



Electro-oxidation of secondary effluents from various wastewater plants for the removal of acetaminophen and dissolved organic matter

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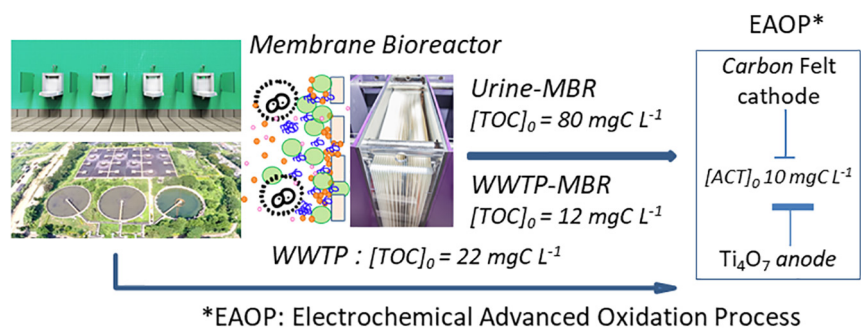
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HIGHLIGHTS

- Biorefractory effluents were successfully treated by EF process coupled to AO.
- 3DEEM could be a global tool to investigate a domestic effluent along its treatment.
- ACT, TOC, acute toxicity and 3DEEM evolution were monitored for different effluents.
- Toxic recalcitrant by-products were identified during Urine MBR effluents treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

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

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1. Introduction

Over the past decade, the effectiveness of wastewater treatment systems has been questioned by many researchers, particularly in terms of

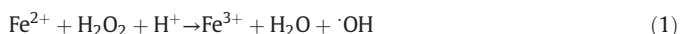
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removing emerging contaminants (pesticides, pharmaceuticals, endocrine disrupting compounds, ...) often detected in treated effluents. Conventional physical, chemical or biological treatment systems are unable to efficiently eliminate these contaminants and there is often a transfer of pollution from one phase to another (liquid to solid phase or vice-versa) or an incomplete degradation of these contaminants. Several researchers have reported that the exposure, especially in long term, to emerging contaminants such as personal care products, pharmaceuticals and hormones causes disruption of aquatic fauna and flora and risks to human health. As reported by [Tiwari et al. \(2017\)](#) and [Solano et al. \(2016\)](#), prolonged exposure to pharmaceutical residues results in a change in the species character and behavior of aquatic organisms. The feminization of male fish due to the presence of estrogen in the aquatic environment is a well-known example of trait change in species ([Gross-Sorokin et al., 2005](#)). The development of bacterial resistance to antibiotics is also a major risk of exposure to pharmaceutical residues in the environment. To overcome this problem, additional, efficient and sustainable treatments of wastewater treatment plant (WWTP) secondary effluents are necessary to improve the quality of the effluents before their release into the environment.

Electrochemical advanced oxidation processes (EAOPs) represent an attractive solution for tertiary treatment of treated effluents ([Solano et al., 2016](#); [Brillas et al., 2016](#); [Sires et al., 2014](#); [Ganzenko et al., 2015](#)). These processes are considered environmentally friendly as they require little or no added chemicals like H_2O_2 for the Fenton reaction or O_3 for ozonation. The advantages of such processes are their non-polluting appearance, ease of automation and reduced processing times. The principle of EAOPs consists into the in situ electrochemical generation of reagents, particularly hydroxyl radicals $\cdot OH$, which are considered as the second most powerful oxidizing species after fluorine ($E^\circ(\cdot OH/H_2O) = 2.80 \text{ V / SHE}$) ([Yahya et al., 2016](#); [Brillas et al., 2009](#)). 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. ([Oturán et al., 2013](#); [Annabi et al., 2016](#); [Panizza et al., 2014](#)). 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 Fe^{2+} initially added is also continuously regenerated (Eq. (3)).

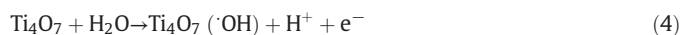


The chemical nature of the anode is also a key parameter for the efficiency of the electrochemical process ([García-Gómez et al., 2014](#)). Several types of anodes can be used during electrolysis, which are divided into two categories, active and non-active ([Komtchou et al., 2015](#); [Jardak et al., 2016](#); [Ouarda et al., 2017](#)). Non-active anodes are characterized by their inert surface and their low adsorption properties, resulting in a weak interaction between the produced hydroxyl radicals and the surface of the anode. Thus, the physisorbed hydroxyl radicals react easily with the organic pollutants, resulting in a complete mineralization of pollutants ([Salazar et al., 2016](#)). On the other hand, hydroxyl radicals are not efficiently formed at active anodes such as Ti/IrO_2 and Ti/RuO_2 . However, they promote efficient conversion of chloride present in wastewater, to hypochlorous acid or hypochlorite ions that can oxidize organic pollutants ([Boudreau et al., 2010](#)).

In this study, we have mainly investigated the treatment of secondary effluents by the electro-Fenton process combined with anodic oxidation (AO) by using sub-stoichiometric titanium oxide anode (Ti_4O_7).

Ti_4O_7 has been reported to be a suitable non-active anode (Eq. (4)) in EF process for the removal of pharmaceuticals such as propranolol and sulfamethoxazole ([Ganiyu et al., 2017](#); [Ganiyu et al., 2018](#); [Trellu et al., 2018a](#)). This material has the potential to be a low cost alternative to the well-known boron-doped diamond electrode ([Ganiyu et al., 2017](#)). Moreover, it is possible to synthesize porous Reactive Electrochemical Membranes (REM), which allow a strong enhancement of mass transport conditions when operated in flow-through mode for the treatment of low concentrations of pollutants. Unprecedented high removal rates of total organic carbon and mineralization current efficiency were achieved on REM (without coupling with EF process) after a single passage through the membrane for ACT, phenol and oxalic acid ([Trellu et al., 2018a](#)). While further development of REM is a promising challenge, it is also important to continue to raise understanding on reaction 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/H_2O_2). For the EF process, a Ti/Pt plate anode was used instead of Ti_4O_7 . For the AO/H_2O_2 , none Fe^{2+} was added, thus avoiding the decomposition for H_2O_2 by the Fenton's reaction.



WWTP secondary effluents were sampled from three different wastewater treatment systems, including an effluent from a full-scale WWTP using activated sludge ($[TOC^\circ] = 17 \text{ mgC L}^{-1}$), another from a full-scale WWTP using a membrane bioreactor (MBR) ($[TOC^\circ] = 7 \text{ mgC L}^{-1}$) and a third from a lab-scale membrane bioreactor (MBR) treating real source-separated urine ($[TOC^\circ] = 75 \text{ mgC L}^{-1}$). The three effluents were then doped with acetaminophen (ACT) as indicator of pharmaceutical pollutant. Results were also compared with a synthetic effluent containing only ACT and Na_2SO_4 as electrolyte. ACT (also known under the name of paracetamol) was selected as pharmaceutical contaminant because it is usually detected in wastewater treatment plants, natural water resources and rivers with concentrations varying from 6 to 65 $\mu\text{g L}^{-1}$ ([Le et al., 2017](#); [García-Mateos et al., 2015](#); [Roberts and Thomas, 2006](#)). Unfortunately, it is impossible to easily determine the degree of mineralization of ACT at a concentration of about 100 $\mu\text{g L}^{-1}$ by TOC analysis in effluents containing from 7 to 75 mgC L^{-1} . Then, based on our previous study ([Le et al., 2017](#)), we used a concentration of ACT of 10 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-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) ([Henderson et al., 2011](#); [Henderson et al., 2009](#); [Hao et al., 2012](#)). 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 ([Jacquin et al., 2017](#)).

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).

2. Materials and methods

2.1. Chemicals

All chemicals were reagent grade purchased from Sigma Aldrich (acetaminophen, Na₂SO₄, trifluoroacetic acid, acetonitrile) or Alfa Aesar (Fe₂SO₄·7H₂O). Synthetic solutions were prepared with pure water (Milli-Q, Millipore Co. Ltd, resistivity > 18.2 MΩ cm).

2.2. Secondary effluents from various wastewater plants

Three different effluents were used in this study. Two effluents were provided by two municipal wastewater treatment plants in the area of Montpellier, France: the first uses conventional activated sludge process (medium organic loading rate) and the second one uses MBR (continuous aeration, chlorinated PES UF membrane (Kubota, Japan)), they are referenced MWWTP and MWWTP MBR respectively. The third effluent was from a lab-scale MBR treating real source-separated urine and is named Urine MBR. A 4-L submerged MBR, equipped with a flat-sheet microfiltration membrane module made of PVDF (A3 Company, USA), was fed with fresh urine for a period of 120 days (Jacquin et al., 2018). More details concerning this effluent could be found in a previous study (Jacquin et al., 2018). 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.

2.3. Electrochemical setup

Experiments were performed using an undivided 500-mL single cylindrical glass with a two-electrode system. Ti₄O₇ plate (for EF/AO and AO/H₂O₂ processes) and platinised titanium mesh (Ti/Pt) (for EF process) anodes with a surface area of 24 cm² (4 cm × 6 cm), were provided by Saint Gobain Research Provence (France) and Goodfellow SARL (France) respectively. The Ti₄O₇ film was synthesized as follow: a mixture of TiOx (x < 2) particles in the range 20–60 μm prepared as described in (Ganiyu et al., 2016) was used to make a plasma coating on a Ti substrate (4 cm × 6 cm) pretreated by sandblasting to create a rough surface. In the conditions described in (Ganiyu et al., 2016), a continuous thick film of 100 μm and 95% density was obtained. X-ray diffraction of the prepared electrode shows that the main phase was Ti₄O₇ with the presence of TiO₂ rutile and Ti₃O₅. The typical electronic conductivity of the plasma-sprayed coating, determined by the four-probes method, is 10⁻³ Ω cm. Carbon-felt cathodes with a surface area of 126 cm² (21 cm × 6 cm) and thickness of 0.5 cm, were provided by Alfa Aesar. In all experiments, the cathode covered the inner wall of the cell while the anode was in the center, similarly to the configuration reported in several articles (Brillas et al., 2009; Oturan et al., 2013; Ganiyu et al., 2018; Sirés et al., 2007; Oturan et al., 2008; Olvera-Vargas et al., 2015). The agitation and homogenization of the solution was carried out using a magnetic PTFE stirrer during electrolysis. Experiments were carried out at room temperature with 250 mL of secondary effluents from various wastewater plants doped with 10 mg L⁻¹ of ACT

as well as with the same volume of a synthetic solution containing 10 mg L⁻¹ of ACT in 50 mM of Na₂SO₄ as supporting electrolyte. The solutions were continuously saturated with O₂ by bubbling compressed air at atmospheric pressure at about 1 L min⁻¹. Iron (II) (0.2 mM) was added as catalyst to perform EF and EF/AO processes. Additions of aliquots of a commercial concentrated solution of sulfuric acid (Sigma Aldrich 96% pure) were done to adjust the pH at 3. The ionic strength (I) was different for the four media. For the synthetic effluent, I was fixed by the 50 mM of Na₂SO₄ used as electrolyte (I = 0.15). For Urine MBR, MWWTP and MWWTP MBR effluents, I was determined from the ionic concentration of 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 MWWTP and I = 0.016 for MWWTP MBR. Because of the difference in ionic strength, the solution resistance varied from one effluent to the other. Resistance of the different systems are 19.6, 19.5, 27.2, 26.6 Ω for the synthetic solution, Urine MBR, MWWTP and MWWTP MBR effluents respectively.

2.4. ACT quantification

Concentrations of ACT and its by-products were analyzed by high-performance liquid chromatography (Waters 717 Autosampler and Waters 616 Pump) with a reverse phase C18 column (Thermo Scientific), thermostated at 30 °C, coupled with a UV detector (photodiode array detector Waters 2996). The injection volumes were 20 μL and the 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 mode in order to ensure the proper separation of acetaminophen and p-benzoquinone (degradation by-product).

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.

2.6. Characterization of the natural organic matter by 3DEEM

Three-dimensional excitation and emission matrix fluorescence (3DEEM) using a Perkin-Elmer LS-55 spectrometer (USA) was used for characterizing DCOM. For 3DEEM analysis, samples were filtered through 1.2 μm glass microfiber filters (Whatman GF/C) and diluted by a factor 60. The procedure reported by (Jacquin et al., 2017) was used for fluorescence spectra acquisition and data extraction based on the division of the 3D fluorescence spectra representation into three different areas corresponding to different groups of fluorophores (Chen et al., 2003). Jacquin et al. have recently developed a semi-quantitative method for the assessment of the amount of fluorophores associated with DCOM in real effluents (Jacquin et al., 2017). This method is based on the calculation of the volume of fluorescence in zones I', II' and III' and was applied in the present work. Zone III' volume of

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

Effluent	pH	σ mS cm ⁻¹	[Cl ⁻] mg L ⁻¹	COD mgO ₂ L ⁻¹	TOC mgC L ⁻¹	[NO ₃ ⁻] mgN L ⁻¹	[NO ₂ ⁻] mgN L ⁻¹	[NH ₄ ⁺] mgN L ⁻¹	MLSS mg L ⁻¹
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

σ: conductivity; LOQ: limit of quantification; MLSS: mixed liquor suspended solid.

fluorescence (HA + FA-like fluorophores) is correlated to humic substances concentration (MW \approx 1000 Da) and degradation by-products from humic substances (hydrophobic compounds, MW \approx 300–500 Da). Similarly, a correlation exists between the volume of fluorescence of zone II' (SMP-like fluorophores) and the concentration of proteins from biopolymers (MW \approx 20,000–7.5 \times 10¹¹ Da). Finally, volume of fluorescence of zone I' is associated with colloidal proteins, which are the bigger and more hydrophilic compounds present in DCOM.

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 fischeri* is directly related to cellular respiration and cell activity. Thus, this method is based on the measure of the inhibition of *Vibrio fischeri* luminescence. Samples were diluted at 45% by adding a 22% NaCl solution. The pH of all samples was adjusted between 6.5 and 7.5 with sodium hydroxide (NaOH, 1 N). Measurements and data extraction were performed as reported in the study of García-Gómez et al. (2014).

2.8. Energy consumption

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

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

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

3. Results and discussion

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 h 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

Table 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. ACT₀ = 10 mg L⁻¹; I = 250 mA; [Na₂SO₄] = 50 mM; [Fe²⁺]₀ = 0.2 mM or 0 mM (for AO/H₂O₂); pH = 3.

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

in wastewater until their complete mineralization (transformation into CO₂) (Sires et al., 2014; Ouarda et al., 2017; Ganiyu et al., 2017; Bejan et al., 2009).

In this study, several current intensities were also tested (100, 250 and 300 mA) for treatment of the synthetic solution (data not shown). The best results, in terms of TOC removal, were obtained using a current intensity of 250 mA. Similar results were reported by Komtchou et al. (2015) during the electrolysis of carbamazepine where the electrodes surface was 113 cm². The highest removal rates were observed with 200 mA compared to 500, 1000 and 2000 mA. Generally, increasing the current intensity has a positive effect on electrochemical degradation of pollutants because a greater amount of hydroxyl radicals is produced when applying higher current intensities. However, researchers have reported that increasing current intensity usually decreases the energy-efficiency of the process because side reactions (mainly oxygen and hydrogen evolution reactions) and parasitic reactions (hydroxyl radical dimerization, reaction of hydroxyl radicals with excess H₂O₂) are also promoted (Quand-Même et al., 2015). Therefore, for the next experiments, a current intensity of 250 mA was chosen as the optimal current intensity for simultaneous regeneration of Fe²⁺, production of H₂O₂ at the cathode and generation 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 three different wastewater treatments plants.

As shown in Fig. 1, a rapid decrease of TOC was observed within the first hour of electrolysis for all the different wastewaters. In fact, a removal rate of 64 ± 0.5%, 56 ± 5.3% and 30 ± 0.5% was obtained for MWWTP MBR (curve B), MWWTP (curve C) and Urine MBR (curve A), respectively. At longer times, mineralization rate slowly increased, which is usually ascribed to the formation of degradation by-products such as short-chain carboxylic presenting lower reaction kinetics with hydroxyl radicals. Similar behaviors were reported in previous studies regarding the removal of propranolol and acetaminophen by EAOPs (Ganiyu et al., 2017; Sirés et al., 2004). The authors reported a similar phenomenon with an initial rapid drop of the TOC concentration during the first hour, which was then 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 8 h of electrolysis, most probably because of the presence of DCOM recalcitrant to oxidation. Under the same experimental conditions, higher mineralization (curve B and C) was obtained for the effluents from

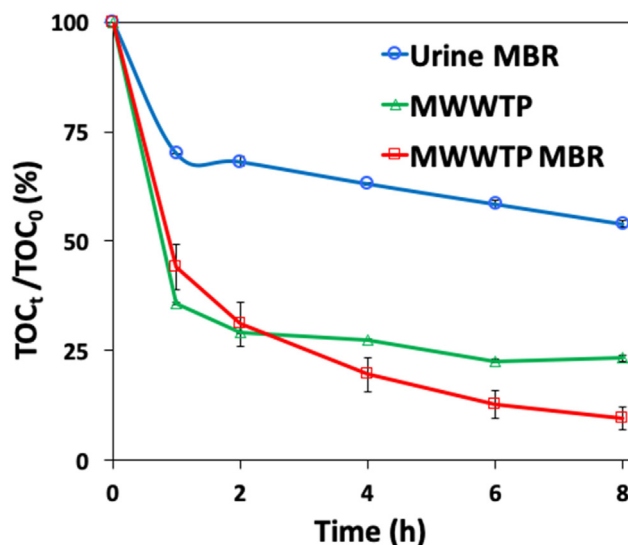


Fig. 1. Mineralization of acetaminophen-doped ([ACT]₀ = 10 mg L⁻¹) real effluents by electro-Fenton/anodic oxidation (EF/AO) process. A - Urine MBR, [TOC]₀ = 80 mgC L⁻¹; B - MWWTP MBR, [TOC]₀ = 12 mgC L⁻¹; C - MWWTP, [TOC]₀ = 22 mgC L⁻¹; I = 250 mA; [Fe²⁺] = 0.2 mM; pH = 3.

MWWTP MBR and MWWTP with a TOC removal of about $76 \pm 1\%$ and $90 \pm 3\%$, respectively. It is important to note that the initial concentration of TOC in Urine MBR effluent doped with ACT was 80 mgC L^{-1} while for the other two effluents this concentration was 22 mgC L^{-1} and 12 mgC L^{-1} for MWWTP and MWWTP MBR, respectively. Thus, 20 to 40% of initial TOC was ascribed to ACT for these latter, while for Urine MBR, 94% of initial TOC was ascribed to the residual DCOM that was not eliminated during the treatment of urine by the MBR.

Fig. 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 similar kinetic for the synthetic solution and MWWTP MBR (Apparent first order kinetic rate: 0.640 min^{-1} and 0.629 min^{-1} respectively) and lower kinetics for MWWTP and Urine MBR (0.374 min^{-1} and 0.314 min^{-1} respectively). Brillas et al. have studied the anodic oxidation of ACT (with concentrations up to 1 g L^{-1}) in a cell with a BDD or Pt anode and a graphite cathode (Brillas et al., 2005). Results showed a complete removal of acetaminophen after 120 to 240 min of electrolysis with the BDD anode and after 240 to 360 min with the Pt anode (pseudo-first order rate constant was $0.013 \pm 0.002 \text{ min}^{-1}$). In both case, the time required for ACT elimination was much longer than in our study. The faster degradation of ACT can be explained by (i) the lower concentration of ACT in our study and (ii) the production of large amount of both heterogeneous and homogeneous hydroxyl radicals from anodic oxidation at the Ti_4O_7 anode (Ganiyu et al., 2017) and electrochemically induced Fenton's reaction in the bulk solution (Eq. (1)). Besides, Sirés et al. (2004) have studied the degradation of ACT solution (157 mg L^{-1}) by electro-Fenton and photo-electro-Fenton processes using a cell with a Pt anode and an O_2 diffusion cathode for H_2O_2 electro-generation. A complete removal was observed after 20–25 min of process. The authors confirmed that ACT was mainly eliminated by the hydroxyl radicals during electrolysis and that UVA lighting did not contributed significantly. The electrolysis time required for the total removal of acetaminophen in the aqueous solution reported was also longer than that obtained in this study (8 min vs 20–25 min). It might be ascribed to (i) the lower concentration level of ACT in our study and (ii) the use of a non-active anode such as Ti_4O_7 , which has a much greater potential than Pt for generating large amounts of hydroxyl radicals at the anode surface (Ganiyu et al., 2017; Bejan et al., 2009).

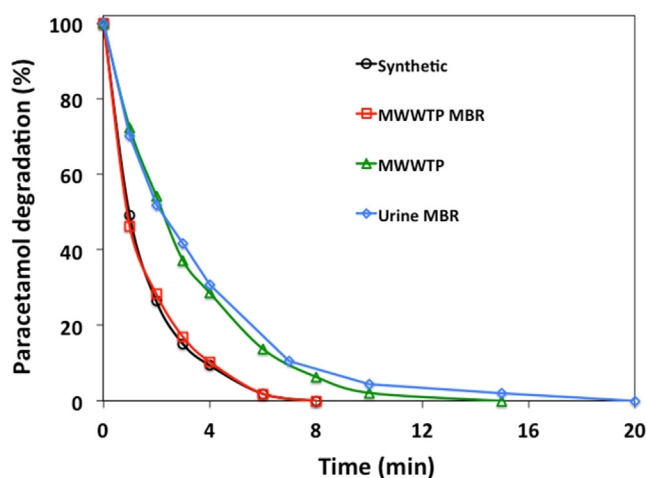


Fig. 2. Degradation of acetaminophen ($[\text{ACT}]_0 = 10 \text{ mgC L}^{-1}$) in synthetic solution ($[\text{Na}_2\text{SO}_4] = 50 \text{ mM}$ + milli-Q water) and acetaminophen-doped real matrix (Urine MBR, $[\text{TOC}]_0 = 80 \text{ mgC L}^{-1}$; MWWTP MBR, $[\text{TOC}]_0 = 12 \text{ mgC L}^{-1}$; MWWTP, $[\text{TOC}]_0 = 20 \text{ mgC L}^{-1}$) by electro-Fenton/anodic oxidation process. $I = 250 \text{ mA}$; $[\text{Fe}^{2+}] = 0.2 \text{ mM}$; $\text{pH} = 3$.

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

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 (Fig. 3). The three raw effluents doped with ACT showed relatively low luminescence inhibition to *V. fischeri* bacteria ($< 10\%$) which is in good accordance with EC_{50} observed in the literature for paracetamol on *V. fischeri* with values around 100 mg L^{-1} (Nunes et al., 2014). However, luminescence inhibition increased rapidly after 1 h of treatment to reach $85\% (+ - 1\%)$ and $65\% (+ - 5\%)$, for MWWTP MBR and Urine MBR effluents respectively. This strong increase in bacterial inhibition can be attributed to the formation of degradation by-products that may be more toxic than parent compounds (Dirany et al., 2011; Dirany et al., 2012). The stronger increase of toxicity in Urine MBR effluent might be ascribed to the formation of further toxic N-containing and

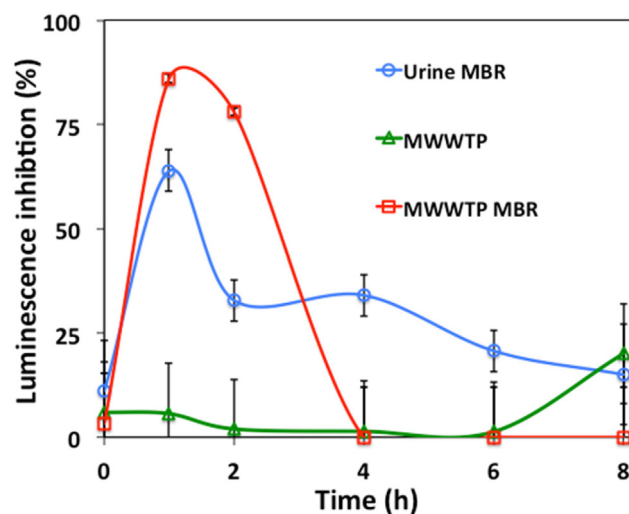


Fig. 3. Microtox® analysis. Evolution of *Vibrio fischeri* luminescence inhibition (15 min exposure) during the treatment of acetaminophen-doped real effluents by anodic oxidation/electro-Fenton process. $I = 250 \text{ mA}$; $[\text{Fe}^{2+}] = 0.2 \text{ mM}$; $\text{pH} = 3$. RSD ($n = 5$): 12% for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

halogenated organic by-products because of the higher N and Cl content of this effluent (Table 1). Luminescence inhibition may also come from the presence of residual oxidants generated during electrolysis such as HClO resulting from the oxidation of Cl⁻ ions present in the effluents. Subsequently, luminescence inhibition decreased during electrolysis to reach around 20% (+5%) for Urine MBR after 8 h of treatment, while a quasi-zero (+12%) luminescence inhibition was observed for MWWTP MBR after 4 h of process. The slower decrease of the toxicity in the Urine MBR effluent might be explained by the formation of toxic degradation by-products that are more recalcitrant to oxidation. This phenomenon is consistent with the slow decrease of the TOC between 1 and 8 h of treatment of this effluent (Fig. 1). Such increase in the toxicity of an ACT solution was also reported by Hamdi El Najjar et al. (2014) during the oxidation by ozone and hydroxyl radicals. The authors observed a gradual increase in toxicity up to nearly 64% inhibition of luminescence bacteria after <20 min because of the formation of degradation by-products more toxic than ACT (Roberts and Thomas, 2006). Recently, García-Gómez et al. identified the aromatic compounds 2-hydroxy-4-(N-acetyl) aminophenol, 1,4-benzoquinone, benzaldehyde and benzoic acid as the toxic sub-products formed from ACT degradation at the first stage of the electrochemical treatment and responsible of toxicity enhancement (García-Gómez et al., 2014).

Luminescence inhibition of the MWWTP effluent during EF/AO process shows a singular behavior. The high concentration of MLSS of this effluent may explain why the toxicity was very low during the first 6 h of treatment (Table 1). Indeed, particulate organic matter might be preferentially oxidized without production of toxic by-products. After 6 h 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.

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

3DEEM has been reported to be a useful tool for characterization of dissolved and colloidal organic matter (DCOM) in real WWTP effluents (Jacquin et al., 2017) and is used in this study to follow the scavenging effect of DCOM during EAOPs (Figs. 4 and 5).

The initial MWWTP and MWWTP MBR effluents show similar 3DEEM 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 (Maghsoodi et al., 2019), 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 Fig. 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 (Trellu et al., 2018a; Maghsoodi et al., 2019). 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 (Sid et al., 2017).

Fluorophores from zone I' and III' present in Urine MBR effluent shows an increase during the first 2 h of treatment. High Cl and N

concentration in Urine MBR led to the quick formation of by-products, which have some fluorophores in those zones. Then, between two to 8 h of treatment, fluorophores from zone I' decreased, while fluorophores from zone III' were stable. It means that by-products from these two zones have different oxidation rates during EAOPs. The stability of zone III' is consistent with the evolution of TOC removal (Fig. 1), which is fast during the first hour of treatment and shows a slight decrease after this first hour.

3.4. Energy consumption

Energy consumption (in term of kWh m⁻³) was calculated for each different effluent according to different objectives. For example, the energy required for >99% degradation of ACT was 1.1, 1.9 and 2.0 kWh m⁻³ for MWWTP MBR, Urine MBR and MWWTP effluents, respectively. By comparison, the average energy consumption of a conventional MWWTP is about 0.6–1 kWh m⁻³ (Sid et al., 2017). The energy consumption can be increased to 2 kWh m⁻³ for a MBR. Overall, the higher energy consumption related to the use of MBR could be almost offset by the cost reduction during the tertiary treatment related to the better quality of the secondary effluent. However, >99% of degradation should not be the only objective because of the potential toxicity of by-products. For an objective related to the acute toxicity (<5%) or the percent of mineralization (>80%), the energy consumption calculated for the MWWTP MBR effluent was strongly increased to 33 and 49 kWh m⁻³. Therefore, it is required to develop more cost-effective electrochemical processes for such application. In fact, the low concentration of pollutants in secondary effluents strongly reduces the efficiency of electro-oxidation processes because of mass transport limitations (Trellu et al., 2018b). Several studies currently focus on different ways to overcome this drawback, including pre-concentration of effluents by combination with the adsorption process (Trellu et al., 2018c) or using reactive electrochemical membranes for convection-enhanced mass transport of pollutants during AO. Another approach related to energy-consumption optimization is to develop milli- or microfluidic reactors in order to reduce the interelectrode distance (Mousset et al., 2019).

4. Conclusions

The electrochemical oxidation of ACT in different secondary effluents was successfully realized using EF/AO process with carbon felt cathode and Ti₄O₇ anode. The complete elimination of acetaminophen was achieved after 20 min of electrolysis for the three types of effluents (MWWTP, MWWTP MBR and Urine MBR). However, lower adverse effect from the organic matrix was observed for the MWWTP MBR effluent because of the higher effectiveness of the secondary treatment (MBR). A relatively high removal of TOC was observed for MWWTP and MWWTP MBR effluents (90 ± 15%, 76 ± 3.8% respectively) after 8 h treatment. However, only 46 ± 1.3% of TOC removal was achieved for Urine MBR effluent under the same conditions. An increase in acute toxicity during ACT oxidation was also observed. A higher increase was observed in Urine MBR effluent. This increase could be attributed to the formation of ACT degradation by-products during electrolysis. Then, further oxidation of these by-products reduced the acute toxicity of the solution and *Vibrio fischeri* luminescence inhibition reached quasi-zero (+12%) for MWWTP MBR and MWWTP. However, toxicity reduction was lower for Urine MBR and luminescence inhibition reached 20% (+5%) at the end of the treatment. Lower TOC removal and higher toxicity during the treatment of Urine MBR might be ascribed to the formation of N-containing and halogenated organic by-products with higher toxicity and lower reactivity for further oxidation by oxidant species generated during the treatment. This hypothesis was confirmed by 3DEEM results, which highlight the formation of recalcitrant degradation by-products during the treatment of Urine MBR. Such phenomenon was not observed during the treatment of MWWTP and MWWTP MBR

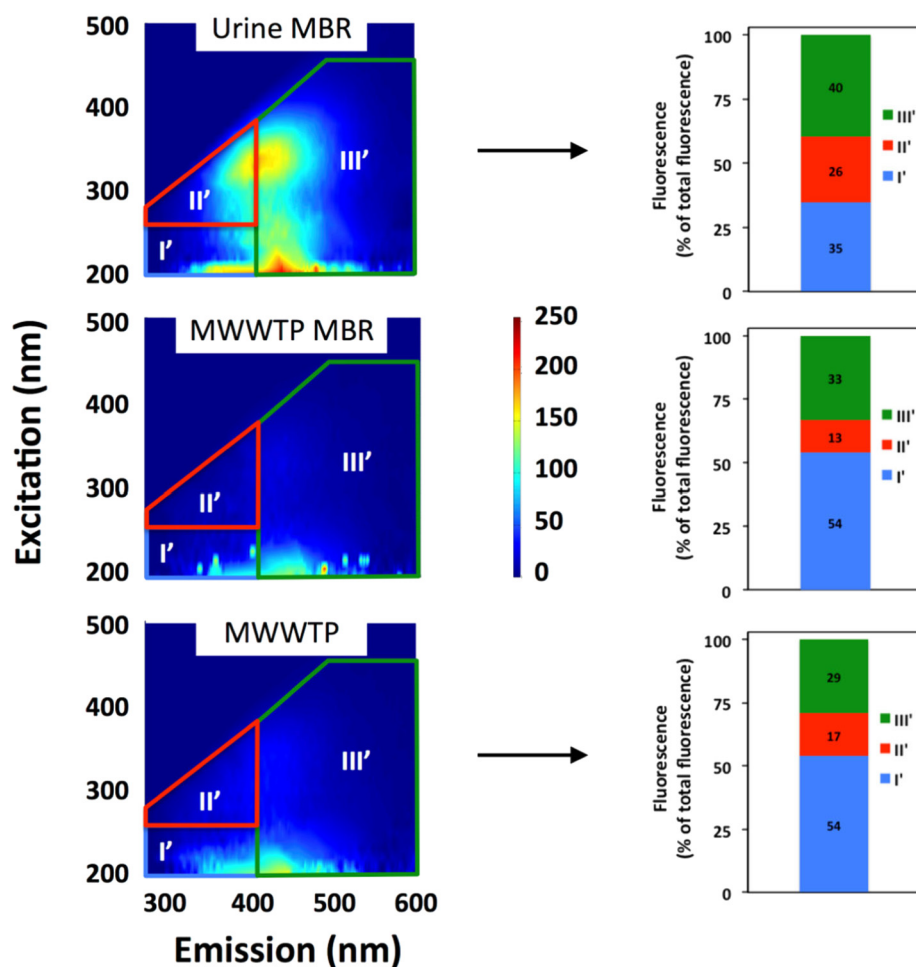


Fig. 4. Initial 3D fluorescence map of acetaminophen-doped real effluents and quantification of volume of fluorescence for zones I', II' and III' (% of total volume of fluorescence).

effluents. Overall, EF/AO process seems to be an effective technology for the treatment of ACT in municipal sewage effluents. Next scientific and technological challenges are related to the treatment of effluents without pre-treatment for pH adjustment. This approach is possible by coupling anodic oxidation with heterogeneous electro-Fenton process on carbon felt modified with iron based compounds like Layer Double

Hydroxide (LDH) as we recently proposed in (Ganiyu et al., 2018; Yang et al., 2020). It will be also necessary to improve the cost-efficiency of these processes, particularly for the treatment of effluents containing a cocktail of pollutants with concentration in the order of $100 \mu\text{g L}^{-1}$. For such low concentration of pollutants, REM operated in flow-through mode might be one of the most promising solutions.

CRedit authorship contribution statement

Yassine Ouarda: Investigation, Visualization. **Clément Trellu:** Investigation, Visualization. **Geoffroy Lesage:** Methodology, Validation, Supervision. **Matthieu Rivallin:** Methodology, Validation. **Patrick Drogui:** Supervision. **Marc Cretin:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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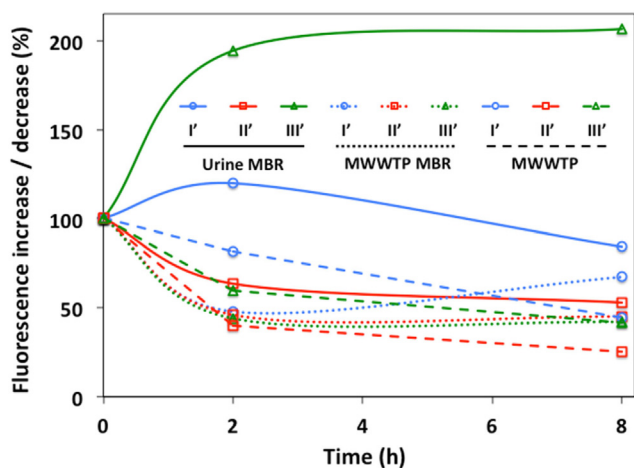


Fig. 5. Volume of fluorescence evolution (zones I', II', III') during the treatment of acetaminophen-doped real effluents by anodic oxidation/electro-Fenton (AO/EF) process. I = 250 mA; [Fe²⁺] = 0.2 mM; pH = 3.

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