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Assessment of a hybrid process coupling ozonation and anodic oxidation in a monophasic configuration

Helios Yasmine, Florence Fourcade, Fares Zouaoui, Pierre-Francois Biard

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24 mineralization rate remained small, even if it allows to enhance even more the alachlor parent
25 molecule degradation rate. The low influence of the hybrid process on the mineralization rate was
26 attributed to the production of aliphatic fatty acids by-products that are poorly reactive with
27 hydroxyl radicals, and whose the degradation by AO is the rate limiting step.

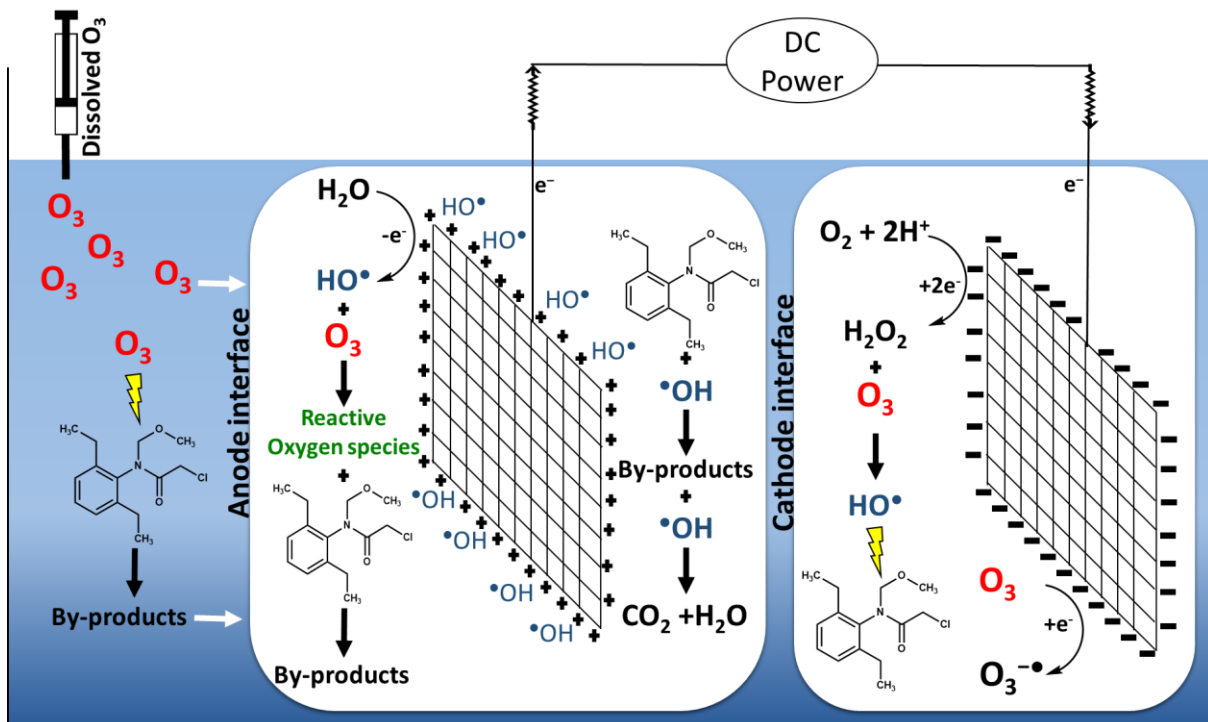
28 **Keywords**

29 Anodic oxidation, ozonation, advanced oxidation process, hydroxyl radicals, alachlor

30 **Highlights**

- 31 • Assessment of an hybrid ozonation/anodic oxidation monophasic process
- 32 • Enhancement of the ozone decomposition rate by the hybrid process
- 33 • Enhancement of the alachlor parent molecule degradation rate by the hybrid process
- 34 • Low influence of the hybrid process on the mineralization rate
- 35 • Pulse reinjections of ozone allows to enhance even more alachlor degradation rate

36 Graphical abstract



37

38

- 40 AO: anodic oxidation
- 41 AOP: advanced oxidation process
- 42 A_{BDD} : BDD anode surface (33 cm²)
- 43 *ARE*: average relative error (-)
- 44 BDD: boron-doped diamond
- 45 C_i : concentration of any species (mol L⁻¹ or mol m⁻³)
- 46 *COD*: chemical oxygen demand (mol_{O₂} L⁻¹)
- 47 *CE*: current efficiency (-)
- 48 D_i : diffusion coefficient of any species *i* (m² s⁻¹)
- 49 DET: direct electron transfer
- 50 *DOC*: dissolved organic carbon (ppm)
- 51 *Eff*: removal efficiency (-)
- 52 EfOM: effluent organic matter
- 53 f_{HO^\bullet} : fraction of hydroxyl radicals reacting with alachlor (-)
- 54 *H*: ozone Henry's law constant (Pa m³ mol⁻¹)
- 55 *I*: current intensity (A)
- 56 *J*: current density (A m⁻² or mA cm⁻²)
- 57 *k*: reaction rate constant (mol¹⁻ⁿ Lⁿ⁻¹ s⁻¹)

- 58 k_m and k_L : mass-transfer coefficient in the liquid phase for COD and O_3 , respectively ($m\ s^{-1}$)
- 59 n : order of reaction (-)
- 60 OM: organic matter
- 61 R_{ct} : ratio of the hydroxyl radical exposure to the ozone exposure (-)
- 62 ROS: reactive oxygen species
- 63 S : gas-liquid interfacial area (m^2)
- 64 $t_{1/2}$ and $t_{0.2}$: half-life time and time for a removal efficiency of 20%, respectively (min or s)
- 65 TOC: total organic carbon (ppm)
- 66 V : volume (L or m^3)
- 67 **Subscripts:**
- 68 al: alachlor
- 69 app: apparent
- 70 H_2O_2 : hydrogen peroxide
- 71 G: in the gas-phase
- 72 i: any species i
- 73 L: in the liquid-phase
- 74 oz: ozone
- 75 0: at t_0

77 Industrial wastewaters treatment needs nowadays technologies, such as ozone-based or
78 electrochemical advanced oxidation processes (AOPs), able to reach extensive mineralization of the
79 organic pollutants. Table S.1 presents the main mature or in development processes to remove
80 organic pollutants from wastewaters. One strategy to improve refractory compounds removal is to
81 combine these processes under a multi-barrier approach.

82 Ozonation is widely used in drinking water production plant and is more and more considered for
83 industrial and urban waste waters treatment, owing to its reactivity on organic matter and emerging
84 pollutants [1–5]. Its reactivity in aqueous solution relies on two pathways, the direct pathway which
85 involves molecular ozone, and the indirect pathway which involves reactive oxygen species (ROS),
86 especially hydroxyl radicals HO^\bullet , generated from the spontaneous ozone decomposition in water
87 [4,6,7]. In natural waters (ground water, surface water, etc.) and waste waters, the ozone
88 decomposition is mainly initiated through the reaction with the hydroxide anion and with some
89 electron-rich moieties of the organic matters, particularly when they have deprotonated functions
90 (such as carboxylates, phenolates, etc.), that electrophilic molecular ozone can easily target [5,8,9].
91 Consequently, the ozone decomposition reaction rate typically increases with the pH. To enhance
92 both the ozone decomposition and ROS generation rates, chemical (catalyst, H_2O_2) or physical (UV,
93 US) initiators can be also added in ozone-based AOPs [7].

94 More recently, several authors investigated the potential of hybrid ozone/electrochemical processes.
95 Electrochemical processes are recognized as versatile, easily automable and are operated in mild
96 conditions [10–14]. There are several ways to combine ozonation and electrochemical processes
97 [10,15–20]. Among them, the most studied are i) the electrochemical production of ozone [16,21,22],
98 ii) the electroperoxone process [23–28] and iii) the combination between anodic oxidation and
99 ozonation.

100 The electroperoxone process is based on the coupling of ozone and *in-situ* produced hydrogen
101 peroxide from the electrochemical reduction of oxygen [14,29,30]. Both the electrochemical
102 reduction of O_3 and the reaction between O_3 and the hydroperoxyde anion (the conjugated base of
103 H_2O_2) generate ROS. Carbon based materials and gas diffusion electrodes are preferentially chosen as
104 cathode materials in this combined process owing to the fact that they favour the H_2O_2 production
105 [14,24,31].

106 Anodic oxidation (AO) has emerged as an efficient, easy, environmentally friendly and cost-effective
107 treatment process for removing persistent organic compounds [32–34]. AO can degrade and
108 mineralize pollutants through both direct and indirect processes. Indeed, on the electrode surface,

109 organic pollutants can be directly oxidized or reduced through the exchange of electrons with the
110 electrode surface. This mechanism is called direct electron transfer (DET). Besides, pollutants can
111 also be oxidized by an indirect oxidation process through the *in-situ* generation of various oxidants,
112 particularly HO[•] radicals produced at the anode surface through the oxidation of H₂O [35,36]. The
113 efficiency of the AO process and the nature and amount of reactive species formed can be affected
114 by various factors, including the material of the electrode, the type of contaminant, the type of
115 electrolyte and the applied current or voltage [37].

116 The limitations of each processes can be surpassed by the combination of the two processes. On one
117 hand, O₃ degradation preferably leads to short chain aldehydes and carboxylic acids, non-reactive
118 with O₃ and poorly reactive with hydroxyl radicals, limiting the mineralization of the pollution [5,38].
119 Electrochemical processes are more potent to mineralize organic compounds than ozonation owing
120 to the DET mechanism that can potentially target organic compounds refractory to reactions with
121 hydroxyl radicals, such as low-chain fatty acids. Furthermore, electrochemical processes might be
122 able to efficiently decompose O₃ even at acidic pH, due to ozone reactions at both the cathode and
123 anode's surface, allowing to increase the pH window of ozone reactivity. On the other hand, the
124 formation of polymer by the electrochemical oxidation of cyclic compounds entails electrode fouling
125 and decreases the current efficiency (CE) [39]. Ozone can react with phenolic compounds by ring
126 opening (cycloaddition mechanism) leading to a reduction of the polymer formation. Biofilm
127 formation at the electrodes surface would be also potentially mitigated by the use of ozone.

128 Thus, the removal of various persistent organic pollutants by hybrid anodic oxidation/ozonation
129 (OA/O₃) processes was studied in aqueous solution [20,23,40,41] and in sludge from wastewater
130 treatment plant [42]. Compared to sole electrooxidation, higher and faster removal yields were
131 obtained highlighting the synergy between ozonation and electrooxidation [19,23,40].

132 The most studied anode material is the boron-doped diamond (BDD) characterized by a good
133 chemical stability and an important production of physisorbed hydroxyl radical [10,20,23,42–44].
134 Ti/PbO₂ anodes are also pertinent candidates because, as for the BDD, the overpotential for O₂
135 evolution is high [40]. The applied current densities were at the same order of magnitude as for the
136 electroperoxone process, from around 10 to 60 mA cm⁻² [20,23,40–42]. Only a few papers
137 investigated the influence of the pH even if it strongly influences the O₃ decomposition [20,40]. Qiu
138 *et al.* assessed the influence of the nature and the concentration of the supporting electrolyte [45]. In
139 Na₂SO₄ electrolyte, the mineralization increased with the concentration and the formation of sulfate
140 radicals was supposed. In NaCl electrolyte, the formation of active chlorine species improved the
141 combined process efficiency but the formation of refractory chlorinated intermediates was
142 suspected. An increase of the current density enhanced the production of hydroxyl radicals at the

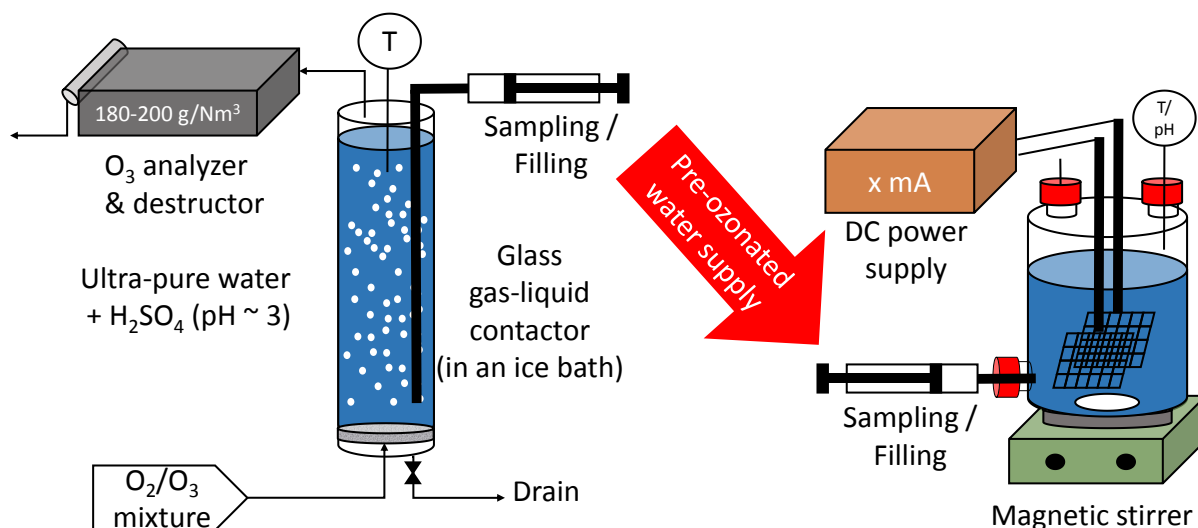
143 anode. They also concluded that, in their study, the O₃ reduction at the cathode played only a minor
144 role on the p-nitrophenol degradation [45].

145 In the majority of the hybrid OA/O₃ process studies, ozone-enriched gas bubbles were used to feed
146 the electrochemical reactor. In that case, the ozone transfer in solution and the oxidation processes
147 were achieved in only one stage. However, particularly in waste waters, which are characterized by a
148 high effluent organic matter (EfOM) content and consequently by a high ozone demand [46], the
149 ozone reaction rate in the boundary layer can be higher than the ozone transfer rate (fast kinetic
150 regime) [7]. Thus, ozone would be completely consumed at the vicinity of the gas-liquid interface and
151 wouldn't be able to reach the surfaces of the anode and cathode. Nonetheless, for other kinds of
152 hybrid ozonation processes, the relevance of mixing a pre-ozonated solution to the water to treat,
153 instead of using ozone-enriched gas bubbles, has been demonstrated [47,48]. It requires to
154 dissociate the ozone transfer step and the oxidation steps. This approach is beneficial to locate the
155 ozone decomposition, and the ROS generation in the liquid bulk, not at the gas-liquid interface.
156 Furthermore, it enables to advantageously control the ozone dose introduced.

157 Consequently, the purpose of the present prospective study is to investigate the potential of a hybrid
158 process coupling ozonation and anodic oxidation in a batch monophasic system, in which a known
159 volume of an ozone stock solution was added to the studied water matrix. BDD anodes and cathodes
160 were used owing to their high potential of HO[•] generation. An acidic pH of 5 was selected in order to
161 limit the ozone decomposition initiated by the hydroxide anions in the bulk and to assess more
162 particularly the mechanisms involved between dissolved ozone and both BDD electrodes. A
163 phosphate buffer as supporting electrolyte was preferred to conventional Na₂SO₄ and NaCl
164 electrolytes, allowing to avoid the formation of chlorine and sulfate radical reactive species, in order
165 to focus only on the mechanisms associated to ROS generation and DET.

166 2. Material and methods

167 2.1. Experimental set-up description



168

169

Figure 1: Scheme of the experimental procedure.

170 A module, already described elsewhere [49], allowed to produce an ozone-enriched oxygen flow (at
171 a concentration in the range 180-200 g Nm⁻³ and a flow rate of 15 NL h⁻¹, under the normal
172 conditions for temperature and pressure). The ozone/oxygen mixture was continuously bubbled in a
173 custom glass bubble column equipped with a gas sparger at the bottom. The bubble column was
174 placed in an ice bath to set a temperature around 1°C. The bubble column contained 1 L of ultra-pure
175 water (UPW) acidified at pH 2 through the addition of 3.75 mL of H₂SO₄ at 1 M, in order to
176 completely suppress ozone decomposition. After ~ 30 min, the gas-liquid equilibrium was reached
177 within the bubble column at a dissolved ozone concentration around 100 ppm.

178 In parallel, 700 mL of the studied aqueous solution (ultra-pure water doped withalachlor and a
179 phosphate buffer to set a pH ~ 5) was introduced in a custom magnetically stirred glass reactor
180 containing 2 BDD grid electrodes (50×50×1.4 mm corresponding to a surface of 33 cm²) connected
181 to a DC power supply unit (Microlab, provided by Micronics-System) by Platinum wires. The
182 electrodes, provided by NeoCoat SA (Switzerland), were composed of 6 μm Boron-Doped Diamond
183 deposited on a niobium substrate (Nb doped with 2500 ppm of boron). The interelectrode distance

184 was set at 1.5 cm. Three current intensity were assessed, 200, 500 and 800 mA, corresponding to
185 current densities J of 6.1, 15.2 and 24.2 mA cm⁻², respectively. A sampling port equipped with a Luer-
186 Lock valve, located at the bottom of the electrochemical reactor, allowed to introduce and
187 withdrawn samples with a set of different gas-tight syringes (provided by Hamilton or SGE).

188 At t_0 , 100 mL of the ozone-stock solution (or of UPW when only anodic oxidation was evaluated) was
189 added as fast as possible (~ 10 s) in the electrochemical reactor to the 700 mL alachlor solution using
190 a 100 mL gas-tight syringe (Hamilton). Thus, it lead to a total liquid volume (V_l) of 800 mL and an
191 initial alachlor concentration around 30 ppm (corresponding to a DOC concentration of ~ 19 ppm), a
192 phosphate buffer concentration of 50 mM and a conductivity of 4.52 mS cm⁻¹ at 20°C. The initial
193 ozone concentration was typically in the range from 10 to 13 ppm. Regular samples were withdrawn
194 but the total amount of solution removed was kept lower than 10% of the initial volume. An excess
195 of sodium bisulfite in powder was used to quench ozone residuals in the vials in which samples for
196 alachlor and TOC quantification were collected.

197 To avoid pressure variations during filling and withdrawing, a metal hub needle was introduced in the
198 top of the reactor, allowing to keep the atmospheric pressure inside the electrochemical reactor but
199 with very limited gas transfer between the gas headspace and the atmosphere outside the reactor.
200 The ozone desorption from the aqueous phase to the gas headspace was previously assessed by
201 measuring the dissolved ozone concentration with an unreactive aqueous solution. The ozone
202 desorption percentage did not exceed 20% in 40 min (See part 3.1.1) and was even lower in reactive
203 systems, prone to consume ozone in lower time ranges.

204 **2.2. Analytical methods**

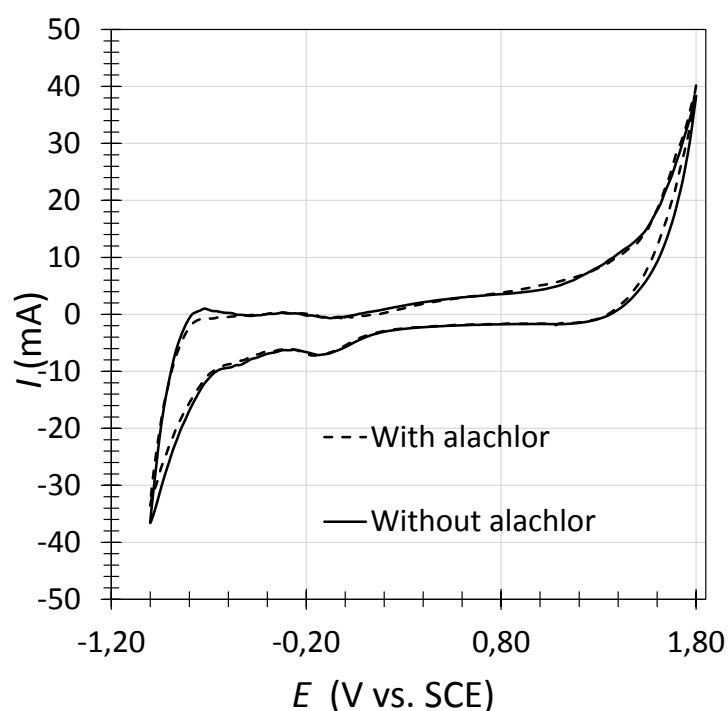
205 Alachlor quantification was achieved with a Waters Acquity UPLC H-Class Plus chromatographic chain
206 equipped with a Waters PDA eλ (Photodiode Array Detector) and a Waters quaternary solvent
207 manager. The separation was performed on a column Acquity UPLC BEH C-18 (1.7 μm; 2.1 × 100 mm)

208 at 45°C with a gradient elution process based on two solvents (A: UPW / Acetonitrile + 0.1% formic
209 acid 10/90 and B: Acetonitrile + 0.1% formic acid). Samples were analyzed after filtering through a
210 0.2 µm membrane filter. The ozone concentration was selectively quantified by the Indigo method
211 [50]. A Helios UV–Vis spectrophotometer (Shimadzu, Japan) was used for the indigo absorbance
212 measurement, performed a few minutes after the sampling ($\lambda = 600$ nm). The H₂O₂ concentration
213 was determined through the potentiometric titration of I₂, generated by the oxidation of KI by H₂O₂,
214 employing sodium thiosulfate as the titrant. Total Organic Carbon was quantified by a Shimadzu COT-
215 meter (TOC-V CPH) with the NPOC method.

216 3. Results and discussion

217 3.1 Direct oxidation study by cyclic voltammetry

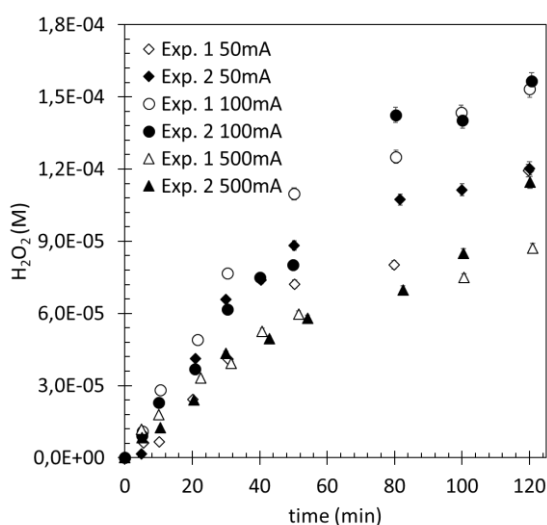
218 Cyclic voltammograms were recorded to examine the electrochemical behavior of alachlor on the
219 BDD electrodes at a scan rate of 100 mV s^{-1} in a $50 \text{ mM H}_3\text{PO}_4$ aqueous solution. Current-potential
220 curves were plotted in the absence and in the presence of 30 ppm of alachlor (Fig. 2). The oxygen
221 evolution potential was observed at around 1.8 V vs. SCE and the hydrogen evolution reaction was
222 observed at around -0.8 V vs. SCE . Oxygen reduction was observed around -0.1 V vs. SCE but no
223 signal appeared for alachlor on the BDD electrode in the electroactivity range of the supporting
224 electrolyte. It shows that direct electron transfer does not occur between BDD electrode surface and
225 alachlor molecule before both oxygen evolution and hydrogen evolution reactions. However, the
226 direct oxidation or reduction of alachlor remains possible at potentials outside the electroactivity
227 range of the BDD electrodes. For instance, He et *al.* demonstrated that alachlor could be reduced on
228 a glassy carbon electrode at -1.25 V vs. SCE [51].



230 **Figure 2. Cyclic voltammograms in 50 mM H₃PO₄ with and without 30 ppm alachlor using BDD**
231 **electrodes.**

232 3.2 H₂O₂ electrochemical generation

233 The combined use of ozone/hydrogen peroxide (O₃/H₂O₂) accelerates the conversion of O₃ to HO[•],
234 which can reduce the reaction time required for pollutants degradation [52]. Therefore, there has
235 been an increased interest in inducing the *in-situ* production of H₂O₂ to enhance O₃ decomposition
236 efficiency. Anodic oxidation generally induces the production of H₂O₂ at the cathode. In the light of
237 this, the production of H₂O₂ in function of the electrolysis duration and the current density (50, 100
238 and 500 mA) is presented in Fig. 3. H₂O₂ generation began as soon as the electrodes were polarized
239 and continued to increase up to 80 minutes regardless of the applied current intensity. After 80
240 minutes, the concentration of H₂O₂ remains almost constant, indicating the establishment of an
241 equilibrium between the cathodic production of H₂O₂ and its anodic oxidation. For low current
242 intensities, the production of H₂O₂ increased with the applied current intensity. However, for 500
243 mA, the production of H₂O₂ is lower than for 50 and 100 mA. This behavior can be explained owing to
244 the fact that for high current intensities, hydrogen evolution and 4 electrons reduction of O₂ into H₂O
245 compete with H₂O₂ formation. According to the state of the art, a similar behavior has been observed
246 with a graphite cathode [53].



247

248 *Figure 3. H₂O₂ concentration evolution in function of the electrolysis duration for different*
249 *current intensities (50, 100 and 500 mA) using BDD electrodes in 800 mL H₃PO₄ at 60 mM.*

250 **3.3. Ozonation alone**

251 **3.3.1 Ozone desorption in the electrochemical reactor**

252 The ozone desorption from the liquid phase to the gas headspace in the electrochemical reactor was
253 firstly evaluated (See Part S.2). The electrochemical reactor was filled with an ultra-pure water
254 acidified at pH 3.5 through 0.1 M H₂SO₄ addition and containing tBuOH (0.005 M) as radical
255 scavenger in order to prevent ozone decomposition [4]. Experiments were performed with or
256 without the non-polarized BDD electrodes. Around 20% of the ozone dose introduced at t_0 was
257 desorbed after 40 min (Fig. S.2) and no significant difference was observed with or without
258 electrodes, showing that no ozone decomposition occurred at the uncharged electrode surface. The
259 time profile of the ozone concentration was modeled according to Eq. S.8 which allowed to
260 determine by numerical resolution the average value of the ozone liquid-side mass-transfer
261 coefficient k_L ($k_L = 1.94 \times 10^{-5} \text{ m s}^{-1}$) at $T = 19 \pm 1^\circ\text{C}$. This value is in good agreement with the value of
262 $1.19 \times 10^{-5} \text{ m s}^{-1}$ found for ozone in a stirred-cell reactor agitated by a Rushton turbine at 20°C [49].

263 **3.3.2 kinetic modeling**

264 Taking into account the ozone desorption from the liquid phase to the gas headspace (part 3.3.1 and
265 part S.2) and the ozone decomposition in the electrochemical reactor, Eq. 1 is obtained:

$$266 \quad -\frac{dC_{L,oz}}{dt} = \frac{k_L S}{V_L} \left(C_{L,oz} - \frac{RT}{H} C_{G,oz} \right) + k_{app} C_{L,oz}^n \quad (\text{Eq. 1})$$

267 With k_{app} ($\text{mol}^{1-n} \text{ L}^{n-1} \text{ s}^{-1}$) the apparent ozone decomposition reaction rate constant and n the order of
268 reaction. S is the surface area between the liquid-phase and the gas-phase, corresponding to the
269 electrochemical reactor section ($7.76 \times 10^{-3} \text{ m}^2$). V_L is the liquid volume (m^3). H ($\text{Pa m}^3 \text{ mol}^{-1}$) is the
270 ozone Henry's law constant in water deduced from the correlation of Ferre-Aracil et al. [54]. The

271 ozone gas-phase concentration $C_{G,oz}$ is related to the ozone liquid-phase concentration $C_{L,oz}$ through
 272 Eq. 2:

$$273 \frac{k_L S}{V_L} \left(C_{L,oz} - \frac{RT}{H} C_{G,oz} \right) = \frac{dC_{G,oz}}{dt} V_G \quad (\text{Eq. 2})$$

274 The best values of n and k_{app} associated to each experiment were determined by numerical
 275 resolution following the procedure presented in supplementary material (Part S.3). The knowledge of
 276 these parameters allowed for each experiments to model $C_{L,oz}$ vs time and to determine both the
 277 ozone half-life time ($t_{1/2}$) according to Eq. 3 and the ozone exposure ($\int C_{L,oz} dt$) according to Eq. 4 [55]:

$$278 t_{1/2} = C_{L,oz,0}^{1-n} \frac{(2^{n-1}-1)}{k_{app}(n-1)} \text{ if } n \neq 1 \text{ and } t_{1/2} = \frac{\ln(2)}{k_{app}} \text{ if } n = 1 \quad (\text{Eq. 3})$$

$$279 \int_{t_0}^t C_{L,oz} dt = \sum_{i=1}^m \frac{C_{L,oz,i-1} + C_{L,oz,i}}{2} \times \Delta t \quad (\text{Eq. 4})$$

280 With m the number of time-interval Δt (fixed to 12 s).

281 The alachlor degradation rate can be modeled according to Eq. 5 considering bimolecular reactions
 282 with both HO^\bullet and O_3 [56]:

$$283 -\frac{dC_{al}}{dt} = k_{O_3} C_{L,oz} C_{al} + k_{HO^\bullet} C_{HO^\bullet} C_{al} \quad (\text{Eq. 5})$$

284 With k_{O_3} the reaction rate constant between O_3 and alachlor and k_{HO^\bullet} the reaction rate constant
 285 between HO^\bullet and alachlor, presumed equal at $2.8 \pm 0.3 \text{ L mol}^{-1} \text{ s}^{-1}$ and $3.2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$,
 286 respectively, according to Beltran et al. [56]. Thus, Eq. 5 can be rearranged leading to Eq. 6:

$$287 \ln \left(\frac{C_{al}}{C_{al,0}} \right) = k_{O_3} \int_{t_0}^t C_{L,oz} dt + k_{HO^\bullet} \int_{t_0}^t C_{HO^\bullet} dt \quad (\text{Eq. 6})$$

288 The HO^\bullet generation can be quantified in ozonation processes with the R_{ct} concept, which
 289 corresponds to the ratio of the HO^\bullet exposure ($\int C_{HO^\bullet} dt$) to the ozone exposure ($\int C_{L,oz} dt$). Thus, Eq. 6
 290 leads to Eq. 7:

291 $\ln\left(\frac{C_{al}}{C_{al,0}}\right) = (k_{O_3} + k_{HO\cdot}R_{ct}) \int_{t_0}^t C_{L,oz} dt \Leftrightarrow C_{al} = C_{al,0} \exp\left(\left(k_{O_3} + k_{HO\cdot}R_{ct}\right) \int_{t_0}^t C_{L,oz} dt\right)$ (Eq.
 292 7)

293 The R_{ct} is usually constant after the instantaneous ozone demand phase in natural and synthetic
 294 waters [57]. It was determined by numerical resolution for each experiment by trying to minimize the
 295 sum of square errors (SSE) between the experimental and modeled values of C_{al} . The knowledge of
 296 the R_{ct} value allowed to determine the fraction of alachlor reacting with $HO\cdot$ ($f_{HO\cdot}$) according to Eq. 8
 297 [57]:

298
$$f_{HO\cdot} = \frac{k_{HO\cdot}R_{ct}}{k_{HO\cdot}R_{ct} + k_{O_3}} \quad (\text{Eq. 8})$$

299 In the present study, in which the water matrix was deprived of natural organic matters, the
 300 instantaneous ozone demand was systematically negligible.

301 **3.3.3 Alachlor degradation by ozonation**

302 Alachlor oxidation by only ozone was assessed in the electrochemical reactor with the non-polarized
 303 BDD electrodes at low ozone doses in the range 0.4-0.6 $g_{O_3} g_{DOC}^{-1}$ (~ 2 -2.5 $mol_{O_3} mol_{al}^{-1}$). The time-
 304 course profiles of both the ozone and alachlor concentrations are provided in Fig. 4. No
 305 mineralization was observed (Fig. S.4) with a constant DOC concentration over time, which is
 306 consistent with the low ozone doses applied.

307 Without radical scavenger (tBuOH) added, the ozone half-life time (Eq. 3), was around 12 min (Table
 308 1). Owing to the low applied ozone dose, the alachlor degradation was not complete and reach a
 309 maximal removal efficiency of around 50-60% after ~ 35 min and the full O_3 decomposition (Fig. 4.a).
 310 The ozone decomposition was well described by a 0.8th-order rate law (Table 1). The ozone
 311 decomposition rate observed was four orders of magnitude higher than the one corresponding to
 312 the initiation reaction of molecular ozone with the hydroxide anion at the low pH applied (*i.e.* k_{O_3/HO^-}
 313 $C_{HO^-}C_{L,oz} \ll k_{app}C_{L,oz}^{0.8}$) [8]. It shows that the ozone decomposition was initiated by another reactions,

314 which involve directly the alachlor parent molecule and/or some of its intermediates. The R_{ct} value of
315 0.76×10^{-10} , is two to three orders of magnitude lower than in natural and waste waters [5,57], which
316 emphasizes a low potential of HO^\bullet generation in the investigated water matrix which is deprived of
317 natural and effluent organic matters acting as potent ozone decomposition initiators. Thus, a fraction
318 of alachlor reacting with HO^\bullet (f_{HO^\bullet}) of 63% was determined (Eq. 8), showing that both the direct
319 (involving molecular ozone) and indirect (involving free hydroxyl radicals) pathways were
320 concomitant. In natural and waste waters in which organic matters would be present, higher R_{ct}
321 would be expected and a complete oxidation by HO^\bullet would be observed [1].

322 With the addition of tBuOH as radical scavenger, both the ozone decomposition and alachlor
323 degradation rates were significantly slowed down compared to the experiments without tBuOH (Fig.
324 4). The ozone half-life time (42 min) was around 3.5 times higher than without radical scavenger
325 (Table 1). More precisely, the alachlor removal efficiency was also a little bit lower, around 43% after
326 40 min but the ozone consumption was not complete yet. Furthermore, the R_{ct} was negligible
327 demonstrating that the tBuOH concentration of 0.01 M was sufficient to efficiently scavenge all the
328 radicals formed by the ozone decomposition in presence of alachlor. The ozone decomposition
329 kinetics was well described by a first-order rate law accounting for molecular O_3 reaction with the
330 alachlor parent molecule and also with some degradation intermediates because the apparent
331 stoichiometry of the reaction was not constant over time and varied between 3 mol and 4.5 mol of
332 O_3 consumed per mol of alachlor consumed. The alachlor concentration-time profile was modeled by
333 Eq. 7, and the alachlor consumption was too sharp using the value of k_{O_3} proposed by Beltran et al.
334 [56], with an average relative error (ARE) of 26% between the experimental and modeled values of
335 C_{al} . Thus, the value of k_{O_3} was recalculated by numerical resolution using Eq. 7 and an alternative
336 lower value of $1.39 \text{ L mol}^{-1} \text{ s}^{-1}$ was determined, associated to an ARE for C_{al} of only 1.9%.

337 Furthermore, a reference experiment with an initial concentration 100 μM of H_2O_2 allowed to
338 simulate the potential influence of the H_2O_2 electrogeneration (See Part 3.2). An enhancement of the

339 ozone decomposition reaction rate, with an ozone half-life time of only 6 min, was observed (Table 1
 340 and Fig. 4.a). The ozone decomposition rate linked to the ozone decomposition by the
 341 hydroperoxyde anion can be estimated through the calculation of the product of the reaction rate
 342 constant k_{O_3/HO_2^-} with the HO_2^- concentration ($k_{O_3/HO_2^-} \times C_{HO_2^-}$), taking into account a maximal
 343 total H_2O_2 concentration ($C_{H_2O_2}$) of 100 μM and a pKa (H_2O_2/HO_2^-) of 11.75 according to Eq. 9 [58]:

$$344 \quad k_{O_3/HO_2^-} C_{HO_2^-} = k_{O_3/HO_2^-} \frac{C_{H_2O_2}}{1+10^{pKa-pH}} = 2.40 \times 10^6 \frac{100 \times 10^{-6}}{1+10^{11.75-5}} = 4.3 \times 10^{-5} \text{ s}^{-1} \text{ (Eq. 9)}$$

345 Thus, the ozone decomposition rate linked to the ozone decomposition by the hydroperoxyde
 346 ($k_{O_3/HO_2^-} C_{HO_2^-} C_{L,oz}$) is around 50 times lower than the apparent ozone decomposition rate
 347 ($k_{app} C_{L,oz}^{0.8}$) considering an average ozone concentration of 100 μM . It shows that the potential H_2O_2
 348 electrogeneration would contribute poorly directly to the ozone decomposition initiation in the liquid
 349 bulk owing to the low pH applied. Nonetheless, the presence of a moderate H_2O_2 concentration can
 350 promote the ozone decomposition owing to the fact that H_2O_2 can react with HO^\bullet leading to the
 351 hydroperoxyl radical HO_2^\bullet , which is in equilibrium with the superoxide radical $O_2^{\bullet-}$ that reacts further
 352 with O_3 leading to the ozonide radical $O_3^{\bullet-}$ ensuing the radical chain [59–62]. Thus, the R_{ct} value was
 353 around twice with H_2O_2 (Table 1). Yong and Lin demonstrated that the R_{ct} corresponds to the ratio of
 354 the total initiation capacity to the total inhibition capacity of a water matrix [63]. Considering that
 355 the inhibition capacity should not depend on the addition of H_2O_2 , it shows that the initiation
 356 capacity is doubled. Consequently, the initiation reaction with the hydroperoxyde anions contributes
 357 almost equally with the other initiation reactions. It also confirms that promotion reactions with
 358 some oxidation intermediates contribute importantly to the ozone decomposition rate, even if they
 359 do not influence the R_{ct} [63]. Nonetheless, with H_2O_2 , associated to a lower ozone exposure because
 360 of the faster ozone decomposition, the final hydroxyl radical exposure ($\int_{t_0}^t C_{HO^\bullet} dt$) and ensuing
 361 alachlor final removal efficiencies were similar with/without H_2O_2 (Table 1). It confirms that addition
 362 of H_2O_2 does not necessarily leads to better removal efficiencies but advantageously allow to speed

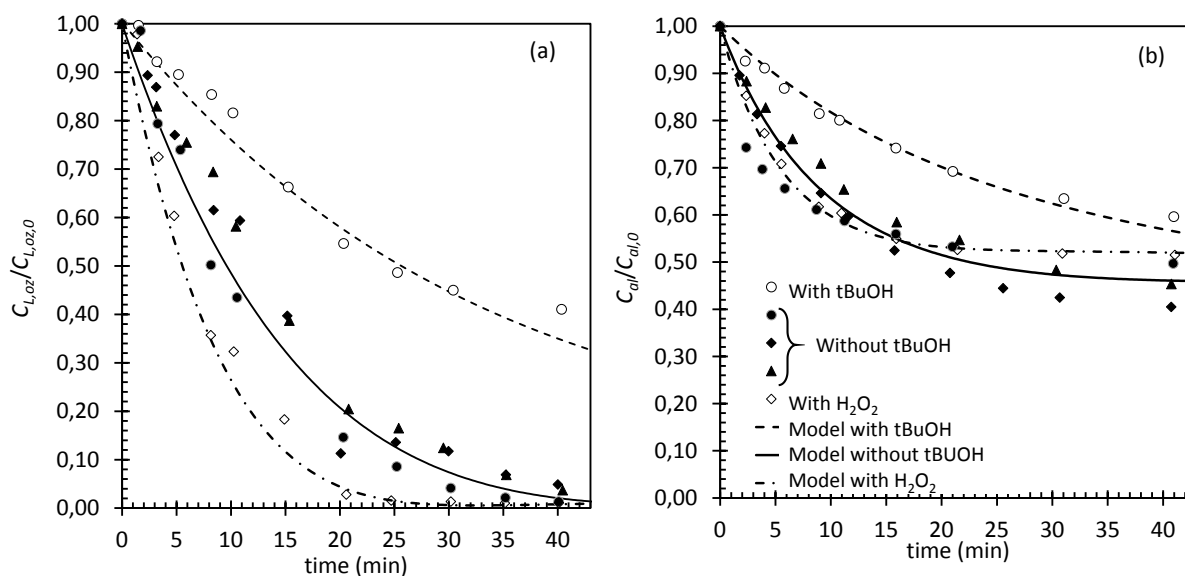
363 up the oxidation process. Finally, evaluation of the fraction of alachlor reacting with HO[•] ($f_{HO^{\bullet}}$) is
364 promoted using H₂O₂ and shift from 63% to 81% (Table 1).

365

366 **Table 1. Values of the apparent reaction rate constants accounting for the ozone**
 367 **decomposition (k_{app}), ozone half-life time,alachlor removal efficiency EFF_{al} after 40 min, R_{ct} , HO^\bullet**
 368 **exposure and f_{HO^\bullet} by only ozonation (non-polarized BDD electrodes, pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108$**
 369 **μ M, $C_{L,oz,0} \sim 200-280 \mu$ M).**

	With tBuOH (0.1 M)	Without tBuOH	With H_2O_2 (100 μ M)
n	1	0.8	0.8
k_{app} ($\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$)	1.81×10^{-4}	2.77×10^{-4}	3.48×10^{-4}
$t_{1/2} O_3$ (min)	42	12	6
ARE (C_{O_3})	4%	9%	16%
Eff_{al} at 40 min	43%	50-60%	48%
ARE (C_{al})	1.9%	1.9%	1.2
$10^{10} \times R_{ct}$		0.76	1.89
f_{HO^\bullet}	Negligible	63%	81%
$10^{11} \times \int_{t_0}^t C_{HO^\bullet} dt$ (M s)		1.6	1.7

370



371

372 **Fig. 4. Time-course profile of $C_{L,oz}/C_{L,oz,0}$ (a) and $C_{al}/C_{al,0}$ (b) by only ozonation (non-polarized**
 373 **BDD electrodes, pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108 \mu$ M, $C_{L,oz,0} \sim 180-280 \mu$ M). Dark symbols: triplicate**
 374 **experiments without H_2O_2 and without tBuOH. Empty circles: reference experiment with tBuOH**
 375 **(0.01 M). Empty diamond: reference experiment with H_2O_2 (100 μ M at t_0). Lines correspond to the**
 376 **model (Eqs. 1,2 and 7).**

377 3.4. Anodic oxidation

378 3.4.1 Alachlor anodic oxidation

379 Contrarily to single ozonation, anodic oxidation enabled to fully degrade alachlor but with a reaction
380 time around 150 min (Fig. 5.a). Surprisingly, the alachlor reaction rate did not depend significantly on
381 the applied current intensity. Anodic oxidation allowed to partly mineralize the alachlor parent
382 molecule, with DOC removal efficiencies in the range 50-80% after 120 min of reaction time (Fig.
383 5.b). In that case, the mineralization rate advantageously increased with the applied current
384 intensity. The alachlor and DOC degradation kinetics were both successfully modeled by a first-order
385 rate law:

$$386 \quad -\frac{dC_i}{dt} = k_{app,i}C_i \Leftrightarrow C_i = C_{i,0}e^{-k_{app,i}t} \quad (\text{Eq. 10})$$

387 The corresponding apparent reaction rate constant ($k_{app,al}$ and $k_{app,DOC}$ in s^{-1}) and half-life times
388 ($\ln(2)/k_{app,i}$) are summarized Table 2. As expected from Fig. 5.a, the alachlor half-life times are erratic
389 and in the range 23-30 min. However, the DOC half-life time significantly dropped with the current
390 intensity, shifting from 120 min at 200 mA to 54 min at 800 mA.

391 The fact that the DOC degradation followed a first-order rate law demonstrates that the
392 electrochemical reactions are diffusion controlled, meaning that alachlor and its intermediates mass-
393 transport to the anode was the rate limiting step and that the imposed current densities are always
394 higher than the limiting current density J_{lim} ($A\ m^{-2}$) [64]. Thus, the apparent reaction rate constant
395 was correlated to the DOC mass-transfer coefficient (k_m in $m\ s^{-1}$) according to Eq. 11 [64]:

$$396 \quad k_{app} = \frac{A_{BDD}k_m}{V_L} \quad (\text{Eq. 11})$$

397 With A_{BDD} the anode surface (m^2). The mass-transfer coefficients calculated have an order of
398 magnitude of $10^{-5}\ m\ s^{-1}$ (Table 2). k_m increased linearly with the current intensity (inset Fig. 5.b), a
399 behavior which has been already observed in the literature [65]. The y-intercept of k_m vs. the current

400 intensity provided the limiting value of k_m ($k_{m,lim} = 1.35 \times 10^{-5} \text{ m s}^{-1}$) in solution when the difference in
 401 potential between the electrodes is null. $k_{m,lim}$ is only slightly lower than the value of k_l of 1.94×10^{-5}
 402 m s^{-1} found for O_3 (Part 3.3.1). According to the Danckwerts theory, the ratio of the mass-transfer
 403 coefficients is proportional to the square root of the ratio of the corresponding diffusion coefficients
 404 according to Eq. 12 [7]:

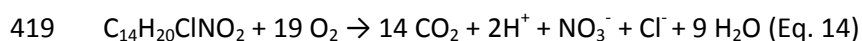
$$405 \frac{k_{m,lim}}{k_{m,oz}} = \sqrt{\frac{D_{oz}}{D_{DOC}}} \quad (\text{Eq. 12})$$

406 Considering $D_{oz} = 1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at $T = 20^\circ \text{C}$ [66], an estimation of D_{DOC} of $0.82 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ can be
 407 determined, which is consistent with the range of $0.9 - 1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ expected for low-chain fatty
 408 acids according to the Wilke-Chang correlation at 20°C [67]. Indeed, Qiang et al. demonstrated that
 409 the main by-products of alachlor oxidation are small aliphatic organic acids such as formic, acetic,
 410 oxalic and propionic acids [68]. These by-products are quite refractory to the hydroxyl radicals attack,
 411 with reaction rate constants in the range $10^6 - 8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ [69], and can be quickly accumulated
 412 in solution [3,34].

413 The knowledge of k_m enabled to determine the limit current density at t_0 ($J_{lim,0}$) over which the
 414 process is diffusion controlled [64]:

$$415 J_{lim,0} = 4Fk_m COD_0 \quad (\text{Eq. 13})$$

416 F is the Faraday's constant. COD_0 is the chemical oxygen demand at t_0 ($2.04 \text{ mmol}_{\text{O}_2} \text{ L}^{-1}$), calculated
 417 from the initial alachlor concentration and considering that alachlor total mineralization consumes 19
 418 equivalent of O_2 according to the following balanced chemical equation:

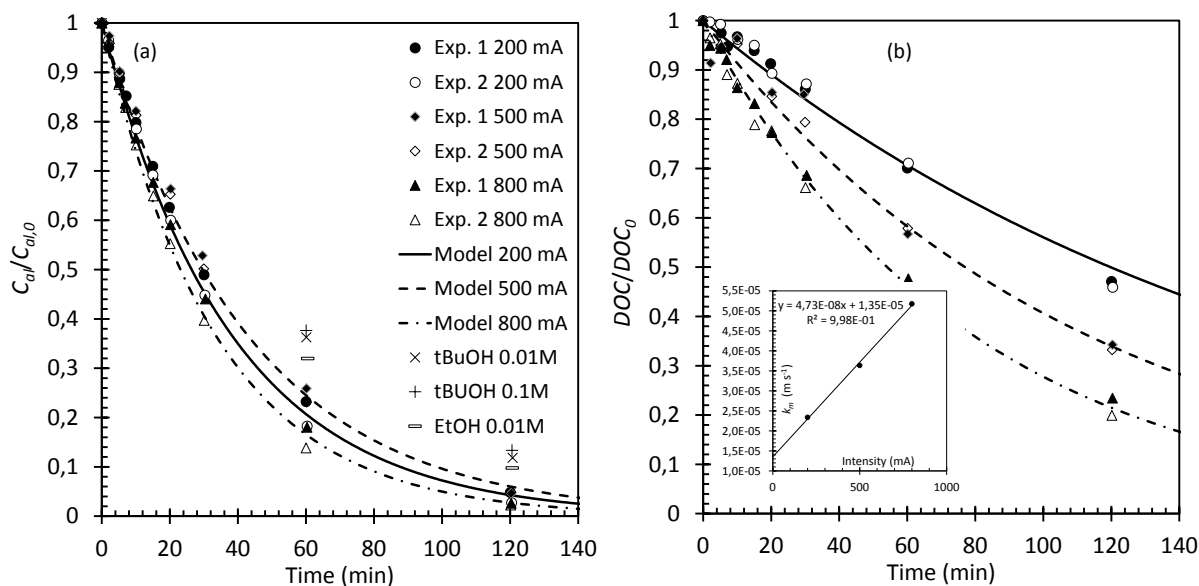


420 The ratio $J_{applied}/J_{lim,0}$ was always higher than 1 (Table 2) confirming that the electrochemical process
 421 is diffusion controlled. Finally, the current efficiency (CE) was determined by Eq. 15 [64]:

422 $CE = \frac{4FVL}{It} (COD_0 - COD_t)$ (Eq. 15)

423 With I the current intensity (A). CE slightly decreased with the reaction time t and was maximal at the
424 lower applied current intensity of 200 mA, which highlights a better tradeoff between the energy
425 consumption and the alachlor mineralization at this intensity (Fig. 6). Indeed, at such a lower
426 intensity, parasite reactions corresponding to both O_2 and N_2 degassing are less significant.

427 Finally, addition of 0.01 M and 0.1 M of tBuOH and 0.01 M ethanol as radical scavengers enables to
428 slightly slow down the alachlor degradation rate (Fig. 5.a). EtOH and tBuOH are both recognized for
429 their ability to scavenge free HO^\bullet [70,71]. Thus, it confirms that free HO^\bullet are produced during anodic
430 oxidation. However, several authors claims that tBuOH should be also able to scavenge surface
431 bounded HO^\bullet [70]. Nonetheless, according to Barazesh et al. [72], saturated alcohols such as tBuOH
432 do not react readily with electrode surfaces. Furthermore, Babu et al. showed that tBuOH can be
433 oxidized through DET using BDD anodes which can affect the conclusions of some authors that used
434 tBUOH to scavenge surface bounded HO^\bullet [71]. Consequently, it remains difficult to conclude about
435 the main mechanism of alachlor oxidation involved, which can happen through reactions with
436 surface HO^\bullet that tBuOH cannot efficiently scavenge and/or by DET at potentials outside the
437 electroactivity range of the BDD electrode.



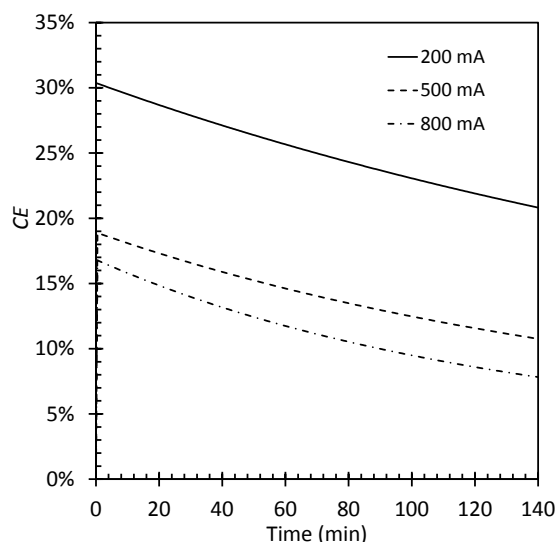
438

439 **Fig. 5. Time-course profile of $C_{al}/C_{al,0}$ (a) and DOC/DOC_0 (b) by anodic oxidation during anodic**
 440 **oxidation without ozone at different current intensity (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108$ μ M, $C_{L,oz,0} \sim 0$**
 441 **μ M). Circles: duplicate experiments at 200 mA, Diamonds: duplicate experiments at 500 mA,**
 442 **Triangles: duplicate experiments at 800 mA. Cross and rod symbols correspond to experiments at**
 443 **200 mA with addition of radical scavengers (tBuOH and EtOH). Fig. 5.b inset: Evolution of k_m vs. the**
 444 **current intensity. Straight and dash lines represent the kinetic model (Eq. 10).**

445 **Table 2. Values of the apparent first-order reaction rate constants accounting for alachlor and**
 446 **DOC oxidation (k_{app}), corresponding half-life times, values of k_m , $J_{lim,0}$ and $J_{applied}/J_{lim,0}$ during anodic**
 447 **oxidation without ozone at different current intensity (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108$ μ M, $C_{L,oz,0} \sim 0$**
 448 **μ M).**

	200 mA	500 mA	800 mA	200 mA with tBuOH
$k_{app,al}$ (s^{-1})	4.37×10^{-4}	3.90×10^{-4}	5.00×10^{-4}	2.8×10^{-4}
$t_{1/2}$ alachlore (min)	26	30	23	42
ARE (C_{al})	4%	5%	4%	4%
$k_{app,DOC}$ (s^{-1})	0.97×10^{-4}	1.50×10^{-4}	2.14×10^{-4}	Not applicable
$t_{1/2}$ DOC (min)	120	77	54	
ARE (DOC)	2%	3%	1%	
$10^5 \times k_m$ ($m s^{-1}$)	2.34	3.64	5.18	
$J_{lim,0}$ ($A m^{-2}$)	18.4	28.7	40.8	
$J_{applied}/J_{lim,0}$	3.3	5.3	5.9	

449



450

451 **Fig. 6. Evolution of the current efficiency vs. time for different current intensity during alachlor**
 452 **anodic oxidation (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108$ μ M, $C_{L,oz,0} \sim 0$ μ M).**

453 3.5. Hybrid ozonation anodic oxidation

454 The ozone concentration time-course profile for different current intensities using the hybrid process
 455 O_3/AO is represented in Fig. 7.a. The ozone consumption rate was significantly enhanced compared
 456 to the experiments with no power input (Fig. 4.a), showing that the anodic oxidation process
 457 contributes to molecular ozone consumption. This consumption can be attributed to several
 458 promotion reactions: the ozone reaction with hydroxyl radicals produced at the anode, which
 459 provides the hydroperoxyl radical HO_2^* , and/or the ozone electroreduction at the cathode which
 460 provides an ozonide radical O_3^* [45]. Local higher pH at the cathode vicinity might be also a way of
 461 enhancing ozone decomposition through the initiation reaction with HO^- . Nonetheless, a pH of ~ 9
 462 would be necessary to get a reaction rate with HO^- similar to the apparent one.

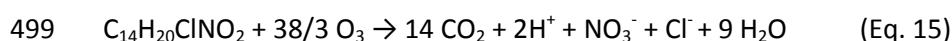
463 There was no statistical difference on the ozone consumption rate (Fig. 7.a) depending on the
 464 applied current intensity, which is in agreement with the observation already done for alachlor
 465 without ozone (Fig. 5.a). The ozone consumption rate was successfully modeled by a first-order
 466 reaction law, with an average half-life time of 4.5 min (Table 3), 2.7 times lower than the half-life
 467 time found for the reference experiment with the non-polarized electrodes (12 min).

468 The enhanced ozone depletion might result in an enhanced ROS generation, which was confirmed by
469 a quick drop of the alachlor concentration (Fig. 5.b). A first-order reaction law poorly described the
470 alachlor depletion. The best agreement was obtained with a second-order reaction law ($k_{app} \times C_{al}^2$),
471 which better described the sharp decreasing observed during the first twenty minutes when residual
472 ozone was still present in the solution. The alachlor degradation rate law was not significantly
473 influenced by the current intensity and the corresponding half-life time was around 12 min, which
474 was half the value found without ozone added to the solution (Tables 2 and 3). It shows that the
475 ozone addition can efficiently enhance the alachlor parent molecule degradation rate.

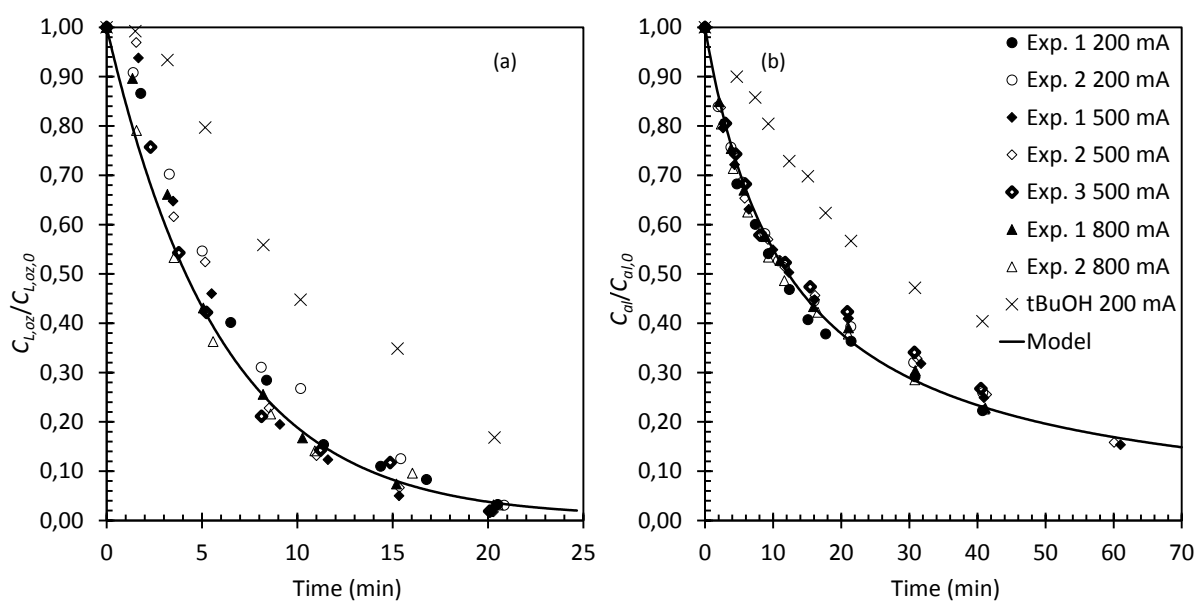
476 Addition of tBuOH as a radical scavenger allowed to slow down the ozone depletion, but with still a
477 rather fast ozone consumption rate, characterized by a half-life time around 10-11 min, whereas a
478 half-life time of 42 min was found with the non-polarized electrodes in presence of tBuOH. tBuOH
479 efficiently scavenges free HO[•] radicals in the solution [70]. Without current intensity, the ozone
480 depletion was therefore only due to reactions between molecular ozone and the parent alachlor
481 molecules and its intermediates when tBuOH was present in the solution. The faster ozone
482 consumption rate observed with the hybrid O₃/AO oxidation process in presence of tBuOH in
483 solution confirms that at least one mechanism contributes to molecular ozone consumption at the
484 anode and/or at the cathode. The alachlor consumption rate was also significantly slowed down
485 using a radical scavenger (Table 3 and Fig. 7.b). This confirms that even if molecular ozone was
486 consumed at the anode and/or the cathode, it results in the formation of free hydroxyl radicals that
487 were efficiently scavenged by tBuOH.

488 In terms of mineralization, assessed through DOC measurement between 0 and 40 min, the results
489 are more difficult to interpret (Fig. 8). The DOC depletion was well described by a first-order reaction
490 law, demonstrating the reaction is still diffusion controlled (Table 3). The mineralization rate at 200
491 mA is identical between AO alone and the hybrid process AO/O₃. However, the mineralization rate is
492 not significantly different at 500 and 800 mA and is between the rate observed at 500 and 800 mA

493 without ozone. This behavior might be due to analytical uncertainties and remains unexplained,
 494 especially because DOC concentration was only followed during a shorter reaction time of 40 min.
 495 Whatever, it shows that the ozone addition poorly influence the mineralization rate. This observation
 496 is in agreement with the fact that the ozone dose introduced (around 2 mol of O₃ per mol of alachlor)
 497 is far from the theoretical ozone consumption of 38/3 mol_{O₃} mol_{ai}⁻¹ in case of a total mineralization,
 498 according to Eq. 15 :

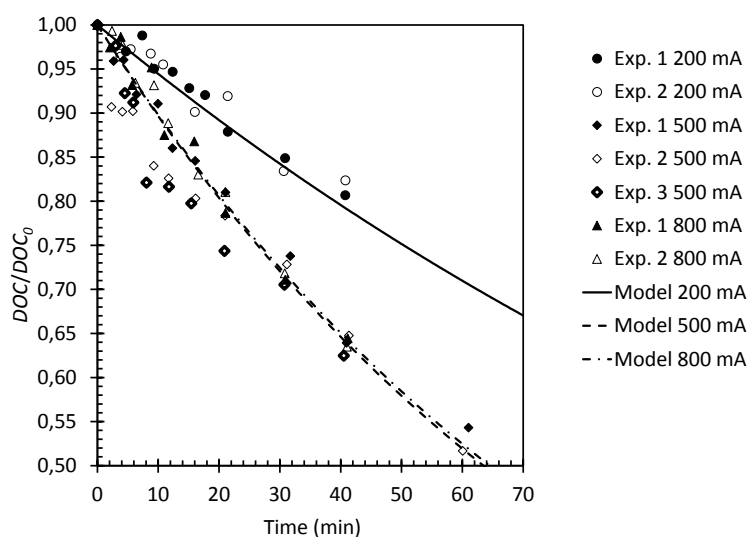


500 Consequently, ozone addition could be a potent solution to enhance the degradation of both the
 501 alachlor parent molecule and maybe the first aromatic intermediates [68], even if O₃ is quickly
 502 consumed in solution (~ 25 min). Nonetheless, low-chain aliphatic acids intermediates must quickly
 503 accumulate in solution after a few tens of minutes. These compounds are quite refractory to
 504 hydroxyl radicals oxidation as mentioned before (Part 3.4.1), and ozonation as well, and cannot end
 505 up fully mineralized by anodic oxidation [71]. They can also reduce the activity of the electrodes due
 506 to poisoning effects caused by polymer production on the electrode surface [71]. Thus, in order to
 507 increase the time window in which ozone is present in solution, pulse injection of ozone could be a
 508 pertinent solution.



509

510 **Fig. 7. Time-course profile of $C_{L,oz}/C_{L,oz,0}$ (a) and $C_{al}/C_{al,0}$ (b) by the hybrid process O_3/AO with**
 511 **various current intensity (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108 \mu\text{M}$, $C_{L,oz,0} \sim 200\text{-}250 \mu\text{M}$). Circles: duplicate**
 512 **experiments at 200 mA, Diamond: triplicate experiments at 500 mA, Triangle: duplicate**
 513 **experiments at 800 mA. Cross symbols correspond to one experiment at 200 mA with addition of a**
 514 **radical scavenger (tBuOH at 0.1 M). Models correspond to first-order (ozone) and second-order**
 515 **(alachlor) reaction laws.**



516

517 **Fig. 8. Time-course profile of DOC/DOC_0 by the hybrid process O_3/AO with various current**
 518 **intensity (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108 \mu\text{M}$, $C_{L,oz,0} \sim 200\text{-}250 \mu\text{M}$). Circles: duplicate experiments at**
 519 **200 mA, Diamond: triplicate experiments at 500 mA, Triangle: duplicate experiments at 800 mA.**
 520 **Models correspond to a first-order reaction law.**

521 **Table 3. Values of the n^{th} -order reaction rate constant accounting for ozone,alachlor and DOC**
 522 **oxidation (k_{app}) and corresponding half-life times by the hybrid process O_3/AO with various current**
 523 **intensity (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 108 \mu\text{M}$, $C_{L,oz,0} \sim 200\text{-}250 \mu\text{M}$). For DOC, the half-life time is**
 524 **replaced by the time necessary to degrade 20% ($t_{0,2}$) owing to the fact that the half-life times were**
 525 **higher than the experiment duration.**

	200 mA	500 mA	800 mA
First-order $k_{app,oz}$ (s^{-1})		2.59×10^{-3}	
$t_{1/2}$ ozone (min)		4.5	
ARE ($C_{L,oz,0}$)		12%	
n_{al}		2	
2 nd -order $k_{app,al}$ ($L \text{ mol}^{-1} s^{-1}$)		12.7	
$t_{1/2}$ alachlore (min)		12	
ARE (C_{al})		5%	
First-order $k_{app,DOC}$ (s^{-1})	0.95×10^{-4}	1.82×10^{-4}	1.79×10^{-4}
$t_{0,2}$ DOC (min)	39	20	21
ARE (DOC)	2%	4%	2%

526 3.6. Hybrid ozonation anodic oxidation with pulse injections of ozone

527 Pulse re-injections of dissolved ozone were achieved every 20 min with the hybrid process O₃/AO at
528 200 mA, leading to:

- 529 • a total ozone dose of 34 ppm (6.7 mol of ozone introduced per mol of alachlor) with two re-
530 injections of ozone (1h of exposure to ozone) for a first experiment
- 531 • a total ozone dose of 57 ppm (11.1 mol of ozone introduced per mol of alachlor) with 9 re-
532 injections of ozone (2h30 of exposure to ozone) for a second experiment.

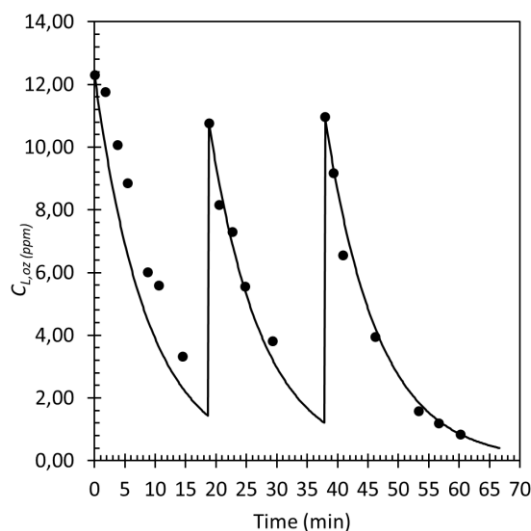
533 The volume of dissolved ozone introduced compensated the volume withdrawn for the samples. The
534 dilution induced by these reinjections were taken into account in the mass-balance to quantify DOC
535 and alachlor concentrations time-profile.

536 Fig. 9 presents the ozone concentration time-course profile for the first experiment. As expected, O₃
537 was fully consumed within 20-25 min of reaction time after each injection. The ozone concentration
538 evolution was successfully modeled by a first-order rate law, with $k_{app} = 1.92 \times 10^{-3} \text{ s}^{-1}$, in agreement
539 with the behavior observed with the single ozone injection method (part 3.5).

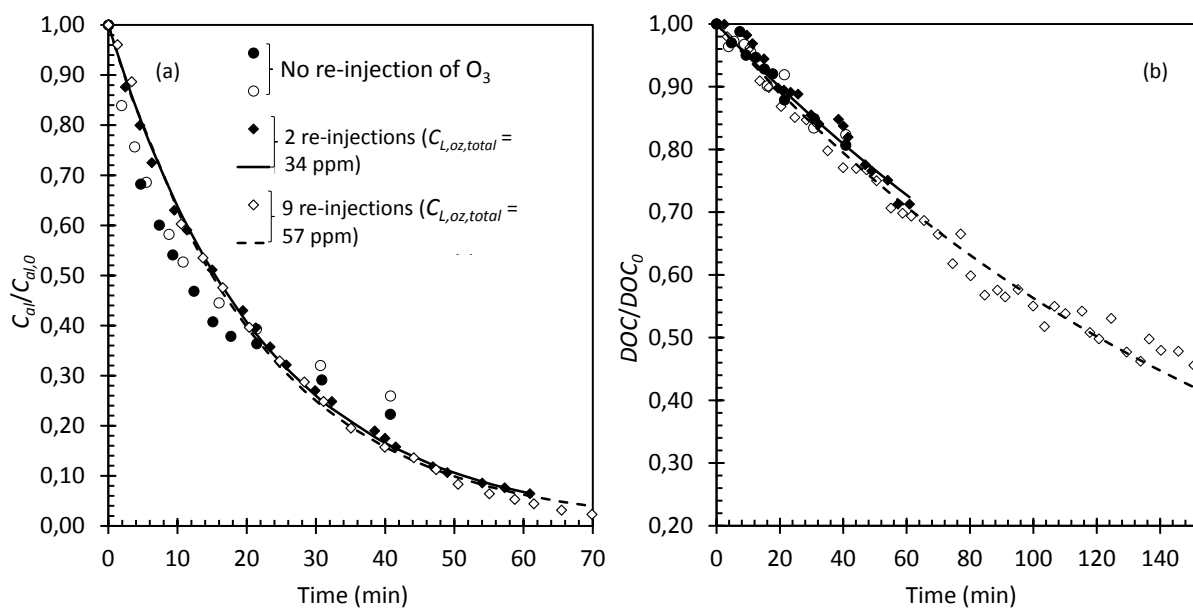
540 The prolonged exposure to dissolved ozone led to faster alachlor degradation consumption rate (Fig.
541 10.a), compared to the experiment with only one dissolved injection at t_0 (Part 3.5). The differences
542 between the pulse ozone injection method and the single ozone injection method only appears after
543 around 30 min, *i.e.* when the dissolved ozone concentration becomes negligible with the single
544 ozone injection method. The alachlor reaction rate was satisfactorily described by a first-order rate
545 law, whereas a second-order rate law was necessary with the single ozone injection method (Part
546 3.5). Thus, after a reaction time of 1h, with the hybrid process at 200 mA, an alachlor removal
547 efficiency around 94% is reached with the pulse ozone injection method (83% for the single ozone
548 injection method, 79% with only anodic oxidation). It confirms that ozone re-injections can be an

549 effective way to enhance the degradation rate of the alachlor parent molecule and probably of the
550 first aromatic intermediates, with advantageously low ozone doses involved.

551 However, the prolonged exposure to ozone had only a slight effect on DOC mineralization rate (Table
552 4 and Fig.10 b). In that case, the rate limiting steps should be the reactions of ROS with the low-chain
553 aliphatic acids [68], that are poorly reactive with hydroxyl radicals and molecular ozone [5]. To
554 confirm this assumption, a monitoring of the main by-products formed should be necessary. Other
555 mechanisms such as DET should justify the higher capacity of OA itself to mineralize these
556 compounds. Nonetheless, owing to the fact that these compounds are easily biodegradable, it do not
557 justify to use energy consuming AOPs to achieve a full mineralization of the effluent. More
558 particularly, prolonged exposure to ozone is not necessary anymore after the breakage of the
559 aromatic structures of the parent and intermediates molecules. Furthermore, DOC mineralization by
560 the hybrid process with pulse ozone injection should be assessed with more realistic water matrixes,
561 containing EfOM and having different pH.



562
563 **Fig. 9. Time-course profile of $C_{L,oz}$ by the hybrid process with pulse injections of dissolved ozone**
564 **(pH 5, $V_L = 800$ mL, $C_{al,0} \sim 110$ μ M, $C_{L,oz,total} \sim 709$ μ M, Intensity = 200 mA). The model corresponds to**
565 **a first-order reaction law with $k_{app} = 1.92 \times 10^{-3} \text{ s}^{-1}$.**



566

567 **Fig. 10. Time-course profile of $C_{al}/C_{al,0}$ (a) and DOC/DOC_0 (b) by the hybrid process with pulse**
 568 **injections of dissolved ozone (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 110$ μ M, Intensity = 200 mA). Circles:**
 569 **Experiments with no ozone re-injection; dark diamonds: experiment with two ozone re-injections**
 570 **($C_{L,oz,total} \sim 709$ μ M, 60 min of ozone exposure) and empty diamonds: experiment with nine ozone re-**
 571 **injections ($C_{L,oz,total} \sim 1.18$ mM, 2h30 of ozone exposure). The models correspond to first-order**
 572 **reaction laws.**

573 **Table 4. Values of the first-order reaction rate constant accounting for alachlor and DOC**
 574 **oxidation (k_{app}) and corresponding half-life times by the hybrid process O_3/AO with pulse injections**
 575 **of dissolved ozone (pH 5, $V_L = 800$ mL, $C_{al,0} \sim 110$ μ M, Intensity = 200 mA).**

	2 re-injections	9 re-injections
$C_{L,oz,total}$ (mM)	0.709	1.18
First-order $k_{app,al}$ (s^{-1})	7.49×10^{-4}	7.71×10^{-4}
$t_{1/2}$ alachlore (min)	15	15
ARE (C_{al})	3%	6%
First-order $k_{app,DOC}$ (s^{-1})	8.84×10^{-5}	9.57×10^{-5}
$t_{1/2}DOC$ (min)	131	121
ARE (DOC)	2%	3%

576

577

578 **3.7. Diphasic vs monophasic hybrid O₃/AO process; what should be used?**

579 **Table 5. Comparison of the monophasic and diphasic hybrid O₃/AO processes.**

	Monophasic configuration	Diphasic configuration
Advantages	<ul style="list-style-type: none"> • Perfect control of the ozone dose and easy optimization of the ozone transfer in a dedicated gaz-liquid contactor • Reactions mainly located in the liquid bulk and at the electrodes surface • Multiple points injection in flow-by or flow-through electrochemical reactors is feasible • Pulse injections or continuous ozone stock solution delivery are both possible in batch electrochemical reactors 	<ul style="list-style-type: none"> • Easier implementation in batch electrochemical reactors • Ozone-enriched bubbles can improve solute mass-transfer in the gas-liquid electrochemical reactor • High ozone doses can be easily implemented
Drawbacks	<ul style="list-style-type: none"> • High ozone dose hardly achievable • Needs of an additional water resource to prepare the ozone-stock solution (but a fraction of the treated water can be devoted to this) • Needs of an additional gas-liquid contactor 	<ul style="list-style-type: none"> • The control of the ozone dose applied is more difficult owing to the fact that the ozone transfer and ozone reactions steps are interdependent • A significant part or the totality of the ozone transferred can react at the gas-liquid interface • The ozone transfer can be hardly optimized

580

581 Parts 3.5 and 3.6 clearly emphasized the pros and cons of the hybrid process O₃/AO. It is noteworthy

582 that an even more enhanced ozone decomposition at the electrode surface might be possible using

583 flow-by or flow-through electrochemical reactors, which are characterized by higher mass-transfer

584 coefficients than conventional agitated electrochemical reactors. These kinds of electrochemical

585 reactors can be easily upgraded for the monophasic configuration of the O₃/AO hybrid process with

586 single or multiple points ozone-stock solution injection. A techno-economical assessment would be

587 pertinent to compare the performances, the energy consumption and the operating and capital

588 expenses of such hybrid processes. Part S.5 in the supplementary material presents some preliminary

589 results regarding these aspects, through the calculation of the Oxygen-equivalent Chemical Oxidation

590 Capacity (OCC), of the Specific Energy Consumption per DOC unit and of the synergy index.

591 Nonetheless, for a full techno-economical assessment, more robust data gathered with realistic

592 industrial wastewaters would be necessary.

593 Table 5 summarizes the main advantages and drawbacks associated to the monophasic and diphasic
594 (use of ozone-enriched gas bubbles) hybrid O₃/AO processes. The superior control of the ozone
595 transfer dose and ozone transfer yield in solution is undoubtedly a salient advantage of the
596 monophasic configuration, allowing to decrease the energy requirement and the operating costs
597 associated to the ozone generation step. Indeed, one of the most challenging issue associated to the
598 use of ozone is the maximization of the ozone transfer yield, which requires a sufficient gas residence
599 time and if possible a low liquid volume (or low liquid flow rate in continuous) owing to the low
600 ozone solubility in water. This constraint can be more easily overcome in a dedicated gas-liquid
601 contactor (agitated vessel, bubble column, static mixer, etc.) than in an electrochemical reactor. In
602 order to maximize the dissolved ozone concentration produced, at a given ozone generator power, a
603 low oxygen flow rate and a large produced ozone concentration should be selected.

604 Another drawback of the diphasic configuration is that ozone transfer directly in the electrochemical
605 reactor might result in a less efficient ROS generation in the liquid bulk. Indeed, depending on the
606 ozone instantaneous ozone demand and on the ozone decomposition rate, a high ozone reaction
607 rate at the gas-liquid interface (fast kinetic regime) is possible [7], which can lead to a poor or even a
608 negligible ozone diffusion in the liquid bulk and at the electrodes surface.

609 The main drawbacks of the monophasic configuration are that supplementary gas-liquid contactor
610 and water resource are necessary for the preparation of the ozone-stock solution. One pertinent
611 solution would be to assess if a fraction of the treated water can be by-passed in the gas-liquid
612 contactor to achieve this operation.

613 5. Conclusion

614 This prospective study investigates the efficiency of a hybrid process that combines ozonation and
615 anodic oxidation (AO/O₃) with two boron-doped diamond (BDD) electrodes to treat a model aqueous
616 solution containing 30 ppm of alachlor at pH 5 in a phosphate buffer. An innovative monophasic
617 configuration, in which an ozone-stock solution was injected at t_0 in the batch electrochemical
618 reactor, was proposed in order to avoid the introduction of ozone-enriched gas bubbles.

619 The results reveal that, even within an acidic water matrix, dissolved ozone injected during the
620 ozonation process was decomposed into hydroxyl radicals allowing to partly degrade alachlor parent
621 molecule but without its mineralization. With the selected water matrix, the hydroxyl radical
622 exposure was particularly low with a R_{ct} value lower than 10^{-10} . The combination of both
623 conventional ozonation and AO processes significantly enhances ozone depletion regardless of the
624 applied current density, resulting in a half-life 2.7 times shorter than the ozonation process alone.
625 This faster ozone decomposition might be related to (i) the ozone oxidation at the anode surface by
626 OH[•] and/or (ii) to its reduction by the cathode and/or (iii) to its reaction with the electrogenerated
627 hydrogen peroxide, in addition to its decomposition in the bulk. Furthermore, the faster ozone
628 decomposition was concomitant with a higher ROS species generation, which leads to a faster
629 alachlor decomposition, with a half-life twice as low than with AO alone. Thus, this hybrid process is
630 part of the process intensification approach, increasing the operational window for processes use
631 and reducing reaction times.

632 Regarding alachlor mineralization, increasing the current intensity from 200 mA to 800 mA during the
633 AO process over 120 minutes leads to a rise in alachlor mineralization efficiency from 50 to 80%.
634 However, the introduction of the hybrid process shows a similar mineralization rate as for AO alone.
635 In this case, the limitation could be attributed to the production of refractory biodegradable
636 compounds, such as small aliphatic intermediates (fatty acids), considered to be poorly reactive with
637 hydroxyl radicals and molecular ozone. Moreover, using a pulse injection of ozone every 20 minutes

638 to extend exposure times and raise the total ozone dose demonstrates only a slight improvement in
639 alachlor mineralization but enhanced the alachlor degradation after the second injection. Thus, the
640 hybrid monophasic AO/O₃ process with a low ozone dose (single ozone injection or a few ozone pulse
641 reinjections) could be sufficient to improve alachlor decomposition into probably more
642 biodegradable compounds that might be more easily removed by a further biological treatment.
643 Nevertheless, further investigation is needed for the identification of the by-products generated.
644 Additionally, using a more realistic water composition containing EfOM, exploring multiple points
645 injection in flow-by or flow-through electrochemical reactors and assessing the feasibility of
646 employing the treated water as a resource for producing stock-ozone solution should be considered.

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653

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