temperature and turbidity) unlike in chemical coagulation. However, electro-coagulation
72 being a non-degradative process, produced flocs should be removed by decantation, flotation

73 or filtration. Moreover, the anodes have to be regularly replaced and electrodes passivation
74 may occur limiting the process efficiency [8]. An enhanced electro-coagulation method
75 (peroxy-coagulation) was reported by Brillas et al. [9]. This method is partially degradative
76 and thus reduces the volume of produced sludge. Coagulation occurs simultaneously with
77 Fenton's reaction between Fe^{2+} ions and cathodically produced H_2O_2 .

78 The anodic oxidation or electro-oxidation is an Electrochemical Advanced Oxidation
79 Process (EAOP) based on the production of a strong oxidant, the hydroxyl radical $\text{M}(\cdot\text{OH})$.
80 The mineralization efficiency depends on three crucial factors: the hydroxyl radical
81 generation, the nature and the stability of the electrode material and the competition of oxygen
82 release. Adsorbed hydroxyl radicals are generated at the anode surface via water oxidation,
83 and interactions between hydroxyl radicals and the anode surface depend on the electrode
84 material. The electrode is considered as "active" when this interaction is strong and
85 characterized by a low oxygen overpotential; it is the case for IrO_2 based electrodes [10]. In
86 this case, oxygen release is favored at the expense of reactions between adsorbed hydroxyl
87 radicals and organic compounds [11] and then mineralization yields are reduced. In the case
88 of strong oxygen overpotential, the oxidation of organic compounds by hydroxyl radicals is
89 favored near the electrode surface, and consequently, the electrode is considered as "non-
90 active". BDD is one of the best material for this type of electrode due to its large O_2 evolution
91 overpotential and high electrochemical stability [12] and was thus largely studied [13-16]. Pt,
92 PbO_2 , SnO_2 electrodes have been also extensively investigated [17-19]. For all these studies,
93 mineralization yields exceeded 75% and reached up to 100% for current densities from 75 to
94 150 mA cm^{-2} .

95 Other electrode materials have also been used for pesticide removal, such as Dimensionally
96 Stable Electrode (DSA), which are constituted of a titanium support covered by a conductive
97 film of metallic oxide or metallic oxides alloys. According to the nature of the conductive

98 film, they can be “active” or “non-active” [20, 21]. In order to increase the mineralization
99 yields, sodium chloride can be added to the electrolyte solution for the production of new
100 oxidant such as Cl_2 or ClO_2 ; this indirect oxidation can be carried out as an alternative to the
101 direct production of hydroxyl radicals [4, 22].

102 In the electro-Fenton process, hydrogen peroxide is generated *in situ* by the two
103 electrons reduction of oxygen at the cathode surface, as well as the regeneration of ferrous
104 ions. Compared to a classical Fenton process, the *in situ* production of reactants prevents from
105 their consumption in large amounts and the regeneration of the catalyst avoids its
106 accumulation as ferric ions, thus decreasing the formation of sludge. At optimized conditions
107 there is no sludge formation since Fe^{3+} does not precipitate at pH 3 for a concentration lower
108 than 0.1 mM, which is used in carbon felt version. Graphite felt cathodes [23-25] and oxygen
109 gas diffusion electrodes [26-29] are the most commonly used electrodes. Various types of
110 Fenton-like processes can be performed [30]; ferrous ions can be directly added to the
111 solution or produced from the oxidation of a sacrificial iron anode (Fered-Fenton). Hydrogen
112 peroxide can also be added to the solution or generated at the cathode surface.

113 Pesticide removal has been largely studied by the electro-Fenton process [31] and
114 mineralization yields are similar to those obtained by electro-oxidation [23]. Electro-Fenton
115 process allows some adaptations especially concerning electrode materials and cell design.
116 For example, a BDD anode can be added in the electrochemical cell to improve the
117 mineralization rate thanks to a concomitant production of hydroxyl radicals [26]. A very good
118 example of the electro-Fenton process using a BDD anode was carried out by Oturan et al.
119 [32] when they studied the mineralization of atrazine and cyanuric acid. More recently, the
120 photoelectro-Fenton process was envisaged to increase the performances of electro-Fenton
121 [28, 29, 33].

122 Electro-oxidation and electro-Fenton are efficient processes leading to high mineralization
123 yields. In order to mineralize organic recalcitrant compounds, an alternative is the coupling of
124 a physico-chemical treatment with a biological process. It can be interesting from an
125 economical point of view since for this type of effluent, the use of an AOP is estimated at 10-
126 20 € m⁻³ at industrial scale, while the coupling of solar photo-Fenton treatment and biological
127 process was recently estimated at 7 € m⁻³ [34].

128 Several electrochemical processes have been carried out after a biological treatment. For
129 example, Ti/RuO₂-IrO₂ electrodes [35] or BDD [36] have been used for the disinfection of
130 biological pretreated domestic effluent, and Ti/BDD was employed during a coke waste water
131 post-treatment [37].

132 An electrochemical process can also be performed as a pre-treatment in order to increase
133 effluent biodegradability and/or reduce its toxicity. To achieve the complete mineralization of
134 the effluent at the end of the combined process, the decrease of DOC should remain limited
135 during this electrochemical pretreatment step. Indeed, significant residual organic carbon
136 should remain available as a carbon substrate for microorganisms during the subsequent
137 biological process [38, 39]. In order to increase industrial effluents biodegradability, various
138 electrode materials have been studied such as platinum [40], stainless steel [41], Ti/RuO₂-IrO₂
139 [42-44] or Pb/PbO₂ [45]. Similarly, electro-oxidation and electro-Fenton have been studied as
140 pretreatments prior to a biological process [42, 44-47].

141 With an integrated system, the risk is to decrease the efficiency of the biological treatment
142 [48], because the production of strong oxidant such as hydroxyl radical can inhibit
143 microorganisms metabolism. In order to prevent this inhibition, both processes can be
144 separated, for instance in the case of Acetomipride (1000 mg L⁻¹) removal; it was first
145 oxidized with a BDD anode and then biologically treated by means of an activated sludge
146 biofilter, with the solution circulating from one to the other [48].

147 In order to improve biodegradability in view of a subsequent biological treatment, namely
148 when total mineralization of the effluent is not needed, direct oxidation or reduction of
149 recalcitrant compounds on an active electrode such as graphite felt can also be considered,
150 even though the corresponding literature remains scarce [49-52]. The aim is to better target
151 the electrochemical reaction, which would be useful not only from an economical point of
152 view, but also in order to control the formation of by-products. A more selective pre-treatment
153 could thus prevent from the formation of more toxic compounds, as it has already been shown
154 in some AOPs and EAOPs processes [51]. Such a direct electrode reaction led to promising
155 results for 2,4-D, a chlorinated phenoxy acid herbicide [51, 52]. Indeed, we have previously
156 shown that mild oxidation of the target compound can be sufficient to improve the
157 biodegradability of 2,4-D solutions [51] allowing a subsequent biological treatment [52]. To
158 complete this previous work and to approach real conditions, the removal of a commercial
159 solution of 2,4-D named U46D[®] has been tested by mild oxidation coupled with activated
160 sludge treatment.

161

162 **2. Materials and Methods**

163 **2.1. Chemicals**

164

165 2,4-dichlorophenoxyacetic acid (2,4-D) (98%) was purchased from Alfa Aesar (Schiltigheim,
166 France) and U46D[®] was commercialized by SAS Nufarm (Gennevilliers, France).
167 Chlorohydroquinone (85%) was purchased from Sigma-Aldrich (Saint-Quentin Fallavier,
168 France). Acetonitrile (ACN) and formic acid were LC/MS grade from JT Baker (Deventer,
169 Netherlands). All standards were prepared with ultra pure water (PurelabOptions-Q7/15, Elga,
170 18.2 M Ω cm).

171

172 2.2. Electrochemical pre-treatment

173

174 The electrochemical pre-treatment was based on a home-made flow cell [51]. Graphite felt
175 used as working electrode was supplied by Le Carbone Lorraine (RVG 4000 – Mersen, Paris
176 La Défense, France). Its specific area, measured by the BET method, was $0.7 \text{ m}^2 \text{ g}^{-1}$; its
177 density was 0.088 g cm^{-3} and its carbon yield was 99.9%.

178 Two interconnected stainless steel plates were used as counter-electrodes and
179 compartments were separated by cationic exchange membranes (Ionac 3470 – Lanxess SAS,
180 Courbevoie, France). The reference electrode (Saturated Calomel Electrode – SCE) was
181 positioned in the middle of the graphite felt, and the potential control was performed using a
182 VersaSTAT 3 potentiostat from Ametek/Princeton Applied (Elancourt, France). To ensure a
183 good homogeneity of the potential distribution in the three dimensional working electrode, the
184 felt was located between the two counter-electrodes [53]. The cell was thoroughly rinsed with
185 distilled water before and after each experiment. The electrolyte solution percolated the
186 porous electrode and flow rate was monitored by a Gilson minipuls 2 peristaltic pump
187 (Middleton, WI, USA).

188

189 2.3. Biological process

190

191 Activated Sludge used in this study was collected from a local wastewater treatment
192 plant in Rennes (Rennes Beaurade, France). It was washed several times by a succession of
193 centrifugations. After each washing, activated sludge was centrifuged at 3000 rpm for five
194 minutes (Jouan, Thermo Fisher Scientifics, Saint Herblain, France). The supernatant was then
195 separated from the sludge to remove any residual carbon or mineral source.

196 Culture medium was prepared in triplicate in 500 mL Erlenmeyer flasks containing
197 250 mL of either pre-treated solutions or pure U46D[®] solutions. Minerals were spiked in the
198 medium as highly concentrated solutions to reach the following initial composition (mg L⁻¹):
199 Na₂HPO₄, 334; K₂HPO₄, 208; KH₂PO₄, 85; CaCl₂, 27.4; MgSO₄·7H₂O, 22.6; NH₄Cl, 75;
200 FeCl₃·6H₂O, 0.26; and the initial pH was adjusted to 7.0 ± 0.2. Activated sludge was added in
201 order to achieve an initial concentration of 0.5 g L⁻¹ of dry matter. Cultures were agitated at
202 250 rpm, and kept at 30°C in aerobic conditions. Samples (5 mL) were taken regularly and
203 filtered through 0.45 µm-syringe filters for measurements.

204

205 **2.3. Analysis**

206

207 Measurements of the residual 2,4-D and chlorohydroquinone concentration were
208 performed by HPLC (High Performance Liquid Chromatography) (Milford, USA) system
209 involving a pump Waters 600, fitted with a Phenomenex Kinetex[®] C18 2.6 µm column (4.6
210 mm × 100 mm), along with a Waters 996 Photodiode array detector, a Waters 717 ph
211 Autosampler and controlled through an Empower[®] 2 program. The mobile phase consisted of
212 acetonitrile and trifluoroacetic acid (TFA) 0.1% in ultra-pure water with a ratio of 30/70 at 1
213 mL min⁻¹.

214 GC/MS/MS measurements were performed with a Perkin Elmer Clarus 500 apparatus
215 coupled with a Variance CB-FFAP 0.25 µm column (25 m × 0.15 mm). Compounds
216 identification was performed with the help of a List database.

217

218 **2.3.1. Dissolved Organic Carbon (DOC) measurements**

219 Solutions were filtered on Satorius Stedim Minisart 0.45 µm GF prefilters
220 (Goettingen, Germany). DOC was measured by means of a TOC-V_{CPH/CPN} Total Organic

221 Analyzer Shimadzu. Organic carbon compounds were combusted and converted to CO₂,
222 which was detected and measured by a non-dispersive infrared detector (NDIR).
223 Reproducible DOC values were always obtained using the standard NPOC (Non Purgeable
224 Organic Carbon) method.

225

226 **2.3.2. Chemical Oxygen Demand (COD) and Biological Oxygen Demand after 5 days** 227 **(BOD₅)**

228 Chemical Oxygen Demand (COD) was measured by means of a Test Nanocolor[®] CSB
229 160 from Macherey-Nagel (Düren, Germany). The amount of oxygen required for the
230 oxidation of the organic and mineral matter at 164°C for 30 min was quantified after
231 oxidation with K₂Cr₂O₇ at acidic pH and heating.

232

233 BOD₅ measurements were carried out in Oxitop IS6 (WTW, Alès, France). Activated sludge
234 provided by a local wastewater treatment plant (Rennes Beaurade, Bretagne, France) was
235 used to inoculate duplicate flasks and the initial microbial concentration was 0.5 g L⁻¹.
236 Control flasks containing easily biodegradable compounds (glucose and glutamic acid at 150
237 mg L⁻¹ each) were run at the same time; and blank flasks, for which the sample was replaced
238 by water, were used to deduce the biological oxygen demand corresponding to the
239 endogenous respiration.

240 Activated sludge solution volume to be added in each flask was deduced from the range of
241 expected BOD₅ values, given by $BOD_5 = COD/1.46$.

242 The following mineral basis was used for all experiments (g L⁻¹): MgSO₄·7H₂O, 22.5; CaCl₂,
243 27.5; FeCl₃, 0.15; NH₄Cl, 2.0; Na₂HPO₄, 6.80; KH₂PO₄, 2.80. Before use, KOH was added to
244 achieve neutral pH (7.0 ± 0.2) and nitrification inhibitor (10 mg L⁻¹ solution of *N*-
245 Allylthiourea) was added.

246

247 **3. Results and Discussion**

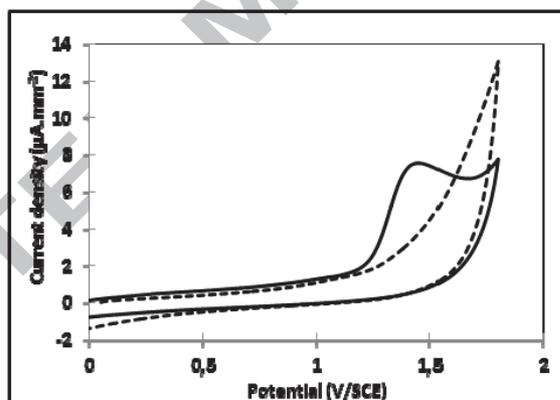
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249 **3.1. Electrochemical pretreatment**

250 GC/MS analysis showed that the commercial herbicide U46D[®] was mainly composed
251 of 2,4-D and dimethylamine salt (data not shown). Other compounds were detected at trace
252 levels, such as 2,4-dichlorophenol or xylene (dimethyl benzene).

253 Previous study [51] highlighted that 2,4-D can be oxidized at 1.6 V/SCE on graphite
254 felt electrode. Figure 1 represents the voltammogram obtained with a solution of U46D[®] (500
255 mg L⁻¹) in Na₂SO₄ 0.1 M, showing similar electrochemical behavior in oxidation to that
256 observed for pure 2,4-D.

257



258

259 Fig.1. Cyclic Voltammetry of U46D[®] (500 mg L⁻¹, continuous line) in 0.1 M Na₂SO₄ (dotted
260 line), 100 mV s⁻¹, glassy carbon electrode (7 mm²).

261

262 An electrochemical pretreatment of the commercial 2,4-D solution was therefore
263 performed and was first investigated at 1.6 V/SCE with 1 mL min⁻¹ flow rate . Electrolysis
264 was then carried out at a constant current intensity of 200 mA, which corresponds to the
265 current intensity measured during the electrolyses at 1.6 V/SCE. Working at a constant

266 current intensity would be helpful for an industrial purpose, since at large scale the reference
267 electrode cannot be used. After electrolysis, high elimination yield, 95.5%, was obtained in
268 only one pass through the flow-cell, similar to those obtained for pure 2,4-D solutions [51].
269 This result confirmed the feasibility of the electrochemical pre-treatment and was promising
270 for the electrolysis of high amounts of pesticides since the recycling of the solution was not
271 needed.

272

273 3.2. Nature of the electrochemical process

274

275 The production of hydroxyl radicals is closely linked to the electrode material used and then
276 to oxygen overvoltage. Mechanisms involving $\bullet\text{OH}$ have been previously proposed in studies
277 based on electrochemical oxidation on graphite felt [54]. If some electrodes (boron doped
278 diamond for instance) are well-known to be powerful candidates for $\bullet\text{OH}$ generation, from a
279 thermodynamic point of view, the formation of hydroxyl radicals on graphite felt seems
280 unlikely for potentials lower than 2 V/SCE. Indeed, with a standard potential of 2.80 V/SHE
281 for $\bullet\text{OH}/\text{H}_2\text{O}$, the oxidation potential at pH 7 reaches 2.38 V/SHE (decrease of 0.06 V per
282 unit of pH) *i.e.* 2.13 V/SCE. Therefore, in order to conclude on the electrochemical oxidation
283 phenomena occurring during the use of such material and to confirm the specificity and
284 selectivity of the considered process, namely a direct oxidation at the electrode surface, the
285 indirect determination of the hydroxyl radicals has been realized.

286 $\bullet\text{OH}$ are known for their strong reactivity with benzene (kinetic rate constant $k = 8 \cdot 10^9 \text{ L mol}^{-1}$
287 s^{-1}), showing the relevance of this compound as a radicals' scavenger [55, 56]. Since phenol
288 is the sole product of benzene hydroxylation, it is possible to deduce the amount of $\bullet\text{OH}$
289 produced from the monitoring of benzene degradation ($\lambda=200 \text{ nm}$) linked to phenol
290 production ($\lambda=270 \text{ nm}$).

291 From this, and after checking the absence of direct benzene oxidation at the electrode at 1.6
292 V/SCE, electrolysis was performed (20 mM initial benzene concentration) in the flow-cell
293 with recycling of the electrolyzed solution. Neither noticeable benzene degradation nor
294 phenol formation could be observed after 140 min of electrolysis. This result clearly
295 confirmed that in the considered experimental conditions and electrolysis time, oxidation of
296 water on graphite felt did not result in $\bullet\text{OH}$ formation. Furthermore and contrarily to
297 electrolysis of the 2,4-D or U46D[®] solutions, the recycling of the electrolysis solution through
298 the cell was considered for this experiment, which was in favor of phenol formation from
299 benzene hydroxylation, confirming unambiguously the absence of radicals formation during
300 2,4-D electrolysis. Consequently, the proposed pretreatment can be considered as a ‘direct’
301 electrochemical process instead of an advanced electrochemical oxidation process.

302

303 **3.3. Impact of the flow rate on pretreatment efficiency**

304 A flow rate of 1 mL min^{-1} was previously considered owing to the high degradation yields
305 obtained if compared to those observed at higher flow rates [49, 50]. The percolation flow rate
306 necessarily impacts the time-contact of the effluent with the polarized surface of the graphite
307 felt. The impact of the percolated flow rate on pretreatment efficiency was therefore
308 investigated, at a constant potential and then at a constant current intensity.

309

310 *3.3.1. Chronoamperometry study*

311 *2,4-D degradation*

312 As seen above, electrolysis of 2,4-D performed at 1.6 V/SCE with 1 mL min^{-1} flow rate led to
313 96% degradation with only a single pass through the cell [51]. To check the influence of the
314 flow rate on the degradation yield, it was examined in the range 1 to 10 mL min^{-1} (Table 1).

315

316

317

Flow rate (mL min ⁻¹)	1	2	3	5	10
2,4-D Degradation yield (%)	>99.9	>99.9	99.3	83.3	46.6
Oxidation yield (%)	54.1	35.6	32.2	24.7	10.3
Mineralization yield (%)	54.2	38.7	35.2	27.2	14.7

318

Table 1: Influence of the flow rate on degradation (2,4-D decrease), oxidation (COD

319

removal) and mineralization (TOC removal) yields during chronoamperometry study.

320

321 Until 3 mL min⁻¹, more than 99% degradation of the 2,4-D present in the commercial
 322 herbicide U46D[®] was observed, and decreased to 83% for 5 mL min⁻¹ and until only 46% for
 323 10 mL min⁻¹.

324 The decrease in the yield is related to insufficient residence time in the graphite felt with less
 325 contact of electro-active species with the electrode surface. Indeed, since the reaction involves
 326 a rapid electron transfer between the substrate and the electrode, an increase of the flow rate
 327 probably leads to the apparition of preferential flow paths through the felt, owing to its high
 328 porosity. Therefore, the decrease of the degradation yield with the flow rate is most likely
 329 linked to the low contact between the solution and the electrode fibers, rather than slow
 330 reaction kinetics.

331 A flow rate of 3 mL min⁻¹ appeared therefore to be a good compromise between the time of
 332 electrolysis, linked to the energy cost, and the efficiency. However, and to confirm the
 333 relevance of this flow rate, other parameters should be examined, such as mineralization,
 334 oxidation, by-products toxicity and biodegradability improvement.

335

336 *Mineralization and oxidation*

337 Impact of the flow rate of percolation on mineralization and oxidation at 1.6 V/SCE is
 338 displayed in table 1, showing that DOC and COD removal followed similar trends (table 1).

339 Mineralization decreased significantly when the flow rates increased from 1 to 2 mL min⁻¹
340 (from 54.2 to 38.7%) and then the decrease was less pronounced; the same trend was
341 observed for oxidation (from 54.1 to 35.6 %). These trends differed from that observed for
342 2,4-D, for which total degradation was observed until 3 mL min⁻¹ (table 1), thus showing the
343 impact of the flow rate on the formed by-products. From this, a flow rate of 3 mL min⁻¹ still
344 appeared to be a good compromise between the pretreatment time and electrolysis efficiency,
345 since it led to an almost total pollutant degradation while mineralization remained limited,
346 both results being in favor of a subsequent biological treatment.

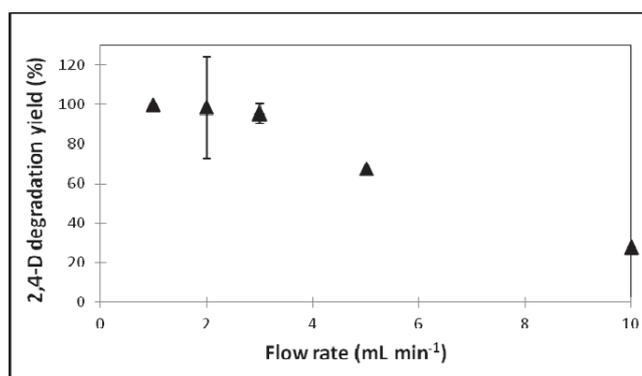
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348 3.3.2. Chronopotentiometry study

349 Although the electrolyses performed at a constant potential were helpful regarding specificity
350 (choice of a relevant potential related to the targeted compounds), it can present some
351 drawbacks regarding possible subsequent industrial application. Indeed, it requires the use of
352 a reference electrode, which is fragile and whose potential can vary with time (salt saturation,
353 porous glass tip fouling...); in addition, with high surface 3-D electrodes, the potential
354 homogeneity can appear difficult to control within all the electrode volume.
355 Chronopotentiometry is therefore needed in view of a possible subsequent industrial
356 implementation, since it does not require a reference electrode, but the problem of the
357 homogenous potential distribution within the electrode volume remains. Indeed, when one
358 counter-electrode is used, the potential field lines decrease rapidly within the felt and hence
359 the reaction occurs only at the electrode surface in front of the counter-electrode. In the flow
360 cell, the two counter-electrodes are positioned each side of the porous electrode, allowing a
361 better linearization of the potential distribution [53]. To work in similar conditions as in the
362 previously described chronoamperometry experiments, the electrode potential was measured

363 and the current intensity adjusted to obtain a potential close to 1.6 V/SCE, leading to applied
364 current values of 200-250 mA.

365 Several electrolyses were performed at various flow rates (Fig. 2). As observed, and similarly
366 to the behavior recorded in potentiostatic mode, high 2,4-D degradation yields were obtained
367 until 3 mL min⁻¹ (above 95%), while they decreased above this flow rate (68 and 28% at 5 and
368 10 mL min⁻¹, respectively) (Fig. 2a).

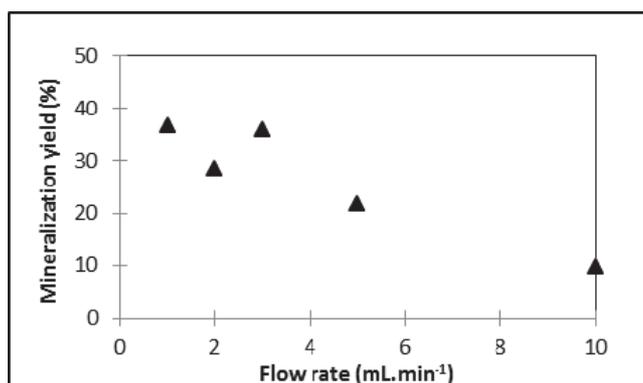


369

370 Fig. 2a. Influence of the flow rate on 2,4-D degradation yield during electrolysis performed at
371 200-250 mA with a single pass through the cell.

372

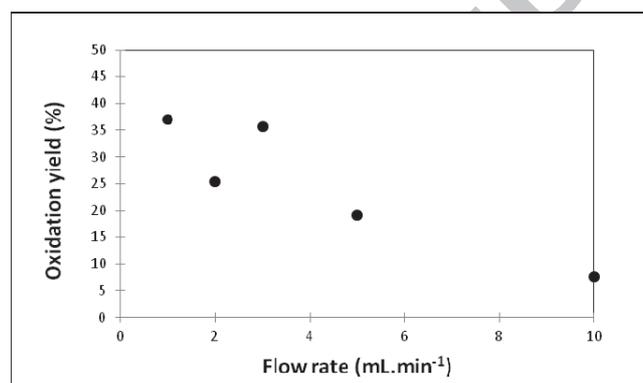
373 As observed in potentiostatic mode, DOC and COD removal followed similar trends:
374 significant decrease of the levels of mineralization and oxidation were observed for 5 and 10
375 mL min⁻¹ (Figs. 2b and c). Therefore, chronopotentiometry can be applied as an
376 electrochemical pretreatment of 2,4-D; and confirming the above results obtained in
377 potentiostatic mode, 3 mL min⁻¹ appeared again to be a good compromise.



378

379 Fig. 2b. Influence of the flow rate on DOC removal during electrolysis performed at 200-250
380 mA with a single pass through the cell.

381



382

383 Fig. 2c. Influence of the flow rate on COD removal during electrolysis performed at 200-250
384 mA with a single pass through the cell.

385

386 3.4. Energy cost

387 For advanced electrochemical oxidation process, the estimation of energy costs is
388 usually based on the COD removal (more especially for 80-85% COD removal) [57]. For
389 example, for an electro-oxidation process carried out with a BDD anode, energy cost varied
390 from 91 to 347 kWh m⁻³ depending on the nature of the treated effluent, since initial COD
391 was in the range 0.1 to 2 g L⁻¹ [58]. For the same electrode material and an initial COD of
392 1.75 g L⁻¹, the energy cost has been estimated to 35 kWh m⁻³ [59]. With a Pb/PbO₂ anode,

393 Panizza et al. [60] have estimated the operating costs at 90 kWh m^{-3} while they increased to
394 681 kWh m^{-3} with a three dimensional carbon bed electrode [61].

395 In this work, the energy cost cannot be estimated from COD removal, since after one
396 pass through the electrolytic cell, COD removal never reached 80% and was more around 30-
397 40%. Considering total 2,4-D degradation after one pass through the graphite felt electrode
398 (2,4-D 500 mg L^{-1} , flow rate of 3 mL min^{-1} and applied current 220 mA), operating costs can
399 be estimated to 5 kWh m^{-3} for the electrochemical pretreatment.

400

401 **3.5. Biological treatment**

402

403 *3.5.1. Biodegradability assessment*

404 Biodegradability of solutions of U46D[®] electrolyzed at 200 mA and 3 mL min^{-1} flow rate was
405 examined. Contrarily to pure 2,4-D for which the BOD₅/COD ratio increased from 0.04 to
406 0.25 [51], electrolysis did not improve the biodegradability of the commercial herbicide
407 solution (Table 2). The initial BOD₅/COD ratio of U46D[®] may be related to the presence of
408 dimethylamine salt, which is obviously more biodegradable than the target compound, 2,4-D,
409 and hence improves the biodegradability of the commercial solution, if compared to pure 2,4-
410 D. The final value nearly similar to that obtained after pure 2,4-D electrolysis may be related
411 to the presence of similar by-products to those obtained after pure 2,4-D electrolysis [51].

412 Even though the BOD₅/COD ratio of 0.4 according to which an effluent can be
413 considered as “easily biodegradable” [62, 63] was not reached, a biological treatment of the
414 commercial U46D[®] solution may be considered owing to the significant ratio measured. Prior
415 to activated sludge cultures, pretreatment in potentiostatic mode at 1 and 3 mL min^{-1} flow rate
416 was therefore considered thereafter.

417

Solution	BOD ₅ /COD
Pure 2,4-D	0.04 [49]
Pure electrolyzed 2,4-D	0.25 [49]
Non-electrolyzed U46D [®] solution	0.21
Electrolyzed U46D [®] solution	0.21

418 **Table 2:** Assessment of the biodegradability of pure and electrolyzed 2,4-D, as well as those
 419 of the commercial herbicide U46D[®] before and after electrolysis (100 mg L⁻¹ 2,4-D)

420

421 3.5.2. Biological treatment of non-pretreated U46D[®]

422 Activated sludge cultures were carried out for two U46D[®] concentrations, 100 and 500 mg L⁻¹
 423 (Fig. 3). A higher mineralization was observed in the beginning of the culture for 500 mg L⁻¹
 424 2,4-D, 33.7% mineralization after 6 days. A rapid DOC decrease was then observed until 8
 425 days culture for both concentrations, until an almost total removal for 100 mg L⁻¹ initial 2,4-D
 426 and 80% degradation for 500 mg L⁻¹ 2,4-D (Fig. 3a). DOC values then remained nearly
 427 constants until cessation of culture, showing that total mineralization could not be achieved
 428 for 500 mg L⁻¹ 2,4-D.

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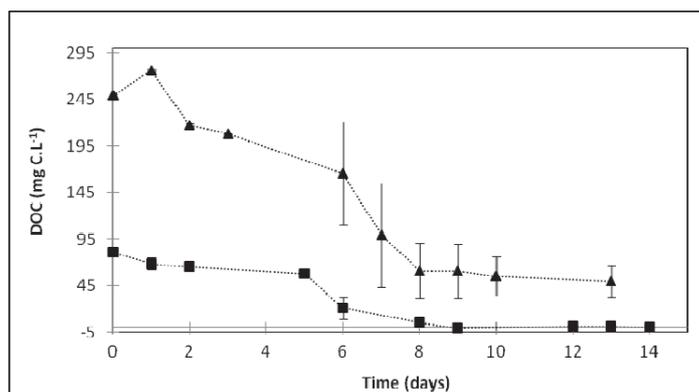
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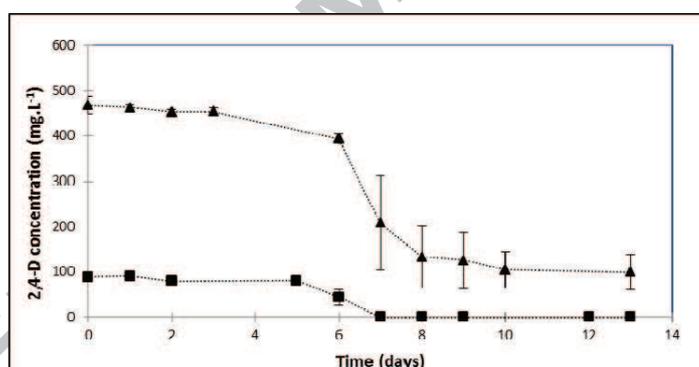
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446 Fig. 3. Time-courses of Dissolved Organic Carbon (a) and 2,4-D concentrations (b) during
 447 biological treatment of U46D[®] corresponding to 500 (▲) and 100 (■) mg L⁻¹ 2,4-D.

448

449 The behavior observed for mineralization was confirmed from 2,4-D monitoring, showing a
 450 low target compound degradation until 5-6 days culture (Fig. 3b), which may be considered as
 451 an acclimation period; a high degradation rate was then observed until 8 days culture before
 452 an almost constant values until the end of culture. Final yields of 2,4-D degradation appeared

453 to be similar to those of mineralization, with an almost total removal for 100 mg L⁻¹ initial
454 2,4-D and 79% degradation for 500 mg L⁻¹ 2,4-D (Fig. 3b). It should be observed that
455 biosorption, which is a rapid phenomenon, was most likely not involved in target compound
456 removal owing to the low decrease observed during the first day of treatment, in agreement
457 with previous results [52].

458 If compared to those obtained during biological treatment of pure 2,4-D solutions, these
459 results were confirmed owing to the similar behavior observed [52]. The higher rates
460 observed on the commercial solution are in agreement with the higher BOD₅/COD ratios
461 described above (0.04 and 0.21 for pure 2,4-D and U46D[®]). These results are most likely
462 related to the presence of dimethylamine salt in the commercial formulation that could
463 increase its “general biodegradability”.

464

465 3.5.3. *Biological treatment of pretreated U46D[®]*

466 Biological treatment was performed on the commercial U46D[®] solution (100 mg L⁻¹ 2,4-D)
467 pretreated at 200 mA, at flow rates of 1 and 3 mL min⁻¹ (Fig.4).

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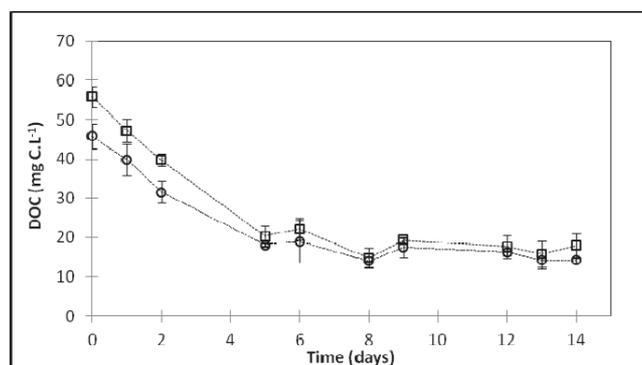
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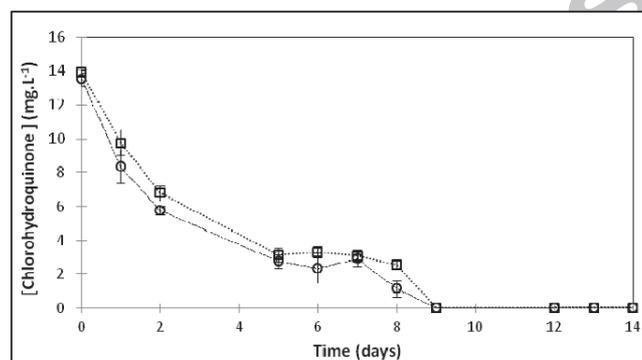
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482 Fig.4. Time-courses of Dissolved Organic Carbon (a) and chlorohydroquinone (b) during
 483 biological treatment of U46D[®] corresponding to 100 mg L⁻¹ 2,4-D, pretreated at 200 mA at a
 484 flow rate of 1 (○) and 3 (□) mL min⁻¹.

485

486 As observed, similar behavior was observed for the two considered flow rates (Fig. 4a): after
 487 one day activated sludge culture, 13.1 and 15.6% DOC decrease were obtained for 1 and 3
 488 mL min⁻¹ flow rates, respectively. This decrease can be attributed to both biosorption and
 489 biodegradation phenomena. However, negligible biosorption of the main by-product,
 490 chlorohydroquinone, was previously demonstrated [52], showing that biodegradation was
 491 mainly involved in DOC decrease. After 5 days culture, 60.3 and 63.7% DOC decrease were
 492 obtained for 1 and 3 mL min⁻¹ flow rates, respectively (Fig. 4a). Low biodegradation rates
 493 were then observed until 70.4 and 72.1% DOC decrease obtained for 1 and 3 mL min⁻¹ after

494 14 days culture (Fig. 4a), leading to overall mineralization yields during the coupled process
495 of 81.3 and 82.1%, respectively.

496 These results should be compared to those recorded for non-pretreated U46D[®] for which
497 98.3% mineralization was observed after 15 days culture, highlighting the persistence of
498 refractory by-products in the pretreated solution, which remained even after 14 days activated
499 sludge culture. As expected [52], this refractory organic matter did not correspond to
500 chlorohydroquinone, since for all studied flow rate, its total removal was observed after 9
501 days of culture (Fig. 4b), showing the presence of other refractory organic compounds
502 accounting for the residual DOC.

503

504

505 If compared to those previously obtained on pure 2,4-D [52], similar trends were observed for
506 the commercial pesticide U46D[®]. Indeed, the electrochemical pretreatment allowed a
507 significant improvement of the mineralization kinetics and by-products degradation rates;
508 however as also previously shown for 2,4-D, the persistence of low concentrated refractory
509 by-products generated during the electrochemical pretreatment was noticed.

510

511 **4. Conclusion**

512 A combined process coupling an electrochemical pretreatment and a biological treatment was
513 applied to a commercial herbicide solution, U46D[®], containing 2,4-D as an active molecule.

514 The electrochemical behavior of U46D[®] was studied by cyclic voltammetry and a similar
515 signal to that of the active molecule 2,4-D was recorded in oxidation around 1.6 V/SCE,
516 confirming that 2,4-D is the major compound in the commercial herbicide. The absence of
517 hydroxyl radicals formation during 2,4-D electrolysis was confirmed suggesting that 2,4-D
518 reacted directly at the electrode surface. Consequently, the proposed pretreatment can be

519 considered as a 'direct' electrochemical process instead of an advanced electrochemical
520 oxidation process. The impact of the flow rate on the pretreatment efficiency was examined in
521 potentiostatic mode and then in amperometric mode to avoid the need for a reference
522 electrode and hence to be more realistic in view of a future industrial implementation. A flow
523 rate of 3 mL min^{-1} appeared to be a good compromise between the pretreatment time (energy
524 cost) and electrolysis efficiency, since it led to an almost total pollutant degradation while
525 mineralization remained limited. Contrarily to pure 2,4-D for which the BOD_5/COD ratio
526 increased, electrolysis did not improve the biodegradability of the commercial herbicide
527 solution. However and even if the limit of biodegradability was not reached (0.4), a biological
528 treatment of the commercial U46D[®] solution was carried out owing to the significant
529 BOD_5/COD ratio measured (0.21).

530 Activated sludge cultures were then performed on the commercial pesticide U46D[®]
531 electrochemically pretreated or not. The electrochemical pretreatment allowed a significant
532 improvement of the mineralization kinetics and by-products degradation rates; however the
533 persistence of refractory by-products from the electrochemical pretreatment in small
534 quantities was highlighted. To remedy the presence of recalcitrant compounds at the end of
535 the electrochemical pretreatment and to degrade these by-products, possible solutions could
536 be the recycling of the solution in the flow cell on the one hand and an acclimation step of the
537 activated sludge to the electrolyzed solution on the other hand.

538

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727 Highlights :

728 •Electrochemical/biodegradation combination was tested for pesticide removal.

729 •Total commercial pesticide U46D[®] degradation and 81.2% mineralization were
730 reached.

731 •A 'direct' electrochemical process was confirmed by the absence of •OH formation.

732 •Biodegradability of the pesticide solution was improved, flow rate was optimized.

733 •The energy cost was found to be similar to those of Advanced Oxidation processes.

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