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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  $[Fe^{2+}] = 0.2$  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<sup>®</sup> 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).

24 **Keywords:**

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

26 Mineralization.

27

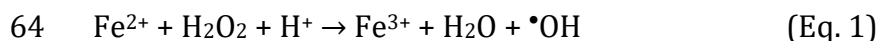
## 28 **1. Introduction**

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  
39 to pharmaceutical residues results in a change in the species character and behavior of  
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.

47 Electrochemical advanced oxidation processes (EAOPs) represent an attractive solution  
48 for tertiary treatment of treated effluents [2, 4-6]. These processes are considered  
49 environmentally friendly as they require little or no added chemicals like  $H_2O_2$  for the  
50 Fenton reaction or  $O_3$  for ozonation. The advantages of such processes are their non-  
51 polluting appearance, ease of automation and reduced processing times. The principle of

52 EAOPs consists into the *in situ* electrochemical generation of reagents, particularly  
53 hydroxyl radicals  $\bullet\text{OH}$ , which are considered as the second most powerful oxidizing  
54 species after fluorine ( $E^\circ (\bullet\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V} / \text{SHE}$ ). [7, 8]. They are non-selective  
55 oxidants that can oxidize pollutants until complete mineralization to water, carbon  
56 dioxide and inorganic ions.

57 Among the EOAPs, electro-Fenton (EF) is widely used in wastewater treatment. Several  
58 studies have reported its efficiency on eliminating different types of pharmaceutical  
59 pollutants such as levofloxacin, enoxacin, amoxicillin, tetracycline, etc. [9-11]. EF process  
60 is based on the continuous production of hydroxyl radicals by the means of  
61 electrochemically generated Fenton's reagent (Eq. 1). Depending on cathode material,  
62  $\text{H}_2\text{O}_2$  can be electro-generated by reduction of dissolved oxygen (Eq. 2), while the  $\text{Fe}^{2+}$   
63 initially added is also continuously regenerated (Eq. 3).

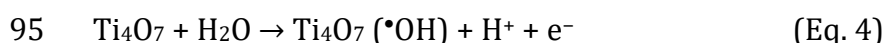


67 The chemical nature of the anode is also a key parameter for the efficiency of the  
68 electrochemical process [12]. Several types of anodes can be used during electrolysis,  
69 which are divided into two categories, active and non-active [13-15]. Non-active anodes  
70 are characterized by their 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  $\text{Ti}/\text{IrO}_2$  and  $\text{Ti}/\text{RuO}_2$ .

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

77 In this study, we have mainly investigated the treatment of secondary effluents by the  
78 electro-Fenton process combined with anodic oxidation (AO) by using sub-  
79 stoichiometric titanium oxide anode (Ti<sub>4</sub>O<sub>7</sub>). Ti<sub>4</sub>O<sub>7</sub> 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  
86 removal rates of total organic carbon and mineralization current efficiency were  
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.

91 Here, the efficiency of this combined process (EF/AO) was also compared with the use of  
92 the EF process as well as with the use of the AO process (AO/H<sub>2</sub>O<sub>2</sub>). For the EF process, a  
93 Ti/Pt plate anode was used instead of Ti<sub>4</sub>O<sub>7</sub>. For the AO/H<sub>2</sub>O<sub>2</sub>, none Fe<sup>2+</sup> was added, thus  
94 avoiding the decomposition for H<sub>2</sub>O<sub>2</sub> by the Fenton's reaction.



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<sup>-1</sup>), an other from a full-scale WWTP using a membrane bioreactor (MBR)  
99 ([TOC°]= 7 mgC L<sup>-1</sup>) and a third from a lab-scale membrane bioreactor (MBR) treating  
100 real source-separated urine ([TOC°]= 75 mgC L<sup>-1</sup>). 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 Na<sub>2</sub>SO<sub>4</sub> 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 µg L<sup>-1</sup> [21-23].  
106 Unfortunately, it is impossible to easily determine the degree of mineralization of ACT at  
107 a concentration of about 100 µg L<sup>-1</sup> by TOC analysis in effluents containing from 7 to 75  
108 mgC L<sup>-1</sup>. Then, based on our previous study [21], we used a concentration of ACT of 10  
109 mg L<sup>-1</sup>, i.e. 6.36 mgC L<sup>-1</sup> to monitor the degree of mineralization of ACT in the real  
110 effluents and to prove the interest and the efficiency of the method coupling electro-  
111 Fenton process and anodic oxidation.

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

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



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

## 129 **2. Materials and Methods**

### 130 **2.1 Chemicals**

131 All chemicals were reagent grade purchased from Sigma Aldrich (acetaminophen,  
132 Na<sub>2</sub>SO<sub>4</sub>, trifluoroacetic acid, acetonitrile) or Alfa Aesar (Fe<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O). Synthetic  
133 solutions were prepared with pure water (Milli-Q, Millipore Co. Ltd, resistivity > 18.2  
134 MΩ 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

145 samples have been collected at stationary phase (stable operating parameters and stable  
146 removal efficiencies) of the systems and the main characteristics of the three effluents  
147 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. Ti<sub>4</sub>O<sub>7</sub> plate (for EF/AO and AO/H<sub>2</sub>O<sub>2</sub> processes) and platinised  
151 titanium mesh (Ti/Pt) (for EF process) anodes with a surface area of 24 cm<sup>2</sup> (4 cm x 6  
152 cm), were provided by Saint Gobain Research Provence (France) and Goodfellow SARL  
153 (France) respectively. The Ti<sub>4</sub>O<sub>7</sub> film was synthesized as follow: a mixture of TiO<sub>x</sub> (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 Ti<sub>4</sub>O<sub>7</sub> with the presence of TiO<sub>2</sub> rutile and Ti<sub>3</sub>O<sub>5</sub>. The typical electronic  
159 conductivity of the plasma-sprayed coating, determined by the four-probes method, is  
160 10<sup>-3</sup> Ω cm. Carbon-felt cathodes with a surface area of 126 cm<sup>2</sup> (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<sup>-1</sup> of ACT as well  
167 as with the same volume of a synthetic solution containing 10 mg L<sup>-1</sup> of ACT in 50 mM of  
168 Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. The solutions were continuously saturated with O<sub>2</sub> by

169 bubbling compressed air at atmospheric pressure at about 1 L min<sup>-1</sup>. 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<sub>2</sub>SO<sub>4</sub> used as electrolyte (I = 0.15). For Urine MBR,  
174 MWWTP 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  
176 I=0.21 for Urine MBR; I=0.0075 for MWWTP and I=0.016 for MWWTP MBR. Because  
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, MWWTP 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  
187 acid. The flow rate was 1 mL min<sup>-1</sup>. The system was operated under gradient elution  
188 mode in order to ensure the proper separation of acetaminophen and p-benzoquinone  
189 (degradation by-product).

#### 190 **2.5 TOC analysis**

191 The total organic carbon (TOC) analysis was performed using TOC-L Shimadzu 1.05.00  
192 analyzer. Total carbon and inorganic carbon were analyzed and TOC was obtained from  
193 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  $\mu\text{m}$  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 ( $\text{MW} \approx 1000 \text{ Da}$ ) and  
206 degradation by-products from humic substances (hydrophobic compounds,  $\text{MW} \approx 300\text{-}500$   
207  $\text{Da}$ ). Similarly, a correlation exists between the volume of fluorescence of zone II' (SMP-like  
208 fluorophores) and the concentration of proteins from biopolymers ( $\text{MW} \approx 20,000 - 7.5 \times 10^{11}$   
209  $\text{Da}$ ). 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**

212 The Microtox<sup>®</sup> bacterial toxicity test was used as an indicator of the acute toxicity of the  
213 effluents during the electrochemical treatment. Bacterial luminescence of *Vibrio fischeri* is  
214 directly related to cellular respiration and cell activity. Thus, this method is based on the

215 measure of the inhibition of *Vibrio fischeri* 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  
218 as reported in the study of Le et al. [12].

## 219 **2.8 Energy consumption**

220 An important concern in EAOPs is to know the energy consumption (EC), expressed as  
221 kWh per m<sup>-3</sup> and calculated from Eq. 5.

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

223 Where  $E_{\text{cell}}$  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<sup>-3</sup>).

225

## 226 **3. Results and Discussion**

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

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

233 The higher TOC removal rate achieved by the EF/AO process can be explained by the  
234 action of hydroxyl radicals produced both at the surface of the Ti<sub>4</sub>O<sub>7</sub> anode and in the  
235 bulk solution from the Fenton's reaction. The use of non-active anodes, such as Ti<sub>4</sub>O<sub>7</sub> or  
236 boron-doped diamond (BDD), instead of active anodes such as mixed metal oxides  
237 (MMO) and dimensionally stable anodes (DSA), allows for a better degradation of

238 organic substances and improves the mineralization of solutions. In fact, several studies  
239 have reported a better removal of pharmaceutical residues like propranolol, ibuprofen,  
240 carbamazepine, venlafaxine and estradiol when using non-active anodes. The non-active  
241 anodes have a great potential for generating hydroxyl radicals which are powerful  
242 oxidants that are able to oxidize pollutants present in wastewater until their complete  
243 mineralization (transformation into CO<sub>2</sub>) [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 cm<sup>2</sup>. 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 H<sub>2</sub>O<sub>2</sub>) 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 Fe<sup>2+</sup>, production of H<sub>2</sub>O<sub>2</sub> at the cathode and generation  
258 of hydroxyl radicals at the anode. The EF/AO process, identified as the most effective  
259 process, was then applied for tertiary treatment of ACT-doped secondary effluents from  
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  $30 \pm 0.5 \%$  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  
269 initial rapid drop of the TOC concentration during the first hour, which was then  
270 followed by a continuous slow decrease over time. The lower mineralization rate was  
271 achieved with Urine MBR (curve A), which reaches only  $46 \pm 1 \%$  of TOC removal after  
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  $80 \text{ mg C L}^{-1}$  while for  
277 the other two effluents this concentration was  $22 \text{ mg C L}^{-1}$  and  $12 \text{ mg C L}^{-1}$  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.

281 Figure 2 shows the degradation of  $10 \text{ mg L}^{-1}$  of ACT over electrolysis time, for the three  
282 secondary effluents and the synthetic solution. A rapid drop of ACT concentration is  
283 observed for the synthetic solution and for the three doped secondary effluents. In fact, a  
284 complete removal of ACT was achieved after 8, 8, 15 and 20 min of treatment for  
285 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:  $0.640 \text{ min}^{-1}$  and  $0.629 \text{ min}^{-1}$  respectively) and lower kinetics for MWWTP and  
288 Urine MBR ( $0.374 \text{ min}^{-1}$  and  $0.314 \text{ min}^{-1}$  respectively). Brillas et al. have studied the  
289 anodic oxidation of ACT (with concentrations up to  $1 \text{ g.L}^{-1}$ ) 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  $0.013 \pm 0.002 \text{ min}^{-1}$ .  
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  $\text{Ti}_4\text{O}_7$  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 ( $157 \text{ mg.L}^{-1}$ ) by electro-Fenton  
299 and photo-electro-Fenton processes using a cell with a Pt anode and an  $\text{O}_2$  diffusion  
300 cathode for  $\text{H}_2\text{O}_2$  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  $\text{Ti}_4\text{O}_7$ , which has a much greater potential than Pt for  
307 generating large amounts of hydroxyl radicals at the anode surface [18, 34].

308 The variation in the required time for the complete removal of ACT in the different  
309 effluents is mainly due to the composition of the treated water as well as to the process  
310 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**

330 The evolution of the toxicity during the treatment of ACT-doped real effluents by EF/AO  
331 was evaluated by the Microtox® method (Figure 3). The three raw effluents doped with  
332 ACT showed relatively low luminescence inhibition to *V. fischeri* bacteria (< 10%) which  
333 is in good accordance with EC50 observed in the literature for paracetamol on *V. fischeri*  
334 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<sup>-</sup> 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].

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

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

364 Overall, these results highlight that the nature and composition of the effluent might be  
365 also crucial parameters for the evolution of the toxicity during a tertiary treatment  
366 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).

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

378 As shown on figure 5, molecules with fluorophores of zone I' are less degraded during  
379 EAOPs than fluorophores associated with zones II' and III'. In previous studies, we have  
380 already observed that EAOPs lead to a slow decrease of colloidal proteins from zone I' due to  
381 lower availability of colloids for reaction with  $\cdot\text{OH}$  in the liquid phase. Besides, a fast  
382 decrease of fluorophores of zone II' and III' was observed because of the degradation and

383 mineralization of these compounds with an aromatic structure that reacts quickly with  $\cdot\text{OH}$   
384 and active chlorine [20; 42]. Humic substances found in WWTP effluent are mainly  
385 biorefractory (because they have not been degraded during secondary treatment) with high  
386 stability and aromaticity. Those substances, known as potentially cytotoxic, are transformed  
387 into more biodegradable and small-molecule DCOM (fulvic-like substances and protein-like  
388 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  $\text{kWh m}^{-3}$ ) 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  $2.0 \text{ kWh m}^{-3}$  for MWWTP MBR, Urine MBR and  
401 MWWTP effluents, respectively. By comparison, the average energy consumption of a  
402 conventional MWWTP is about  $0.6\text{-}1 \text{ kWh m}^{-3}$  [43]. The energy consumption can be  
403 increased to  $2 \text{ kWh m}^{-3}$  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<sup>-3</sup>. 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 Ti<sub>4</sub>O<sub>7</sub> 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  
425 TOC was observed for MWWTP and MWWTP MBR effluents (90 ± 15 %, 76 ± 3.8 %  
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 fischeri* 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<sup>-1</sup>. 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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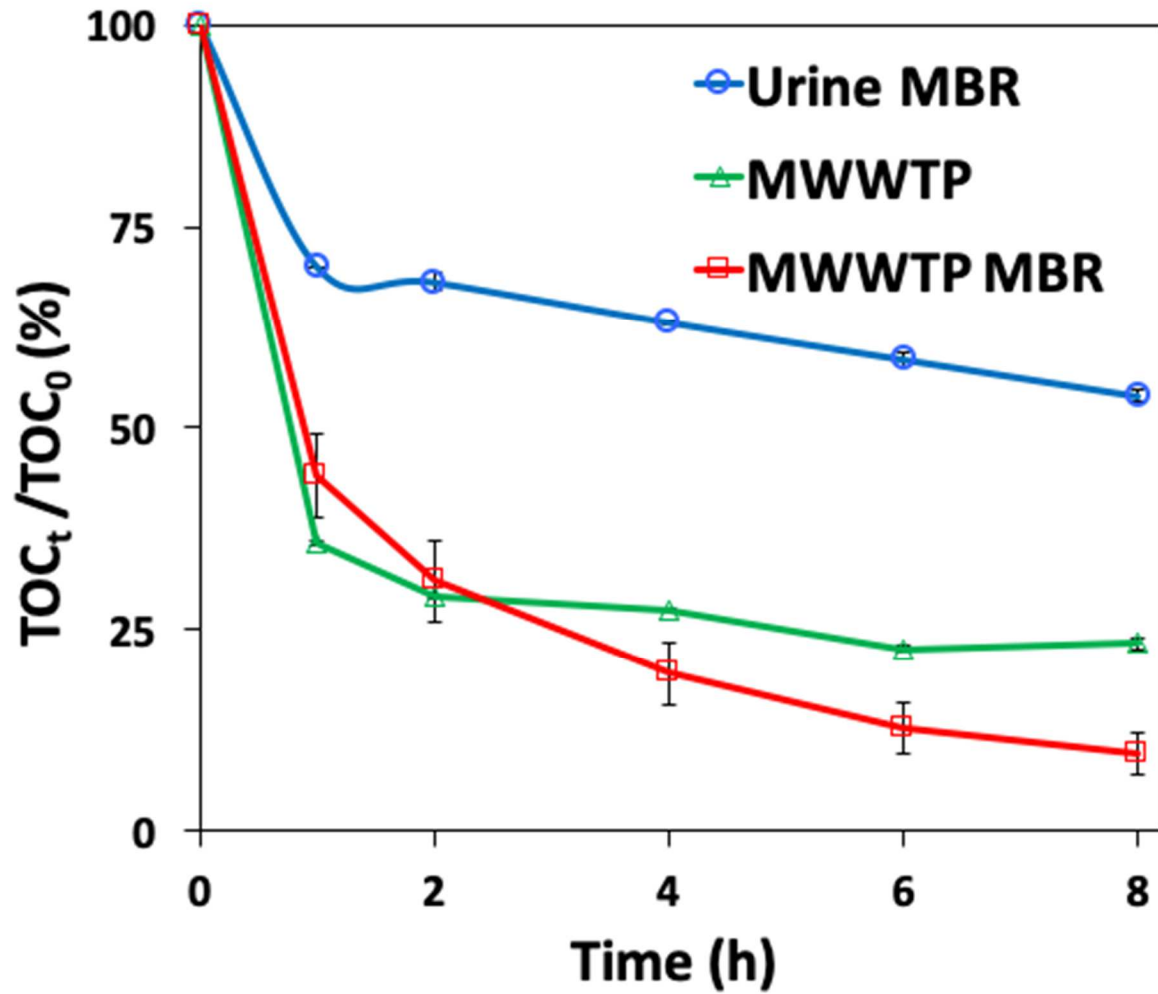


Figure 1: Mineralization of acetaminophen-doped ( $[ACT]_0 = 10 \text{ mg L}^{-1}$ ) real effluents by electro-Fenton/anodic oxidation (EF/AO) process. A – Urine MBR,  $[TOC]_0 = 80 \text{ mgC L}^{-1}$ ; B – MWWTP MBR,  $[TOC]_0 = 12 \text{ mgC L}^{-1}$ ; C – MWWTP,  $[TOC]_0 = 22 \text{ mgC L}^{-1}$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

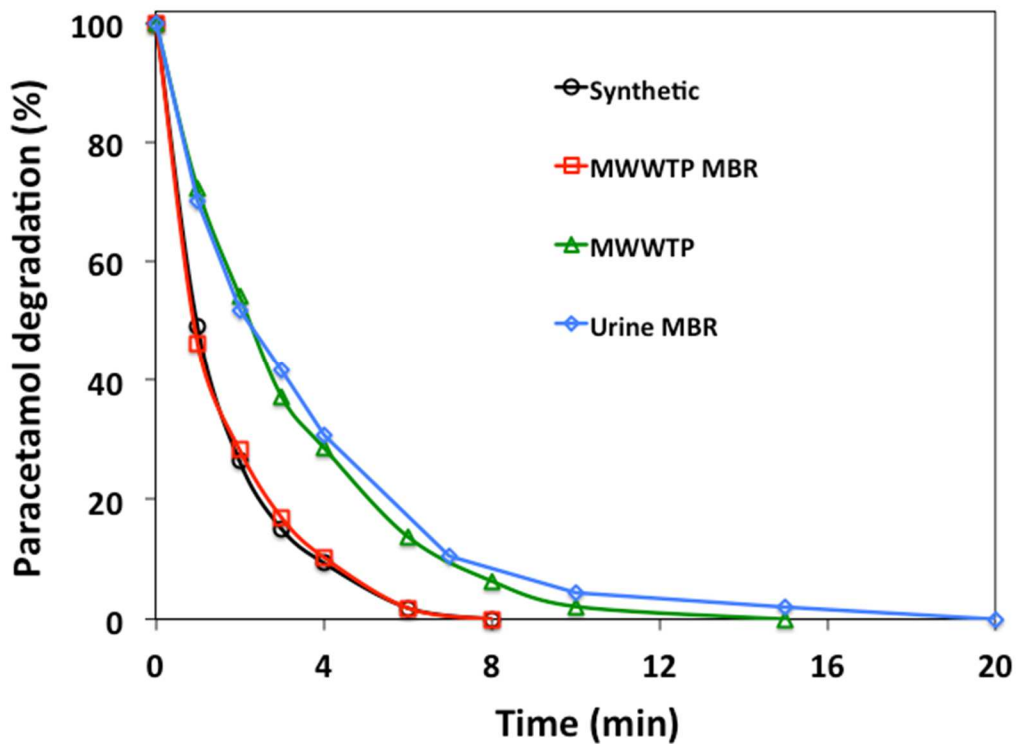


Figure 2: Degradation of acetaminophen ( $[ACT]_0 = 10 \text{ mgC L}^{-1}$ ) in synthetic solution ( $[Na_2SO_4] = 50 \text{ mM}$  + milli-Q water) and acetaminophen-doped real matrix (Urine MBR,  $[TOC]_0 = 80 \text{ mgC L}^{-1}$ ; MWWTP MBR,  $[TOC]_0 = 12 \text{ mgC L}^{-1}$ ; MWWTP,  $[TOC]_0 = 20 \text{ mgC L}^{-1}$ ) by electro-Fenton/anodic oxidation process.  $I = 250 \text{ mA}$  ;  $[Fe^{2+}] = 0.2 \text{ mM}$  ;  $pH = 3$ .

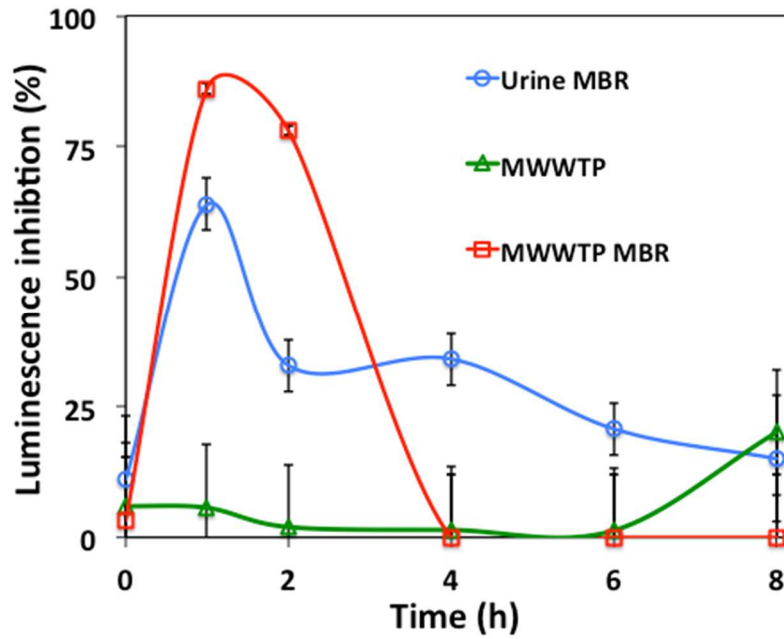


Figure 3: Mircrotox® analysis. Evolution of *Vibrio fisheri* luminescence inhibition (15 min exposure) during the treatment of acetaminophen-doped real effluents by anodic oxidation/electro-Fenton process.  $I = 250 \text{ mA}$  ;  $[\text{Fe}^{2+}] = 0.2 \text{ mM}$  ;  $\text{pH} = 3$ . RSD ( $n = 5$ ): 12% for inhibition  $< 20\%$ ; 5% for  $20\% < \text{inhibition} < 70\%$  and 1% for inhibition  $> 70\%$ .

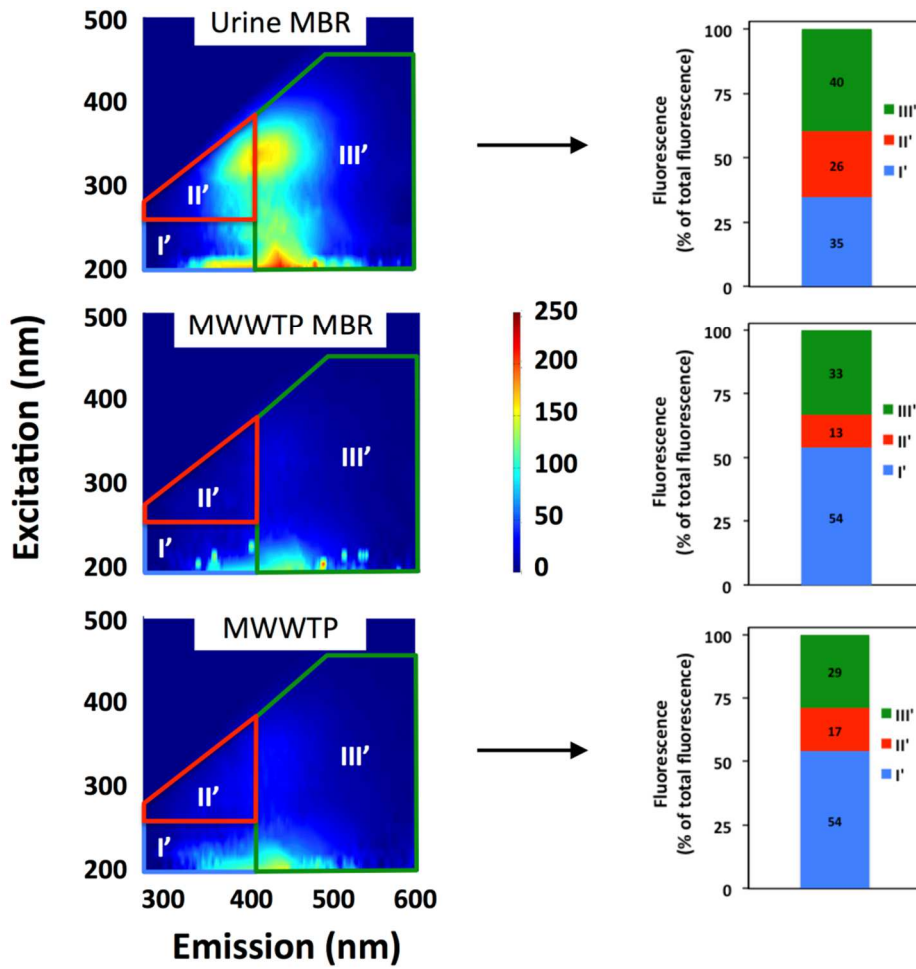


Figure 4 – Initial 3D fluorescence map of acetaminophen-doped real effluents and quantification of volume of fluorescence for zones I', II' and III' (% of total volume of fluorescence).



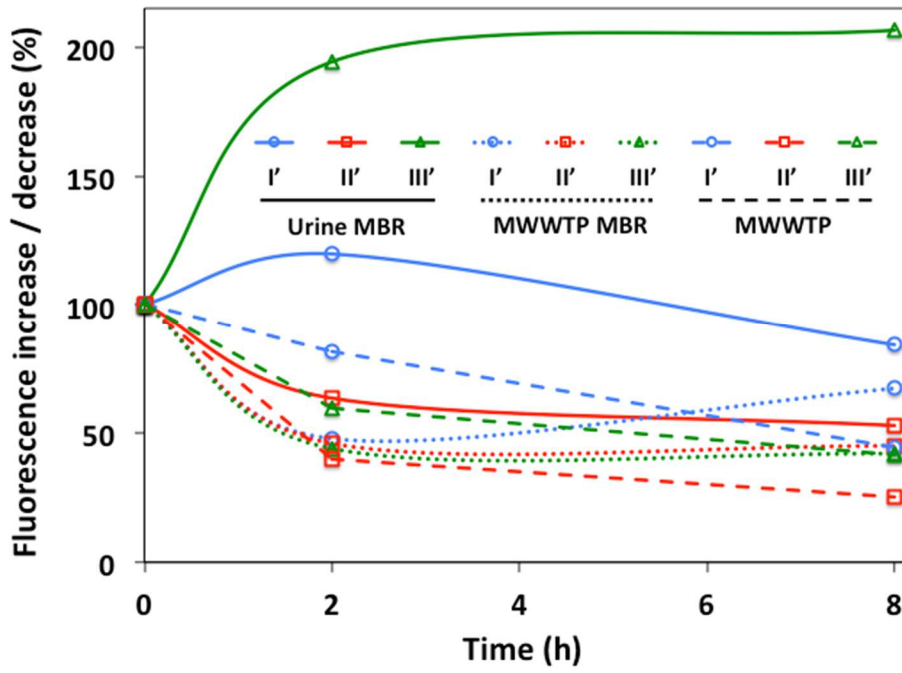


Figure 5 – Volume of fluorescence evolution (zones I', II', III') during the treatment of acetaminophen-doped real effluents by anodic oxidation/electro-Fenton (AO/EF) process.

$I = 250 \text{ mA}$  ;  $[\text{Fe}^{2+}]_0 = 0.2 \text{ mM}$  ;  $\text{pH} = 3$ .

Table 1 – MWWTP, MWWTP MBR and Urine MBR effluents main characteristics

Effluent	pH	$\sigma$ mS cm <sup>-1</sup>	[Cl <sup>-</sup> ] mg L <sup>-1</sup>	COD mgO <sub>2</sub> L <sup>-1</sup>	TOC mgCL <sup>-1</sup>	[NO <sub>3</sub> <sup>-</sup> ] mgNL <sup>-1</sup>	[NO <sub>2</sub> <sup>-</sup> ] mgNL <sup>-1</sup>	[NH <sub>4</sub> <sup>+</sup> ] mgNL <sup>-1</sup>	MLSS mg L <sup>-1</sup>
Urine MBR	7.0 ±0.2	12.8 ±2.6	4380 ±481	150 ±11.2	75.2 ±5.3	1200 ±160	<LOQ	38 ±12	2.3 ±1.0
MWWTP	7.2 ±0.2	4.1 ±0.5	267 ±37	50.3 ±8.1	17.2 ±1.2	1.8 ±0.9	<LOQ	55 ±14	33.2 ±2.1
MWWTP MBR	7.4 ±0.3	3.2 ±0.3	586 ±65	19.1 ±2.7	7.4 ±0.8	5.8 ±1.9	0.1 ±0.1	1.8 ±1.7	1.5 ±1.0

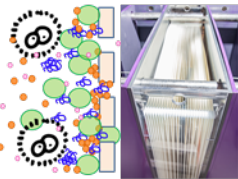
$\sigma$ : Conductivity ; LOQ: Limit of Quantification ; MLSS: Mixed Liquor Suspended Solid

Tableau 2: Comparison of TOC removal of the synthetic solution of ACT after 8 h of treatment by electro-Fenton (EF), anodic oxidation/H<sub>2</sub>O<sub>2</sub> (AO/H<sub>2</sub>O<sub>2</sub>) and electro-Fenton/anodic oxidation (EF/AO) processes. ACT<sub>0</sub> = 10 mg L<sup>-1</sup> ; I = 250 mA ; [Na<sub>2</sub>SO<sub>4</sub>] = 50 mM ; [Fe<sup>2+</sup>]<sub>0</sub> = 0.2 mM or 0 mM (for AO/H<sub>2</sub>O<sub>2</sub>) ; pH = 3.

TOC removal after 8 h (%)	
EF	76 ± 5
AO/H <sub>2</sub> O <sub>2</sub>	81.0 ± 3.4
EF/AO	87 ± 2.7



## Membrane Bioreactor



*Urine-MBR*

$[TOC]_0 = 80 \text{ mgC L}^{-1}$

*WWTP-MBR*

$[TOC]_0 = 12 \text{ mgC L}^{-1}$

*WWTP :  $[TOC]_0 = 22 \text{ mgC L}^{-1}$*

EAOP\*

*Carbon Felt  
cathode*

$[ACT]_0 10 \text{ mgC L}^{-1}$

*Ti<sub>4</sub>O<sub>7</sub> anode*

\*EAOP: Electrochemical Advanced Oxidation Process