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Electro-oxidation of secondary effluents from various wastewater plants for the removal of acetaminophen

and dissolved organic matter

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1 Abstract

2 Electro-oxidation of acetaminophen (ACT) in three different doped secondary effluents 3 collected from a conventional Municipal Waste Water Treatment Plant (MWWTP), a 4 MWWTP using a membrane bioreactor (WWTP MBR) and a lab-scale MBR treating 5 source-separated urine (Urine MBR) was investigated by electro-Fenton (EF) coupled 6 with anodic oxidation (AO) using sub-stoichiometric titanium oxide anode (Ti_4O_7). After 7 8 h of treatment, 90 \pm 15 %, 76 \pm 3.8 % and 46 \pm 1.3 % of total organic carbon removal 8 was obtained for MWWTP, MWWTP-MBR and Urine-MBR respectively, at a current 9 intensity of 250 mA, pH of 3 and [Fe²⁺]=0.2 mM. Faster degradation of ACT was 10 observed in the WWTP MBR because of the lower amount of competitive organic matter, 11 however, >99% degradation of ACT was obtained after 20 min for all effluents. The 12 acute toxicity of the treated effluent was measured using Microtox® tests. Results 13 showed an initial increase in toxicity, which could be assigned to formation of more 14 toxic by-products than parent compounds. From 3D excitation and emission matrix 15 fluorescence (3DEEM), different reactivity was observed according to the nature of the 16 organic matter. Particularly, an increase of low molecular weight organic compounds 17 fluorescence was observed during Urine MBR treatment. This could be linked to the 18 slow decrease of the acute toxicity during Urine MBR treatment and ascribed to the 19 formation and recalcitrance of toxic organic nitrogen and chlorinated organic by-20 products. By comparison, the acute toxicity of other effluents decreased much more 21 rapidly. Finally, energy consumption was calculated according to the objective to 22 achieve (degradation, absence of toxicity, mineralization).

23

24 Keywords:

- 25 Organic pollutants ; Electro-Fenton ; Anodic oxidation ; Magneli phases ; 3D EEM ;
- 26 Mineralization.

27

28 **1. Introduction**

29 Over the past decade, the effectiveness of wastewater treatment systems has been 30 questioned by many researchers, particularly in terms of removing emerging 31 contaminants (pesticides, pharmaceuticals, endocrinal disrupting compounds, ...) often 32 detected in treated effluents. Conventional physical, chemical or biological treatment 33 systems are unable to efficiently eliminate these contaminants and there is often a 34 transfer of pollution from one phase to another (liquid to solid phase or vice-versa) or 35 an incomplete degradation of these contaminants. Several researchers have reported 36 that the exposure, especially in long term, to emerging contaminants such as personal 37 care products, pharmaceuticals and hormones causes disruption of aquatic fauna and 38 flora and risks to human health. As reported by Tiwari et al. [1, 2], prolonged exposure to pharmaceutical residues results in a change in the species character and behavior of 39 40 aquatic organisms. The feminization of male fish due to the presence of estrogen in the 41 aquatic environment is a well-known example of trait change in species [3]. The 42 development of bacterial resistance to antibiotics is also a major risk of exposure to 43 pharmaceutical residues in the environment. To overcome this problem, additional, 44 efficient and sustainable treatments of wastewater treatment plant (WWTP) secondary 45 effluents are necessary to improve the quality of the effluents before their release into 46 the environment.

Electrochemical advanced oxidation processes (EAOPs) represent an attractive solution for tertiary treatment of treated effluents [2, 4-6]. These processes are considered environmentally friendly as they require little or no added chemicals like H₂O₂ for the Fenton reaction or O₃ for ozonation. The advantages of such processes are their nonpolluting appearance, ease of automation and reduced processing times. The principle of EAOPs consists into the *in situ* electrochemical generation of reagents, particularly hydroxyl radicals •OH, which are considered as the second most powerful oxidizing species after fluorine (E^{0} (•OH/H₂O) = 2.80 V / SHE). [7, 8]. They are non-selective oxidants that can oxidize pollutants until complete mineralization to water, carbon dioxide and inorganic ions.

Among the EOAPs, electro-Fenton (EF) is widely used in wastewater treatment. Several studies have reported its efficiency on eliminating different types of pharmaceutical pollutants such as levofloxacin, enoxacin, amoxicillin, tetracycline, etc. [9-11]. EF process is based on the continuous production of hydroxyl radicals by the means of electrochemically generated Fenton's reagent (Eq. 1). Depending on cathode material, H_2O_2 can be electro-generated by reduction of dissolved oxygen (Eq. 2), while the Fe²⁺ initially added is also continuously regenerated (Eq. 3).

64
$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH$$
 (Eq. 1)

$$65 \quad O_2 + 2H^+ + 2e^- \to H_2O_2 \tag{Eq. 2}$$

66
$$Fe^{3+} + e^- \to Fe^{2+}$$
 (Eq. 3)

67 The chemical nature of the anode is also a key parameter for the efficiency of the electrochemical process [12]. Several types of anodes can be used during electrolysis, 68 69 which are divided into two categories, active and non-active [13-15]. Non-active anodes 70 are characterized by their inert surface and their low adsorption properties, resulting in 71 a weak interaction between the produced hydroxyl radicals and the surface of the anode. 72 Thus, the physisorbed hydroxyl radicals react easily with the organic pollutants, 73 resulting in a complete mineralization of pollutants [16]. On the other hand, hydroxyl 74 radicals are not efficiently formed at active anodes such as Ti/IrO₂ and Ti/RuO₂.

However, they promote efficient conversion of chloride present in wastewater, tohypochlorous acid or hypochlorite ions that can oxidize organic pollutants [17].

In this study, we have mainly investigated the treatment of secondary effluents by the 77 electro-Fenton process combined with anodic oxidation (AO) by using sub-78 79 stoichiometric titanium oxide anode (Ti₄O₇). Ti₄O₇ has been reported to be a suitable 80 non-active anode (Eq. 4) in EF process for the removal of pharmaceuticals such as 81 propranolol and sulfamethoxazole [18-20]. This material has the potential to be a low 82 cost alternative to the well-known boron-doped diamond electrode [18]. Moreover, it is 83 possible to synthesize porous Reactive Electrochemical Membranes (REM), which allow 84 a strong enhancement of mass transport conditions when operated in flow-through 85 mode for the treatment of low concentrations of pollutants. Unprecedented high removal rates of total organic carbon and mineralization current efficiency were 86 87 achieved on REM (without coupling with EF process) after a single passage through the 88 membrane for ACT, phenol and oxalic acid [20]. While further development of REM is a 89 promising challenge, it is also important to continue to raise understanding on reaction 90 and competition mechanisms thanks to batch experiments.

Here, the efficiency of this combined process (EF/AO) was also compared with the use of
the EF process as well as with the use of the AO process (AO/H₂O₂). For the EF process, a
Ti/Pt plate anode was used instead of Ti₄O₇. For the AO/H₂O₂, none Fe²⁺ was added, thus
avoiding the decomposition for H₂O₂ by the Fenton's reaction.

95 $Ti_4O_7 + H_2O \rightarrow Ti_4O_7 (^{\bullet}OH) + H^+ + e^-$ (Eq. 4)

96 WWTP secondary effluents were sampled from three different wastewater treatment
97 systems, including an effluent from a full-scale WWTP using activated sludge ([TOC°]=

98 17 mgC L⁻¹), an other from a full-scale WWTP using a membrane bioreactor (MBR) 99 $([TOC^{\circ}] = 7 \text{ mgC } L^{-1})$ and a third from a lab-scale membrane bioreactor (MBR) treating 100 real source-separated urine ($[TOC^{\circ}] = 75 \text{ mgC } \text{L}^{-1}$). The three effluents were then doped 101 with acetaminophen (ACT) as indicator of pharmaceutical pollutant. Results were also 102 compared with a synthetic effluent containing only ACT and Na₂SO₄ as electrolyte. ACT 103 (also known under the name of paracetamol) was selected as pharmaceutical 104 contaminant because it is usually detected in wastewater treatment plants, natural 105 water resources and rivers with concentrations varying from 6 to 65 μ g L⁻¹ [21-23]. 106 Unfortunately, it is impossible to easily determine the degree of mineralization of ACT at 107 a concentration of about 100 μ g L⁻¹ by TOC analysis in effluents containing from 7 to 75 108 mgC L⁻¹. Then, based on our previous study [21], we used a concentration of ACT of 10 109 mg L⁻¹, i.e. 6.36 mgC L⁻¹ to monitor the degree of mineralization of ACT in the real effluents and to prove the interest and the efficiency of the method coupling electro-110 111 Fenton process and anodic oxidation.

Three-dimensional fluorescence excitation-emission matrix (3DEEM) is increasingly employed to understand dissolved and colloidal organic matter (DCOM) evolution and distinguish the effects of different types of DCOM on wastewater treatment technologies (i.e., membrane fouling, AOP scavenging, and disinfection by-product formation) [24-26]. A recent study also demonstrated that 3DEEM can be used to distinguish proteins from biopolymers and humic substances and to quantify building blocks, with potential use as an on-line indicator to describe DOM fate and behavior [27].

The performance of the different EAOPs was first evaluated in the synthetic effluent. The
effectiveness of the EF/AO process was then evaluated in terms of ACT degradation and
TOC removal over time for all secondary effluents. The evolution of three dimensional

excitation-emission matrix (3DEEM) was also assessed during the process in order to characterize dissolved and colloidal organic matter (DCOM) from wastewater treatment effluents, raise the understanding of reaction mechanisms in such complex effluent and more especially the interactions between DCOM and EAOP efficiencies. The evolution of the toxicity of the three effluents was evaluated using the Microtox[®] method. Finally, energy consumption was calculated according to the objective to achieve (degradation, mineralization, toxicity removal).

129 **2. Materials and Methods**

130 **2.1 Chemicals**

131 All chemicals were reagent grade purchased from Sigma Aldrich (acetaminophen, 132 Na₂SO₄, trifluoroacetic acid, acetonitrile) or Alfa Aesar (Fe₂SO₄,7H₂O). Synthetic 133 solutions were prepared with pure water (Milli-Q, Millipore Co. Ltd, resisitivity > 18.2 134 M Ω cm).

135 **2.2 Secondary effluents from various wastewater plants**

136 Three different effluents were used in this study. Two effluents were provided by two 137 municipal wastewater treatment plants in the area of Montpellier, France: the first uses 138 conventional activated sludge process (medium organic loading rate) and the second 139 one uses MBR (continuous aeration, chlorinated PES UF membrane (Kubota, Japan)), 140 they are referenced MWWTP and MWWTP MBR respectively. The third effluent was 141 from a lab-scale MBR treating real source-separated urine and is named Urine MBR. A 4-142 L submerged MBR, equipped with a flat-sheet microfiltration membrane module made 143 of PVDF (A3 Company, USA), was fed with fresh urine for a period of 120 days [28]. 144 More details concerning this effluent could be found in a previous study [28]. All samples have been collected at stationary phase (stable operating parameters and stable
removal efficiencies) of the systems and the main characteristics of the three effluents
are presented in table 1.

148 **2.3 Electrochemical setup**

149 Experiments were performed using an undivided 500-mL single cylindrical glass with a 150 two-electrode system. Ti₄O₇ plate (for EF/AO and AO/H₂O₂ processes) and platinised 151 titanium mesh (Ti/Pt) (for EF process) anodes with a surface area of 24 cm² (4 cm x 6 152 cm), were provided by Saint Gobain Research Provence (France) and Goodfellow SARL 153 (France) respectively. The Ti_4O_7 film was synthesized as follow: a mixture of TiOx (x<2) 154 particles in the range 20-60 µm prepared as described in [29] was used to make a 155 plasma coating on a Ti substrate (4 cm x 6 cm) pretreated by sandblasting to create a 156 rough surface. In the conditions described in [29], a continuous thick film of 100 µm and 157 95% density was obtained. X-ray diffraction of the prepared electrode shows that the 158 main phase was Ti₄O₇ with the presence of TiO₂ rutile and Ti₃O₅. The typical electronic 159 conductivity of the plasma-sprayed coating, determined by the four-probes method, is 160 $10^{-3} \Omega$ cm. Carbon-felt cathodes with a surface area of 126 cm² (21 cm x 6 cm) and 161 thickness of 0.5 cm, were provided by Alfa Aesar. In all experiments, the cathode 162 covered the inner wall of the cell while the anode was in the center, similarly to the 163 configuration reported in several articles [8, 9, 19, 30-32]. The agitation and 164 homogenization of the solution was carried out using a magnetic PTFE stirrer during 165 electrolysis. Experiments were carried out at room temperature with 250 mL of 166 secondary effluents from various wastewater plants doped with 10 mg L⁻¹ of ACT as well 167 as with the same volume of a synthetic solution containing 10 mg L⁻¹ of ACT in 50 mM of 168 Na₂SO₄ as supporting electrolyte. The solutions were continuously saturated with O₂ by

169 bubbling compressed air at atmospheric pressure at about 1 L min⁻¹. Iron (II) (0.2 mM) 170 was added as catalyst to perform EF and EF/AO processes. . Additions of aliquots of a 171 commercial concentrated solution of sulfuric acid (Sigma Aldrich 96% pure) were done to 172 adjust the pH at 3. The ionic strength (I) was different for the four media. For the synthetic 173 effluent, I was fixed by the 50 mM of Na_2SO_4 used as electrolyte (I = 0.15). For Urine MBR, 174 MWWWTP and MWWTP MBR effluents, I was determined from the ionic concentration of 175 salts listed in Table 1 (taking the hypothesis of monovalent cations as counter-ions). Then I=0.21 for Urine MBR; I=0.0075 for MWWWTP and I=0.016 for MWWTP MBR. Because 176 177 of the difference in ionic strength, the solution resistance varied from one effluent to the 178 other. Resistance of the different systems are 19.6, 19.5, 27.2, 26.6 Ω for the synthetic 179 solution, Urine MBR, MWWWTP and MWWTP MBR effluents respectively.

180

181 **2.4 ACT quantification**

182 Concentrations of ACT and its by-products were analyzed by high-performance liquid 183 chromatography (Waters 717 Autosampler and Waters 616 Pump) with a reverse phase 184 C18 column (Thermo Scientific), thermostated at 30 °C, coupled with a UV detector 185 (photodiode array detector Waters 2996). The injection volumes were 20 µL and the 186 mobile phase was a mixture of water and acetonitrile, with 0.1% (v/v) of trifluoroacetic acid. The flow rate was 1 mL min⁻¹. The system was operated under gradient elution 187 188 mode in order to ensure the proper separation of acetaminophen and p-benzoquinone 189 (degradation by-product).

190 **2.5 TOC analysis**

The total organic carbon (TOC) analysis was performed using TOC-L Shimadzu 1.05.00
analyzer. Total carbon and inorganic carbon were analyzed and TOC was obtained from
the difference between total carbon and inorganic carbon.

194 **2.6 Characterization of the natural organic matter by 3DEEM**

195 Three-dimensional excitation and emission matrix fluorescence (3DEEM) using a 196 Perkin-Elmer LS-55 spectrometer (USA) was used for characterizing DCOM. For 3DEEM 197 analysis, samples were filtered through 1.2 µm glass microfiber filters (Whatman GF/C) 198 and diluted by a factor 60. The procedure reported by [27] was used for fluorescence 199 spectra acquisition and data extraction based on the division of the 3D fluorescence 200 spectra representation into three different areas corresponding to different groups of 201 fluorophores [33]. Jacquin et al. have recently developed a semi-quantitative method for 202 the assessment of the amount of fluorophores associated with DCOM in real effluents 203 [27]. This method is based on the calculation of the volume of fluorescence in zones I', II' 204 and III' and was applied in the present work. Zone III' volume of fluorescence (HA+FA-205 like fluorophores) is correlated to humic substances concentration (MW ≈ 1000 Da) and 206 degradation by-products from humic substances (hydrophobic compounds, MW \approx 300-500 207 Da). Similarly, a correlation exists between the volume of fluorescence of zone II' (SMP-like 208 fluorophores) and the concentration of proteins from biopolymers (MW $\approx 20,000 - 7.5 \times 10^{11}$ 209 Da). Finally, volume of fluorescence of zone I' is associated with colloidal proteins, which 210 are the bigger and more hydrophilic compounds present in DCOM.

211 **2.7 Acute toxicity assessments**

The Microtox[®] bacterial toxicity test was used as an indicator of the acute toxicity of the effluents during the electrochemical treatment. Bacterial luminescence of *Vibrio fisheri* is directly related to cellular respiration and cell activity. Thus, this method is based on the

- 215 measure of the inhibition of *Vibrio fisheri* luminescence. Samples were diluted at 45% by
 216 adding a 22% NaCl solution. The pH of all samples was adjusted between 6.5 and 7.5
- 217 with sodium hydroxide (NaOH, 1N). Measurements and data extraction were performed
- as reported in the study of Le et al. [12].

219 2.8 Energy consumption

An important concern in EAOPs is to know the energy consumption (EC), expressed as
kWh per m⁻³ and calculated from Eq. 5.

222
$$EC(kWh.m^{-3}) = \frac{Ecell \times I \times t}{V}$$
 (5)

223 Where E_{cell} is the average cell voltage (V), I the applied current (A), t the duration of 224 electrolysis (h), V the volume of treated solution (m⁻³).

225

3. Results and Discussion

227 **3.1. Degradation and mineralization of ACT**

The degradation of ACT was first studied for the synthetic solution using the three different EAOPs: EF, AO/H₂O₂ and EF/AO. The electrolyses were carried out at 250 mA for 8 hours using the electrochemical cell previously described. The performance of the treatment was evaluated by following TOC removal (Table 2). Results showed that the highest TOC removal was obtained using AO/EF.

The higher TOC removal rate achieved by the EF/AO process can be explained by the action of hydroxyl radicals produced both at the surface of the Ti₄O₇ anode and in the bulk solution from the Fenton's reaction. The use of non-active anodes, such as Ti₄O₇ or boron-doped diamond (BDD), instead of active anodes such as mixed metal oxides (MMO) and dimensionally stable anodes (DSA), allows for a better degradation of organic substances and improves the mineralization of solutions. In fact, several studies have reported a better removal of pharmaceutical residues like propanol, ibuprofen, carbamazepine, venlafaxine and estradiol when using non-active anodes. The non-active anodes have a great potential for generating hydroxyl radicals which are powerful oxidants that are able to oxidize pollutants present in wastewater until their complete mineralization (transformation into CO₂) [5, 15, 18, 34].

244 In this study, several current intensities were also tested (100, 250 and 300 mA) for 245 treatment of the synthetic solution (data not shown). The best results, in terms of TOC 246 removal, were obtained using a current intensity of 250 mA. Similar results were 247 reported by Komtchou et al [13] during the electrolysis of carbamazepine where the 248 electrodes surface was 113 cm². The highest removal rates were observed with 200 mA 249 compared to 500, 1000 and 2000 mA. Generally, increasing the current intensity has a 250 positive effect on electrochemical degradation of pollutants because a greater amount of 251 hydroxyl radicals is produced when applying higher current intensities. However, 252 researchers have reported that increasing current intensity usually decreases the 253 energy-efficiency of the process because side reactions (mainly oxygen and hydrogen 254 evolution reactions) and parasitic reactions (hydroxyl radical dimerization, reaction of 255 hydroxyl radicals with excess H₂O₂) are also promoted [35]. Therefore, for the next 256 experiments, a current intensity of 250 mA was chosen as the optimal current intensity 257 for simultaneous regeneration of Fe²⁺, production of H₂O₂ at the cathode and generation 258 of hydroxyl radicals at the anode. The EF/AO process, identified as the most effective process, was then applied for tertiary treatment of ACT-doped secondary effluents from 259 260 three different wastewater treatments plants.

261 As shown in figure 1, a rapid decrease of TOC was observed within the first hour of 262 electrolysis for all the different wastewaters. In fact, a removal rate of $64 \pm 0.5\%$, $56 \pm$ 263 5.3 % and 30 ± 0.5 % was obtained for MWWTP MBR (curve B), MWWTP (curve C) and 264 Urine MBR (curve A), respectively. At longer times, mineralization rate slowly increased, 265 which is usually ascribed to the formation of degradation by-products such as short-266 chain carboxylic presenting lower reaction kinetics with hydroxyl radicals. Similar 267 behaviors were reported in previous studies regarding the removal of propranolol and 268 acetaminophen by EAOPs [18, 36]. The authors reported a similar phenomenon with an initial rapid drop of the TOC concentration during the first hour, which was then 269 270 followed by a continuous slow decrease over time. The lower mineralization rate was achieved with Urine MBR (curve A), which reaches only 46 ± 1 % of TOC removal after 271 272 8h of electrolysis, most probably because of the presence of DCOM recalcitrant to 273 oxidation. Under the same experimental conditions, higher mineralization (curve B and 274 C) was obtained for the effluents from MWWTP MBR and MWWTP with a TOC removal 275 of about 76 \pm 1 % and 90 \pm 3 %, respectively. It is important to note that the initial 276 concentration of TOC in Urine MBR effluent doped with ACT was 80 mg C L⁻¹ while for 277 the other two effluents this concentration was 22 mg C L⁻¹ and 12 mg C L⁻¹ for MWWTP 278 and MWWTP MBR, respectively. Thus, 20 to 40% of initial TOC was ascribed to ACT for 279 these latter, while for Urine MBR, 94% of initial TOC was ascribed to the residual DCOM 280 that was not eliminated during the treatment of urine by the MBR.

Figure 2 shows the degradation of 10 mg L⁻¹ of ACT over electrolysis time, for the three secondary effluents and the synthetic solution. A rapid drop of ACT concentration is observed for the synthetic solution and for the three doped secondary effluents. In fact, a complete removal of ACT was achieved after 8, 8, 15 and 20 min of treatment for synthetic solution, MWWTP MBR, MWWTP and Urine MBR respectively with then a

286 similar kinetic for the synthetic solution and MWWTP MBR (Apparent first order kinetic 287 rate: 0.640 min⁻¹ and 0.629 min⁻¹ respectively) and lower kinetics for MWWTP and 288 Urine MBR (0.374 min⁻¹ and 0.314 min⁻¹ respectively). Brillas et al. have studied the 289 anodic oxidation of ACT (with concentrations up to 1 g.L⁻¹) in a cell with a BDD or Pt 290 anode and a graphite cathode [37]. Results showed a complete removal of 291 acetaminophen after 120 to 240 min of electrolysis with the BDD anode and after 240 to 292 360 min with the Pt anode (pseudo-first order rate constant was $0.013 + - 0.002 \text{ min}^{-1}$. 293 In both case, the time required for ACT elimination was much longer than in our study. 294 The faster degradation of ACT can be explained by (i) the lower concentration of ACT in 295 our study and (ii) the production of large amount of both heterogeneous and 296 homogeneous hydroxyl radicals from anodic oxidation at the Ti₄O₇ anode [18] and 297 electrochemically induced Fenton's reaction in the bulk solution (Eq. (1)). Besides, Sirès 298 et al. [36] have studied the degradation of ACT solution (157 mg.L⁻¹) by electro-Fenton 299 and photo-electro-Fenton processes using a cell with a Pt anode and an O₂ diffusion 300 cathode for H₂O₂ electro-generation. A complete removal was observed after 20-25 min 301 of process. The authors confirmed that ACT was mainly eliminated by the hydroxyl 302 radicals during electrolysis and that UVA lighting did not contributed significantly. The 303 electrolysis time required for the total removal of acetaminophen in the aqueous 304 solution reported was also longer than that obtained in this study (8 min vs 20-25 min). 305 It might be ascribed to (i) the lower concentration level of ACT in our study and (ii) the 306 use of a non-active anode such as Ti₄O₇, which has a much greater potential than Pt for 307 generating large amounts of hydroxyl radicals at the anode surface [18, 34].

The variation in the required time for the complete removal of ACT in the different effluents is mainly due to the composition of the treated water as well as to the process applied for the secondary treatment (activated sludge for WWTP effluent, MBR for

311 WWTP MBR effluent and for Urine MBR effluent). Hydroxyl radicals are known to be 312 non-selective and may react with DCOM (natural organic matter, microbial residues), 313 inorganic species, suspended solids, which constitutes radical scavengers and can 314 increase the time required for ACT degradation. During the treatment of MWWTP MBR 315 effluent, it was not observed any significant effect of the real effluent matrix on the 316 degradation rate of ACT. It might be ascribed to the high effectiveness of the MBR used 317 as secondary treatment, which strongly reduces the presence of particulate and colloidal 318 radical scavengers in the solution. Besides, a significant reduction of the degradation 319 kinetic of ACT was observed in MWWTP and Urine MBR effluents, most probably 320 because of the higher TOC and MLSS (for MWWTP) content that promotes hydroxyl 321 radical scavenging. However, from the much higher TOC content of Urine MBR effluent, a 322 stronger adverse effect could have been expected. The similar adverse effect observed 323 from both MWWTP and Urine MBR might be ascribed to the lower reactivity of the 324 organic compounds in the Urine MBR effluent, as it was observed from the lower TOC 325 decrease. Thus, both the amount and the nature/reactivity of the organic compounds 326 must be considered for understanding hydroxyl radical scavenging. Moreover, these 327 results also highlight that the effectiveness of the secondary treatment might be crucial 328 for the removal of organic micropollutants during tertiary treatment by EAOP.

329 **3.2. Evolution of the toxicity of treated effluents**

The evolution of the toxicity during the treatment of ACT-doped real effluents by EF/AO was evaluated by the Microtox[®] method (Figure 3). The three raw effluents doped with ACT showed relatively low luminescence inhibition to *V. fischeri* bacteria (< 10%) which is in good accordance with EC50 observed in the literature for paracetamol on *V. fischeri* with values around 100 mg/L [38]. However, luminescence inhibition increased rapidly

335 after 1 hour of treatment to reach 85% (+- 1%) and 65% (+-5%), for MWWTP MBR and 336 Urine MBR effluents respectively. This strong increase in bacterial inhibition can be 337 attributed to the formation of degradation by-products that may be more toxic than 338 parent compounds [39, 40]. The stronger increase of toxicity in Urine MBR effluent 339 might be ascribed to the formation of further toxic N-containing and halogenated 340 organic by-products because of the higher N and Cl content of this effluent (Table 1). 341 Luminescence inhibition may also come from the presence of residual oxidants 342 generated during electrolysis such as HClO resulting from the oxidation of Cl⁻ ions 343 present in the effluents. Subsequently, luminescence inhibition decreased during 344 electrolysis to reach around 20% (+-5%) for Urine MBR after 8 hours of treatment, 345 while a quasi-zero (+- 12%) luminescence inhibition was observed for MWWTP MBR 346 after 4 hours of process. The slower decrease of the toxicity in the Urine MBR effluent 347 might be explained by the formation of toxic degradation by-products that are more 348 recalcitrant to oxidation. This phenomenon is consistent with the slow decrease of the 349 TOC between 1 and 8 h of treatment of this effluent (Figure 1). Such increase in the 350 toxicity of a ACT solution was also reported by Hamdi El Najjar et al. [41] during the 351 oxidation by ozone and hydroxyl radicals. The authors observed a gradual increase in 352 toxicity up to nearly 64% inhibition of luminescence bacteria after less than 20 minutes 353 because of the formation of degradation by-products more toxic than ACT [23]. Recently, 354 Le et al. identified the aromatic compounds 2-hydroxy-4-(N-acetyl) aminophenol, 1,4-355 benzoquinone, benzaldehyde and benzoic acid as the toxic sub-products formed from 356 ACT degradation at the first stage of the electrochemical treatment and responsible of 357 toxicity enhancement [12].

Luminescence inhibition of the MWWTP effluent during EF/AO process shows a singularbehavior. The high concentration of MLSS of this effluent may explain why the toxicity

was very low during the first six hours of treatment (Table 1). Indeed, particulate
organic matter might be preferentially oxidised without production of toxic by-products.
After 6 hours of treatment of MWWTP effluent, oxidation of soluble organic matter (like
ACT) and Cl- ions might promote a slight increase of luminescence inhibition.

Overall, these results highlight that the nature and composition of the effluent might be
also crucial parameters for the evolution of the toxicity during a tertiary treatment
based on EAOPs.

367 **3.3. Evolution of dissolved and colloidal organic matter by 3DEEM**

368 3DEEM has been reported to be a useful tool for characterization of dissolved and colloidal 369 organic matter (DCOM) in real WWTP effluents [27] and is used in this study to follow the 370 scavenging effect of DCOM during EAOPS (Figures 4 and 5).

The initial MWWTP and MWWTP MBR effluents show similar 3DDEM spectrums and percentages of volume of fluorescence of the three different zones. Colloidal proteins fluorophores from zone I', which are known to exert quenching effect on AOPs [42], represent around 54% of fluorescent DCOM of those effluents. Urine MBR has the higher content of DCOM fluorophores (higher 3DEEM intensities) because of its higher TOC concentrations (Table 1) and its DCOM composition is relatively well distributed between the three different fluorescence zones.

As shown on figure 5, molecules with fluorophores of zone I' are less degraded during EAOPs than fluorophores associated with zones II' and III'. In previous studies, we have already observed that EAOPs lead to a slow decrease of colloidal proteins from zone I' due to lower availability of colloids for reaction with 'OH in the liquid phase. Besides, a fast decrease of fluorophores of zone II' and III' was observed because of the degradation and mineralization of these compounds with an aromatic structure that reacts quickly with 'OH and active chlorine [20; 42]. Humic substances found in WWTP effluent are mainly biorefractory (because they have not been degraded during secondary treatment) with high stability and aromaticity. Those substances, known as potentially cytotoxic, are transformed into more biodegradable and small-molecule DCOM (fulvic-like substances and protein-like substances) by oxidants generated during EAOPs [43].

389 Fluorophores from zone I' and III' present in Urine MBR effluent shows an increase during 390 the first two hours of treatment. High Cl and N concentration in Urine MBR led to the quick 391 formation of by-products, which have some fluorophores in those zones. Then, between two 392 to eight hours of treatment, fluorophores from zone I' decreased, while fluorophores from 393 zone III' were stable. It means that by-products from these two zones have different oxidation 394 rates during EAOPs. The stability of zone III' is consistent with the evolution of TOC 395 removal (Figure 1), which is fast during the first hour of treatment and shows a slight 396 decrease after this first hour.

397 **3.4. Energy consumption**

398 Energy consumption (in term of kWh m⁻³) was calculated for each different effluent 399 according to different objectives. For example, the energy required for >99% 400 degradation of ACT was 1.1, 1.9 and 2.0 kWh m⁻³ for MWWTP MBR, Urine MBR and 401 MWWTP effluents, respectively. By comparison, the average energy consumption of a 402 conventional MWWTP is about 0.6-1 kWh m⁻³ [43]. The energy consumption can be 403 increased to 2 kWh m⁻³ for a MBR. Overall, the higher energy consumption related to the 404 use of MBR could be almost offset by the cost reduction during the tertiary treatment 405 related to the better quality of the secondary effluent. However, >99% of degradation 406 should not be the only objective because of the potential toxicity of by-products. For an 407 objective related to the acute toxicity (<5%) or the percent of mineralization (>80%), 408 the energy consumption calculated for the MWWTP MBR effluent was strongly 409 increased to 33 and 49 kWh m⁻³. Therefore, it is required to develop more cost-effective 410 electrochemical processes for such application. In fact, the low concentration of 411 pollutants in secondary effluents strongly reduces the efficiency of electro-oxidation 412 processes because of mass transport limitations [44]. Several studies currently focus on 413 different ways to overcome this drawback, including pre-concentration of effluents by 414 combination with the adsorption process [45] or using reactive electrochemical 415 membranes for convection-enhanced mass transport of pollutants during AO. Another 416 approach related to energy-consumption optimization is to develop milli- or 417 microfluidic reactors in order to reduce the interelectrode distance [46].

418 4. Conclusions

419 The electrochemical oxidation of ACT in different secondary effluents was successfully 420 realized using EF/AO process with carbon felt cathode and Ti₄O₇ anode. The complete 421 elimination of acetaminophen was achieved after 20 minutes of electrolysis for the three 422 types of effluents (MWWTP, MWWTP MBR and Urine MBR). However, lower adverse 423 effect from the organic matrix was observed for the MWWTP MBR effluent because of 424 the higher effectiveness of the secondary treatment (MBR). A relatively high removal of TOC was observed for MWWTP and MWWTP MBR effluents (90 \pm 15 %, 76 \pm 3.8 % 425 426 respectively) after 8h treatment. However, only 46 ± 1.3 % of TOC removal was achieved 427 for Urine MBR effluent under the same conditions. An increase in acute toxicity during 428 ACT oxidation was also observed. A higher increase was observed in Urine MBR effluent. 429 This increase could be attributed to the formation of ACT degradation by-products 430 during electrolysis. Then, further oxidation of these by-products reduced the acute

431 toxicity of the solution and Vibrio fisheri luminescence inhibition reached quasi-zero (+-432 12%) for MWWTP MBR and MWWTP. However, toxicity reduction was lower for Urine 433 MBR and luminescence inhibition reached 20% (+-5%) at the end of the treatment. 434 Lower TOC removal and higher toxicity during the treatment of Urine MBR might be 435 ascribed to the formation of N-containing and halogenated organic by-products with 436 higher toxicity and lower reactivity for further oxidation by oxidant species generated 437 during the treatment. This hypothesis was confirmed by 3DEEM results, which highlight 438 the formation of recalcitrant degradation by-products during the treatment of Urine 439 MBR. Such phenomenon was not observed during the treatment of MWWTP and 440 MWWTP MBR effluents. Overall, EF/AO process seems to be an effective technology for 441 the treatment of ACT in municipal sewage effluents. Next scientific and technological 442 challenges are related to the treatment of effluents without pre-treatment for pH 443 adjustment. This approach is possible by coupling anodic oxidation with heterogeneous 444 electro-Fenton process on carbon felt modified with iron based compounds like Layer 445 Double Hydroxyde (LDH) as we recently proposed in [19] and [47]. It will be also 446 necessary to improve the cost-efficiency of these processes, particularly for the 447 treatment of effluents containing a cocktail of pollutants with concentration in the order 448 of 100 µg L⁻¹. For such low concentration of pollutants, REM operated in flow-through 449 mode might be one of the most promising solutions.

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Figure 1: Mineralization of acetaminophen-doped ($[ACT]_0 = 10 \text{ mg } L^{-1}$) real effluents by electro-Fenton/anodic oxidation (EF/AO) process. A – Urine MBR, $[TOC]_0 = 80 \text{ mgC } L^{-1}$; B – MWWTP MBR, $[TOC]_0 = 12 \text{ mgC } L^{-1}$; C – MWWTP, $[TOC]_0 = 22 \text{ mgC } L^{-1}$; I = 250 mA; $[Fe^{2+}] = 0.2 \text{ mM}$; pH = 3.



Figure 2: Degradation of acetaminophen ([ACT]₀ = 10 mgC L⁻¹) in synthetic solution
([Na₂SO₄] = 50 mM + milli-Q water) and acetaminophen-doped real matrix (Urine MBR,
[TOC]₀ = 80 mgC L⁻¹; MWWTP MBR, [TOC]₀ = 12 mgC L⁻¹; MWWTP, [TOC]₀ = 20 mgC L⁻¹) by
electro-Fenton/anodic oxidation process. I = 250 mA ; [Fe²⁺] = 0.2 mM ; pH = 3.



Figure 3: Mircrotox® analysis. Evolution of Vibrio fisheri luminescence inhibition (15 min exposure) during the treatment of acetaminophen-doped real effluents by anodic
oxidation/electro-Fenton process. I = 250 mA; [Fe²⁺] = 0.2 mM; pH = 3. RSD (n = 5): 12% for inhibition < 20%; 5% for 20% < inhibition < 70% and 1% for inhibition > 70%.





fluorescence).



Figure 5 – Volume of fluorescence evolution (zones I', II', III') during the treatment of acetaminophen-doped real effluents by anodic oxidation/electro-Fenton (AO/EF) process. I = 250 mA; [Fe2+]0 = 0.2 mM; pH = 3.

Effluont	nЦ	-	[[[]]]	COD	TOC	$[NO_{a}-1]$	[NO ₂ -]	[NH.+]	MISS
Linuent	pn	0	[CI-]	COD	IUC		[NO ₂]		MLSS
		mS cm ⁻¹	mg L-1	mgO ₂ L ⁻¹	mgC L-1	mgN L-1	mgN L-1	mgN L-1	mg L-1
Urine MBR	7.0	12.8	4380	150	75.2	1200	<loq< td=""><td>38</td><td>2.3</td></loq<>	38	2.3
	±0.2	±2.6	±481	±11.2	±5.3	±160		±12	±1.0
MWWTP	7.2	4.1	267	50.3	17.2	1.8	<loq< td=""><td>55</td><td>33.2</td></loq<>	55	33.2
	±0.2	±0.5	±37	±8.1	±1.2	±0.9		±14	±2.1
MWWTP	7.4	3.2	586	19.1	7.4	5.8	0.1	1.8	1.5
MBR	±0.3	±0.3	±65	±2.7	±0.8	±1.9	±0.1	±1.7	±1.0

 σ : Conductivity ; LOQ: Limit of Quantification ; MLSS: Mixed Liquor Suspended Solid

Tableau 2: Comparison of TOC removal of the synthetic solution of ACT after 8 h of treatment by electro-Fenton (EF), anodic oxidation/H₂O₂ (AO/H₂O₂) and electro-Fenton/anodic oxidation (EF/AO) processes. $ACT_0 = 10 \text{ mg } L^{-1}$; I = 250 mA; $[Na_2SO_4] = 50 \text{ mM}$; $[Fe^{2+}]_0 = 0.2 \text{ mM}$ or 0 mM (for AO/H_2O_2); pH = 3.

TOC removal after 8 h (%)				
76 ± 5				
81.0 ± 3.4				
87± 2.7				



*EAOP: Electrochemical Advanced Oxidation Process