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

Helios YASMINE<sup>a</sup>, Florence FOURCADE<sup>a</sup>, Fares ZOUAOUI<sup>a</sup>, Pierre-François BIARD<sup>a\*</sup>

4 <sup>a</sup>Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 5 Rennes, France

6 \*corresponding author: Pierre-François BIARD, pierre-francois.biard@ensc-rennes.fr

#### Abstract 7

This prospective study assessed a hybrid process that combines ozonation with anodic oxidation 8 9  $(AO/O_3)$  with two boron-doped diamond (BDD) electrodes to treat a model aqueous solution 10 containing 30 ppm of alachlor at pH 5 in a phosphate buffer. An innovative monophasic 11 configuration, operated batch-wise, in which an ozone-stock solution was injected at  $t_0$  in the 12 electrochemical reactor, was proposed in order to avoid introduction of ozone-enriched gas bubbles. 13 The alachlor parent molecule was almost entirely degraded within around 150 min of reaction time 14 by anodic oxidation alone, whatever the applied current intensity (200, 500 and 800 mA). The 15 mineralization efficiency varied from 50% at 200 mA to 80% at 800 mA after 120 min. The results 16 emphasized that the anodic oxidation was a diffusion-controlled process. Addition of ozone at a low 17 ozone dose of 1.9-2.3 mol of ozone per mol of alachlor allowed to decrease the ozone half-life time 2.7 times with the hybrid process compared to ozonation alone. This faster ozone consumption was 18 19 concomitant with an enhanced alachlor degradation rate, with a corresponding half-life time around 20 two-times lower. However, owing to the low ozone dose applied and the short ozone lifetime in solution (around 25-30 min), similar mineralization efficiencies were noticed for both AO/O<sub>3</sub> and AO 21 22 processes. Thus, the application of pulse ozone-stock solution re-injections every 20 min to prolong 23 the ozone exposure was assessed to overcome this limitation. However, the effect on the 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

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

#### Graphical abstract



#### Nomenclature

40 AO: anodic oxidation

- 41 AOP: advanced oxidation process
- 42  $A_{BDD}$ : BDD anode surface (33 cm<sup>2</sup>)
- 43 ARE: average relative error (-)
- 44 BDD: boron-doped diamond
- 45  $C_i$ : concentration of any species (mol L<sup>-1</sup> or mol m<sup>-3</sup>)
- 46 *COD*: chemical oxygen demand ( $mol_{0_2} L^{-1}$ )
- 47 CE: current efficiency (-)
- 48  $D_i$ : diffusion coefficient of any species i (m<sup>2</sup> s<sup>-1</sup>)
- 49 DET: direct electron transfer
- 50 DOC: dissolved organic carbon (ppm)
- 51 *Eff*: removal efficiency (-)
- 52 EfOM: effluent organic matter
- 53  $f_{HO}$ : fraction of hydroxyl radicals reacting with alachlor (-)
- 54 *H*: ozone Henry's law constant (Pa  $m^3 mol^{-1}$ )
- 55 *I*: current intensity (A)
- 56 J: current density (A  $m^{-2}$  or mA cm<sup>-2</sup>)
- 57 k: reaction rate constant (mol<sup>1-n</sup> L<sup>n-1</sup> s<sup>-1</sup>)

- 58  $k_m$  and  $k_L$ : mass-transfer coefficient in the liquid phase for COD and O<sub>3</sub>, respectively (m s<sup>-1</sup>)
- 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<sup>2</sup>)
- 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<sub>2</sub>O<sub>2</sub>: 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*<sub>0</sub>

#### 76 **1. Introduction**

Industrial wastewaters treatment needs nowadays technologies, such as ozone-based or electrochemical advanced oxidation processes (AOPs), able to reach extensive mineralization of the organic pollutants. Table S.1 presents the main mature or in development processes to remove organic pollutants from wastewaters. One strategy to improve refractory compounds removal is to 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), especially hydroxyl radicals HO<sup>•</sup>, generated from the spontaneous ozone decomposition in water 86 [4,6,7]. In natural waters (ground water, surface water, etc.) and waste waters, the ozone 87 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<sub>2</sub>O<sub>2</sub>) or physical (UV, 93 US) initiators can be also added in ozone-based AOPs [7].
- More recently, several authors investigated the potential of hybrid ozone/electrochemical processes. Electrochemical processes are recognized as versatile, easily automable and are operated in mild conditions [10–14]. There are several ways to combine ozonation and electrochemical processes [10,15–20]. Among them, the most studied are i) the electrochemical production of ozone [16,21,22], ii) the electroperoxone process [23–28] and iii) the combination between anodic oxidation and 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].

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

organic pollutants can be directly oxidized or reduced through the exchange of electrons with the electrode surface. This mechanism is called direct electron transfer (DET). Besides, pollutants can also be oxidized by an indirect oxidation process through the *in-situ* generation of various oxidants, particularly HO<sup>•</sup> radicals produced at the anode surface through the oxidation of H<sub>2</sub>O [35,36]. The efficiency of the AO process and the nature and amount of reactive species formed can be affected by various factors, including the material of the electrode, the type of contaminant, the type of 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,  $O_3$  degradation preferably leads to short chain aldehydes and carboxylic acids, non-reactive 118 with O<sub>3</sub> 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  $O_3$  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 formation at the electrodes surface would be also potentially mitigated by the use of ozone. 127

Thus, the removal of various persistent organic pollutants by hybrid anodic oxidation/ozonation (OA/O<sub>3</sub>) processes was studied in aqueous solution [20,23,40,41] and in sludge from wastewater treatment plant [42]. Compared to sole electrooxidation, higher and faster removal yields were 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].  $Ti/PbO_2$  anodes are also pertinent candidates because, as for the BDD, the overpotential for  $O_2$ 134 evolution is high [40]. The applied current densities were at the same order of magnitude as for the 135 electroperoxone process, from around 10 to 60 mA cm<sup>-2</sup> [20,23,40-42]. Only a few papers 136 investigated the influence of the pH even if it strongly influences the O<sub>3</sub> decomposition [20,40]. Qiu 137 et al. assessed the influence of the nature and the concentration of the supporting electrolyte [45]. In 138 139 Na<sub>2</sub>SO<sub>4</sub> electrolyte, the mineralization increased with the concentration and the formation of sulfate radicals was supposed. In NaCl electrolyte, the formation of active chlorine species improved the 140 141 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 anode. They also concluded that, in their study, the  $O_3$  reduction at the cathode played only a minor role on the p-nitrophenol degradation [45].

145 In the majority of the hybrid  $OA/O_3$  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, instead of using ozone-enriched gas bubbles, has been demonstrated [47,48]. It requires to 153 154 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<sup>•</sup> 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 Na<sub>2</sub>SO<sub>4</sub> and NaCl electrolytes, allowing to avoid the formation of chlorine and sulfate radical reactive species, in order 164 165 to focus only on the mechanisms associated to ROS generation and DET.

#### 166 2. Material and methods







Figure 1: Scheme of the experimental procedure.

170 A module, already described elsewhere [49], allowed to produce an ozone-enriched oxygen flow (at a concentration in the range 180-200 g Nm<sup>-3</sup> and a flow rate of 15 NL h<sup>-1</sup>, under the normal 171 conditions for temperature and pressure). The ozone/oxygen mixture was continuously bubbled in a 172 173 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 water (UPW) acidified at pH 2 through the addition of 3.75 mL of  $H_2SO_4$  at 1 M, in order to 175 completely suppress ozone decomposition. After ~ 30 min, the gas-liquid equilibrium was reached 176 177 within the bubble column at a dissolved ozone concentration around 100 ppm.

In parallel, 700 mL of the studied aqueous solution (ultra-pure water doped with alachlor and a phosphate buffer to set a pH ~ 5) was introduced in a custom magnetically stirred glass reactor containing 2 BDD grid electrodes ( $50 \times 50 \times 1.4$  mm corresponding to a surface of 33 cm<sup>2</sup>) connected to a DC power supply unit (Microlab, provided by Micronics-System) by Platinum wires. The electrodes, provided by NeoCoat SA (Switzerland), were composed of 6 µm Boron-Doped Diamond deposited on a niobium substrate (Nb doped with 2500 ppm of boron). The interlectrode distance was set at 1.5 cm. Three current intensity were assessed, 200, 500 and 800 mA, corresponding to
current densities *J* of 6.1, 15.2 and 24.2 mA cm<sup>-2</sup>, respectively. A sampling port equipped with a LuerLock valve, located at the bottom of the electrochemical reactor, allowed to introduce and
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 initial alachlor concentration around 30 ppm (corresponding to a DOC concentration of ~ 19 ppm), a 191 phosphate buffer concentration of 50 mM and a conductivity of 4.52 mS cm<sup>-1</sup> at 20 °C. The initial 192 193 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.

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

#### 204 2.2. Analytical methods

Alachlor quantification was achieved with a Waters Acquity UPLC H-Class Plus chromatographic chain equipped with a Waters PDA  $e\lambda$  (Photodiode Array Detector) and a Waters quaternary solvent manager. The separation was performed on a column Acquity UPLC BEH C-18 (1.7  $\mu$ m; 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 measurement, performed a few minutes after the sampling ( $\lambda$  = 600 nm). The H<sub>2</sub>O<sub>2</sub> concentration 212 213 was determined through the potentiometric titration of  $I_2$ , generated by the oxidation of KI by  $H_2O_2$ , 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 voltamogramms were recorded to examine the electrochemical behavior of alachlor on the BDD electrodes at a scan rate of 100 mV s<sup>-1</sup> in a 50 mM H<sub>3</sub>PO<sub>4</sub> aqueous solution. Current-potential 219 220 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 signal appeared for alachlor on the BDD electrode in the electroactivity range of the supporting 223 224 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 a glassy carbon electrode at -1.25 V vs. SCE [51]. 228



230 231

# Figure 2. Cyclic voltammograms in 50 mM $H_3PO_4$ with and without 30 ppm alachlor using BDD electrodes.

232

#### 3.2 H<sub>2</sub>O<sub>2</sub> electrochemical generation

233 The combined use of ozone/hydrogen peroxide  $(O_3/H_2O_2)$  accelerates the conversion of  $O_3$  to HO<sup>•</sup>, 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  $H_2O_2$  to enhance  $O_3$  decomposition 236 efficiency. Anodic oxidation generally induces the production of H<sub>2</sub>O<sub>2</sub> at the cathode. In the light of 237 this, the production of  $H_2O_2$  in function of the electrolysis duration and the current density (50, 100 238 and 500 mA) is presented in Fig. 3.  $H_2O_2$  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  $H_2O_2$  remains almost constant, indicating the establishment of an 241 equilibrium between the cathodic production of  $H_2O_2$  and its anodic oxidation. For low current 242 intensities, the production of  $H_2O_2$  increased with the applied current intensity. However, for 500 mA, the production of  $H_2O_2$  is lower than for 50 and 100 mA. This behavior can be explained owing to 243 244 the fact that for high current intensities, hydrogen evolution and 4 electrons reduction of  $O_2$  into  $H_2O$ 245 compete with H<sub>2</sub>O<sub>2</sub> formation. According to the state of the art, a similar behavior has been observed 246 with a graphite cathode [53].



Figure 3.  $H_2O_2$  concentration evolution in function of the electrolysis duration for different current intensities (50, 100 and 500 mA) using BDD electrodes in 800 mL  $H_3PO_4$  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 H<sub>2</sub>SO<sub>4</sub> addition and containing tBuOH (0.005 M) as radical 255 scavenger in order to prevent ozone decomposition [4]. Experiments were performed with or without the non-polarized BDD electrodes. Around 20% of the ozone dose introduced at  $t_0$  was 256 257 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 determine by numerical resolution the average value of the ozone liquid-side mass-transfer 260 coefficient  $k_L$  ( $k_L = 1.94 \times 10^{-5}$  m s<sup>-1</sup>) at  $T = 19 \pm 1^{\circ}$ C. This value is in good agreement with the value of 261 1.19×10<sup>-5</sup> m s<sup>-1</sup> found for ozone in a stirred-cell reactor agitated by a Rushton turbine at 20°C [49]. 262

263

#### 3.3.2 kinetic modeling

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

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

With  $k_{app}$  (mol<sup>1-n</sup> L<sup>n-1</sup> s<sup>-1</sup>) the apparent ozone decomposition reaction rate constant and *n* the order of reaction. *S* is the surface area between the liquid-phase and the gas-phase, corresponding to the electrochemical reactor section (7.76×10<sup>-3</sup> m<sup>2</sup>).  $V_L$  is the liquid volume (m<sup>3</sup>). *H* (Pa m<sup>3</sup> mol<sup>-1</sup>) is the 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 
$$\frac{k_L S}{V_L} \left( C_{L,oz} - \frac{RT}{H} C_{G,oz} \right) = \frac{dC_{G,oz}}{dt} V_G \qquad \text{(Eq. 2)}$$

The best values of *n* and  $k_{app}$  associated to each experiment were determined by numerical resolution following the procedure presented in supplementary material (Part S.3). The knowledge of these parameters allowed for each experiments to model  $C_{L,oz}$  vs time and to determine both the 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 
$$t_{1/2} = C_{L,oz,0}^{1-n} \frac{(2^{n-1}-1)}{k_{app}(n-1)}$$
 if  $n \neq 1$  and  $t_{1/2} = \frac{\ln(2)}{k_{app}}$  if  $n = 1$  (Eq. 3)

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

#### 280 With *m* the number of time-interval $\Delta t$ (fixed to 12 s).

The alachlor degradation rate can be modeled according to Eq. 5 considering bimolecular reactions with both HO<sup>•</sup> and  $O_3$  [56]:

283 
$$-\frac{dC_{al}}{dt} = k_{O_3}C_{L,OZ}C_{al} + k_{HO} \cdot C_{HO} \cdot C_{al}$$
(Eq. 5)

With  $k_{O_3}$  the reaction rate constant between O<sub>3</sub> and alachlor and  $k_{HO}$  the reaction rate constant between HO<sup>•</sup> and alachlor, presumed equal at 2.8 ± 0.3 L mol<sup>-1</sup> s<sup>-1</sup> and 3.2×10<sup>10</sup> L mol<sup>-1</sup> s<sup>-1</sup>, respectively, according to Beltran et al. [56]. Thus, Eq. 5 can be rearranged leading to Eq. 6:

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

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

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

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

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

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

**301 3.3.3 Alachlor degradation by ozonation** 

Alachlor oxidation by only ozone was assessed in the electrochemical reactor with the non-polarized BDD electrodes at low ozone doses in the range 0.4-0.6  $g_{0_3} g_{DOC}^{-1}$  (~ 2-2.5 mol<sub>03</sub> mol<sub>al</sub><sup>-1</sup>). The timecourse profiles of both the ozone and alachlor concentrations are provided in Fig. 4. No mineralization was observed (Fig. S.4) with a constant DOC concentration over time, which is consistent with the low ozone doses applied.

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

which involve directly the alachlor parent molecule and/or some of its intermediates. The R<sub>ct</sub> value of 314  $0.76 \times 10^{-10}$ , is two to three orders of magnitude lower than in natural and waste waters [5,57], which 315 316 emphasizes a low potential of HO<sup>•</sup> 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 of alachlor reacting with HO<sup>•</sup> ( $f_{HO}$ •) of 63% was determined (Eq. 8), showing that both the direct 318 (involving molecular ozone) and indirect (involving free hydroxyl radicals) pathways were 319 320 concomitant. In natural and waste waters in which organic matters would be present, higher R<sub>ct</sub> 321 would be expected and a complete oxidation by HO<sup>•</sup> 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<sub>ct</sub> 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<sub>3</sub> 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<sub>3</sub> consumed per mol of alachlor consumed. The alachlor concentration-time profile was modeled by Eq. 7, and the alachlor consumption was too sharp using the value of  $k_{O_3}$  proposed by Beltran et al. 333 334 [56], with an average relative error (ARE) of 26% between the experimental and modeled values of  $C_{al}$ . Thus, the value of  $k_{O_3}$  was recalculated by numerical resolution using Eq. 7 and an alternative 335 lower value of 1.39 L mol<sup>-1</sup> s<sup>-1</sup> was determined, associated to an ARE for  $C_{al}$  of only 1.9%. 336

Furthermore, a reference experiment with an initial concentration 100  $\mu$ M of H<sub>2</sub>O<sub>2</sub> allowed to simulate the potential influence of the H<sub>2</sub>O<sub>2</sub> electrogeneration (See Part 3.2). An enhancement of the

ozone decomposition reaction rate, with an ozone half-life time of only 6 min, was observed (Table 1 and Fig. 4.a). The ozone decomposition rate linked to the ozone decomposition by the hydroperoxyde anion can be estimated through the calculation of the product of the reaction rate constant  $k_{O_3/HO_2^-}$  with the HO<sub>2</sub><sup>-</sup> concentration ( $k_{O_3/HO_2^-} \times C_{HO_2^-}$ ), taking into account a maximal total H<sub>2</sub>O<sub>2</sub> concentration ( $C_{H_2O_2}$ ) of 100 µM and a *pKa* (H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup>) of 11.75 according to Eq. 9 [58]:

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

345 Thus, the ozone decomposition rate linked to the ozone decomposition by the hydroperoxyde  $(k_{O_3/HO_2}-C_{HO_2}-C_{L,oz})$  is around 50 times lower than the apparent ozone decomposition rate 346 347  $(k_{app}C_{L,oz}^{0.8})$  considering an average ozone concentration of 100  $\mu$ M. It shows that the potential H<sub>2</sub>O<sub>2</sub> electrogeneration would contribute poorly directly to the ozone decomposition initiation in the liquid 348 349 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<sub>2</sub>O<sub>2</sub> can react with HO<sup>•</sup> leading to the hydroperoxyl radical  $HO_2^{\bullet}$ , which is in equilibrium with the superoxide radical  $O_2^{\bullet}$  that reacts further 351 with  $O_3$  leading to the ozonide radical  $O_3^{\bullet}$  ensuing the radical chain [59–62]. Thus, the  $R_{ct}$  value was 352 353 around twice with  $H_2O_2$  (Table 1). Yong and Lin demonstrated that the  $R_{ct}$  corresponds to the ratio of the total initiation capacity to the total inhibition capacity of a water matrix [63]. Considering that 354 355 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 of the faster ozone decomposition, the final hydroxyl radical exposure  $(\int_{t_0}^t C_{HO} \cdot dt)$  and ensuing 360 361 alachlor final removal efficiencies were similar with/without H<sub>2</sub>O<sub>2</sub> (Table 1). It confirms that addition 362 of H<sub>2</sub>O<sub>2</sub> 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<sup>•</sup> ( $f_{HO•}$ ) is
- 364 promoted using  $H_2O_2$  and shift from 63% to 81% (Table 1).

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<sub>al</sub> after 40 min,  $R_{cb}$  HO<sup>•</sup> exposure and  $f_{H0}^{\circ}$  by only ozonation (non-polarized BDD electrodes, pH 5,  $V_L$  = 800 mL,  $C_{al,0} \sim 108$ 368 369

	With tBuOH (0.1 M)	Without tBuOH	With $H_2O_2$ (100 $\mu$ M)
n	1	0.8	0.8
<i>k<sub>app</sub></i> (mol <sup>1-n</sup> L <sup>n-1</sup> s <sup>-1</sup> )	$1.81 \times 10^{-4}$	2.77×10 <sup>-4</sup>	$3.48 \times 10^{-4}$
<i>t<sub>1/2</sub></i> O <sub>3</sub> (min)	42	12	6
ARE ( <i>C<sub>03</sub></i> )	4%	9%	16%
<i>Eff<sub>al</sub></i> at 40 min	43%	50-60%	48%
ARE (Cal)	1.9%	1.9%	1.2
$10^{10} \times R_{ct}$		0.76	1.89
f <sub>нo</sub> •	Negligible	63%	81%
$10^{11} \times \int_{t_0}^t C_{HO} dt (M s)$	2.0	1.6	1.7

μM, C<sub>L.oz.0</sub> ~ 200-280 μM).

37	0
----	---



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 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 373 experiments without H<sub>2</sub>O<sub>2</sub> and without tBuOH. Empty circles: reference experiment with tBuOH 374 375 (0.01 M). Empty diamond: reference experiment with  $H_2O_2$  (100  $\mu$ M at  $t_0$ ). Lines correspond to the model (Eqs. 1,2 and 7). 376

#### 377 **3.4. Anodic oxidation**

378

#### 3.4.1 Alachlor anodic oxidation

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

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

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

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

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

With  $A_{BDD}$  the anode surface (m<sup>2</sup>). The mass-transfer coefficients calculated have an order of magnitude of 10<sup>-5</sup> m s<sup>-1</sup> (Table 2).  $k_m$  increased linearly with the current intensity (inset Fig. 5.b), a 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  $k_m$  ( $k_{m,lim} = 1.35 \times 10^{-5}$  m s<sup>-1</sup>) 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  $1.94 \times 10^{-5}$ 402 m s<sup>-1</sup> found for O<sub>3</sub> (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 
$$\frac{k_{m,lim}}{k_{m,oz}} = \sqrt{\frac{D_{oz}}{D_{Doc}}}$$
 (Eq. 12)

406 Considering  $D_{oz} = 1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at T = 20 °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  $10^6 - 8 \times 10^8 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$  [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 
$$J_{lim,0} = 4Fk_m COD_0$$
 (Eq. 13)

416 *F* is the Faraday's constant.  $COD_0$  is the chemical oxygen demand at  $t_0$  (2.04 mmol<sub>02</sub> L<sup>-1</sup>), calculated 417 from the initial alachlor concentration and considering that alachlor total mineralization consumes 19 418 equivalent of O<sub>2</sub> according to the following balanced chemical equation:

419  $C_{14}H_{20}CINO_2 + 19O_2 \rightarrow 14CO_2 + 2H^+ + NO_3^- + CI^- + 9H_2O$  (Eq. 14)

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

With *I* the current intensity (A). CE slightly decreased with the reaction time *t* and was maximal at the lower applied current intensity of 200 mA, which highlights a better tradeoff between the energy consumption and the alachlor mineralization at this intensity (Fig. 6). Indeed, at such a lower 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<sup>•</sup> [70,71]. Thus, it confirms that free HO<sup>•</sup> are produced during anodic oxidation. However, several authors claims that tBuOH should be also able to scavenge surface 430 431 bounded HO<sup>•</sup> [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<sup>•</sup> [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<sup>•</sup> that tBuOH cannot efficiently scavenge and/or by DET at potentials outside the 437 electroactivity range of the BDD electrode.



Fig. 5. Time-course profile of  $C_{al}/C_{al,0}$  (a) and DOC/DOC<sub>0</sub> (b) by anodic oxidation during anodic 439 440 oxidation without ozone at different current intensity (pH 5,  $V_L$  = 800 mL,  $C_{al,0} \sim 108 \mu$ M,  $C_{L,oz,0} \sim 0$ 441 μM). 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 200 mA with addition of radical scavengers (tBuOH and EtOH). Fig. 5.b inset: Evolution of  $k_m$  vs. the 443 current intensity. Straight and dash lines represent the kinetic model (Eq. 10). 444 445 Table 2. Values of the apparent first-order reaction rate constants accounting for alachlor and

DOC oxidation  $(k_{app})$ , corresponding half-life times, values of  $k_m$ ,  $J_{lim,0}$  and  $J_{applied}/J_{lim,0}$  during anodic 446 oxidation without ozone at different current intensity (pH 5,  $V_L$  = 800 mL,  $C_{al,0} \sim 108 \mu$ M,  $C_{L,oz,0} \sim 0$ 447 448

μM).

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



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,  $C_{al,0} \sim 108 \mu$ M,  $C_{L,oz,0} \sim 0 \mu$ M).

#### 453 **3.5. Hybrid ozonation anodic oxidation**

450

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<sub>2</sub>, 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<sup>-</sup>. Nonetheless, a pH of ~ 9 462 would be necessary to get a reaction rate with HO<sup>-</sup> similar to the apparent one.

There was no statistical difference on the ozone consumption rate (Fig. 7.a) depending on the applied current intensity, which is in agreement with the observation already done for alachlor without ozone (Fig. 5.a). The ozone consumption rate was successfully modeled by a first-order reaction law, with an average half-life time of 4.5 min (Table 3), 2.7 times lower than the half-life 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 alachlor depletion. The best agreement was obtained with a second-order reaction law  $(k_{app} \times C_{al}^{2})$ , 470 which better described the sharp decreasing observed during the first twenty minutes when residual 471 472 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<sup>•</sup> 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 O<sub>3</sub>/AO oxidation process in presence of tBuOH in 483 solution confirms that at least one mechanism contributes to molecular ozone consumption at the anode and/or at the cathode. The alachlor consumption rate was also significantly slowed down 484 485 using a radical scavenger (Table 3 and Fig. 7.b). This confirms that even if molecular ozone was consumed at the anode and/or the cathode, it results in the formation of free hydroxyl radicals that 486 487 were efficiently scavenged by tBuOH.

In terms of mineralization, assessed through DOC measurement between 0 and 40 min, the results are more difficult to interpret (Fig. 8). The DOC depletion was well described by a first-order reaction law, demonstrating the reaction is still diffusion controlled (Table 3). The mineralization rate at 200 mA is identical between AO alone and the hybrid process AO/O<sub>3</sub>. However, the mineralization rate is 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 O<sub>3</sub> per mol of alachlor) 497 is far from the theoretical ozone consumption of 38/3 mol<sub>O3</sub> mol<sub>al</sub><sup>-1</sup> in case of a total mineralization, 498 according to Eq. 15 :

499 
$$C_{14}H_{20}CINO_2 + 38/3 O_3 \rightarrow 14 CO_2 + 2H^+ + NO_3^- + CI^- + 9 H_2O$$
 (Eq. 15)

Consequently, ozone addition could be a potent solution to enhance the degradation of both the 500 501 alachlor parent molecule and maybe the first aromatic intermediates [68], even if O<sub>3</sub> is quickly 502 consumed in solution (~ 25 min). Nonetheless, low-chain aliphatic acids intermediates must quickly accumulate in solution after a few tens of minutes. These compounds are quite refractory to 503 hydroxyl radicals oxidation as mentioned before (Part 3.4.1), and ozonation as well, and cannot end 504 505 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 increase the time window in which ozone is present in solution, pulse injection of ozone could be a 507 508 pertinent solution.



510Fig. 7. Time-course profile of  $C_{L,oz}/C_{L,oz,0}$  (a) and  $C_{al}/C_{al,0}$  (b) by the hybrid process  $O_3/AO$  with511various current intensity (pH 5,  $V_L = 800 \text{ mL}$ ,  $C_{al,0} \sim 108 \mu$ M,  $C_{L,oz,0} \sim 200-250 \mu$ M). Circles: duplicate512experiments at 200 mA, Diamond: triplicate experiments at 500 mA, Triangle: duplicate513experiments at 800 mA. Cross symbols correspond to one experiment at 200 mA with addition of a514radical scavenger (tBuOH at 0.1 M). Models correspond to first-order (ozone) and second-order515(alachlor) reaction laws.



516

Fig. 8. Time-course profile of DOC/DOC<sub>0</sub> by the hybrid process O<sub>3</sub>/AO with various current
 intensity (pH 5, V<sub>L</sub> = 800 mL, C<sub>al,0</sub> ~ 108 μM, C<sub>L,oz,0</sub> ~ 200-250 μM). Circles: duplicate experiments at
 200 mA, Diamond: triplicate experiments at 500 mA, Triangle: duplicate experiments at 800 mA.
 Models correspond to a first-order reaction law.

521Table 3. Values of the nth-order reaction rate constant accounting for ozone, alachlor and DOC522oxidation  $(k_{app})$  and corresponding half-life times by the hybrid process  $O_3/AO$  with various current523intensity (pH 5,  $V_L = 800$  mL,  $C_{al,0} \sim 108 \mu M$ ,  $C_{L,oz,0} \sim 200-250 \mu M$ ). For DOC, the half-life time is524replaced by the time necessary to degrade 20% ( $t_{0.2}$ ) owing to the fact that the half-life times were525higher than the experiment duration.

	200 mA	500 mA	800 mA
First-order <i>k<sub>app,oz</sub></i> (s <sup>-1</sup> )		2.59×10 <sup>-3</sup>	
<i>t</i> <sub>1/2</sub> ozone (min)	4.5		
ARE (C <sub>L,oz,0</sub> )	12%		
n <sub>al</sub>		2	
$2^{nd}$ -order $k_{app,al}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	12.7		
t <sub>1/2</sub> alachlore (min)	12		
ARE (Cal)		5%	
First-order <i>k<sub>app,DOC</sub></i> (s <sup>-1</sup> )	$0.95 \times 10^{-4}$	$1.82 \times 10^{-4}$	$1.79 \times 10^{-4}$
<i>t<sub>0.2</sub>DOC</i> (min)	39	20	21
ARE (DOC)	2%	4%	2%

#### 526

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

- Pulse re-injections of dissolved ozone were achieved every 20 min with the hybrid process O<sub>3</sub>/AO at
  200 mA, leading to:
- a total ozone dose of 34 ppm (6.7 mol of ozone introduced per mol of alachlor) with two re injections of ozone (1h of exposure to ozone) for a first experiment
- a total ozone dose of 57 ppm (11.1 mol of ozone introduced per mol of alachlor) with 9 re injections of ozone (2h30 of exposure to ozone) for a second experiment.

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

Fig. 9 presents the ozone concentration time-course profile for the first experiment. As expected,  $O_3$ was fully consumed within 20-25 min of reaction time after each injection. The ozone concentration evolution was successfully modeled by a first-order rate law, with kapp =  $1.92 \times 10^{-3}$  s<sup>-1</sup>, in agreement 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 around 30 min, *i.e.* when the dissolved ozone concentration becomes negligible with the single 543 ozone injection method. The alachlor reaction rate was satisfactorily described by a first-order rate 544 545 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 efficiency around 94% is reached with the pulse ozone injection method (83% for the single ozone 547 548 injection method, 79% with only anodic oxidation). It confirms that ozone re-injections can be an 549 effective way to enhance the degradation rate pf 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, containing EfOM and having different pH. 561



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



567Fig. 10. Time-course profile of  $C_{al}/C_{al,0}$  (a) and  $DOC/DOC_0$  (b) by the hybrid process with pulse568injections of dissolved ozone (pH 5,  $V_L = 800 \text{ mL}$ ,  $C_{al,0} \sim 110 \mu$ M, Intensity = 200 mA). Circles:569Experiments with no ozone re-injection; dark diamonds: experiment with two ozone re-injections570 $(C_{L,oz,total} \sim 709 \mu$ M, 60 min of ozone exposure) and empty diamonds: experiment with nine ozone re-571injections ( $C_{L,oz,total} \sim 1.18 \text{ mM}$ , 2h30 of ozone exposure). The models correspond to first-order572reaction 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,  $C_{al,0} \sim 110 \mu$ M, Intensity = 200 mA).

	2 re-injections	9 re-injections
C <sub>L,oz,total</sub> (mM)	0.709	1.18
First-order $k_{app,al}$ (s <sup>-1</sup> )	7.49×10 <sup>-4</sup>	7.71×10 <sup>-4</sup>
t <sub>1/2</sub> alachlore (min)	15	15
ARE (C <sub>al</sub> )	3%	6%
First-order k <sub>app,DOC</sub> (s <sup>-1</sup> )	8.84×10⁻⁵	9.57×10⁻⁵
t <sub>1/2</sub> DOC (min)	131	121
ARE (DOC)	2%	3%

576

#### 3.7. Diphasic vs monophasic hybrid O<sub>3</sub>/AO process; what should be used?

#### Table 5. Comparison of the monophasic and diphasic hybrid $O_3$ /AO processes.

	Monophasic configuration	Diphasic configuration
Advantages	<ul> <li>Perfect control of the ozone dose and easy optimization of the ozone transfer in a dedicated gaz-liquid contactor</li> <li>Reactions mainly located in the liquid bulk and at the electrodes surface</li> <li>Multiple points injection in flow-by or flow-through electrochemical reactors is feasible</li> <li>Pulse injections or continuous ozone stock solution delivery are both possible in batch electrochemical reactors</li> </ul>	<ul> <li>Easier implementation in batch electrochemical reactors</li> <li>Ozone-enriched bubbles can improve solute mass-transfer in the gas-liquid electrochemical reactor</li> <li>High ozone doses can be easily implemented</li> </ul>
Drawbacks	<ul> <li>High ozone dose hardly achievable</li> <li>Needs of an additional water resource to prepare the ozone-stock solution (but a fraction of the treated water can be devoted to this)</li> <li>Needs of an additional gas-liquid contactor</li> </ul>	<ul> <li>The control of the ozone dose applied is more difficult owing to the fact that the ozone transfer and ozone reactions steps are interdependent</li> <li>A significant part or the totality of the ozone transferred can react at the gas-liquid interface</li> <li>The ozone transfer can be hardly optimized</li> </ul>

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581 Parts 3.5 and 3.6 clearly emphasized the pros and cons of the hybrid process O<sub>3</sub>/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  $O_3/AO$  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 (use of ozone-enriched gas bubbles) hybrid O<sub>3</sub>/AO processes. The superior control of the ozone 594 transfer dose and ozone transfer yield in solution is undoubtedly a salient advantage of the 595 596 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.

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

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

#### 613 **5. Conclusion**

This prospective study investigates the efficiency of a hybrid process that combines ozonation and anodic oxidation (AO/O<sub>3</sub>) with two boron-doped diamond (BDD) electrodes to treat a model aqueous solution containing 30 ppm of alachlor at pH 5 in a phosphate buffer. An innovative monophasic configuration, in which an ozone-stock solution was injected at  $t_0$  in the batch electrochemical 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 exposure was particularly low with a  $R_{ct}$  value lower than  $10^{-10}$ . The combination of both 622 623 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<sup>•</sup> 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.

Regarding alachlor mineralization, increasing the current intensity from 200 mA to 800 mA during the AO process over 120 minutes leads to a rise in alachlor mineralization efficiency from 50 to 80%. However, the introduction of the hybrid process shows a similar mineralization rate as for AO alone. In this case, the limitation could be attributed to the production of refractory biodegradable compounds, such as small aliphatic intermediates (fatty acids), considered to be poorly reactive with 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  $AO/O_3$  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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