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# Dynamic cross-flow electro-Fenton process coupled to anodic oxidation for wastewater treatment: Application to the degradation of acetaminophen

Hugo Olvera-Vargas<sup>a</sup>, Jean-Christophe Rouch<sup>a</sup>, Clémence Coetsier<sup>a,\*</sup>, Marc Cretin<sup>b</sup>,  
Christel Causserand<sup>a</sup>

<sup>a</sup> Laboratoire de Génie Chimique, CNRS, INPT, UPS, Université de Toulouse, 118 route de Narbonne, F-31062 Toulouse, France

<sup>b</sup> IEM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

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## A B S T R A C T

### Keywords:

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Electrocatalytic membranes  
Sub-stoichiometric Ti<sub>4</sub>O<sub>7</sub> anode  
Membrane technology  
Acetaminophen

In this work, we present an integrated dynamic cross-flow electro-Fenton (DCF-EF) system for the treatment of the pharmaceutical, acetaminophen (paracetamol), in aqueous medium. A carbonaceous electrocatalytic membrane was used as cathode, allowing the continuous production of H<sub>2</sub>O<sub>2</sub> during EF in dynamic filtration mode. The transmembrane pressure (TMP) and current were the two driving forces of the system, whose influence strongly affected the global efficiency. It was found that H<sub>2</sub>O<sub>2</sub> production from the electrochemical reduction of dissolved O<sub>2</sub> was favoured at higher TMP values as a consequence of an increase of the O<sub>2</sub> partial pressure, and higher H<sub>2</sub>O<sub>2</sub> amounts entailed an increase in the efficiency of the process. Current also had a positive effect on H<sub>2</sub>O<sub>2</sub> production and acetaminophen degradation and mineralization efficiencies up to an optimal value. Complete degradation of the drug and 44% mineralization were achieved under optimal conditions (2.0 bar and 100 mA). On the other hand, the results pointed out that the use of a Ti<sub>4</sub>O<sub>7</sub> rod as counter electrode (anode) had an important contribution to the mineralization of the acetaminophen's solutions owing to the formation of hydroxyl radicals ( $\cdot$ OH) on its surface, which highlighted the oxidative power of this anode material. The oxidation mechanisms involved during the process were assessed by electrochemical measurements with both electrodes (carbon membrane and Ti<sub>4</sub>O<sub>7</sub> rod), and a degradation pathway for paracetamol oxidation was proposed based on the identification of the main aromatic and aliphatic degradation by-products. This DCF-EF process is presented as a potential alternative for water treatment and reuse in which the integration of membrane and electrochemical technologies brings together separation science and advanced oxidation.

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## 1. Introduction

The critical worldwide water situation demands the development of more efficient and sustainable technologies for wastewater treatment [1]. In this scenario, the unambiguous presence of a variety of persistent organic pollutants (POPs) in the aquatic environment has boosted research in the field of wastewater treatment during the last decades [2,3]. POPs are substances refractory to conventional physicochemical and biological degradative treatment methods, and physical processes such as membrane filtration, adsorption and coagulation/flocculation are separation technologies that do not involve structural changes. POPs include pharmaceuticals, personal care products, industrial chemicals, pesticides and so on. Some organic pollutants of this kind are categorized as contaminants of “emerging concern” because they have only been recently detected in the environment.

Advanced oxidation processes (AOPs) are powerful technologies

that were developed for the degradation of refractory contaminants. They are based on the production of highly reactive species, mainly hydroxyl radicals ( $\cdot$ OH), which are capable of mineralizing the organic matter present in the wastewater [4,5]. When AOPs are performed by means of electrochemistry (EAOPs), numerous advantages arise, such as high efficiency, operability at mild conditions, economic feasibility, ease of automation and environmental compatibility. These characteristics have positioned them as potential alternatives for large scale applications [6,7]. However, some EAOPs intrinsic limitations still restrain further industrial implementation; mainly the stability and elevated costs of the electrode materials, mass transport restrictions, reactor design and other engineering issues [6 10].

EAOPs include direct electrochemical oxidation methods, commonly referred as anodic oxidation (AO), and indirect electro oxidation (IEO). AO is based on the electrochemical oxidation of organics at the anode surface through two different mechanisms: (i) direct electron

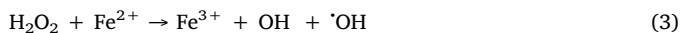
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\* Corresponding author.

E-mail address: coetsier@chimie.ups-tlse.fr (C. Coetsier).

transfer and (ii) indirect oxidation via the “chemisorbed oxygen” ( $M(\cdot OH)$ ) formed from water discharge (Eq. (1)). The oxidative mechanism depends on the characteristics of the anode material [6,7,11] and boron doped diamond (BDD) electrodes are the most efficient and preferred materials for AO [11–13]. On the other hand, in recent years  $Ti_nO_{n-1}$  ( $n \geq 3$ ) sub stoichiometric ceramic anodes, specially  $Ti_4O_7$ , have emerged for water remediation applications due to their ability to generate “quasi free”  $M(\cdot OH)$  via Eq. (1) in a similar way to BDD [14–16]. In recent publications,  $Ti_4O_7$  anodes have even been reported to show similar or better performances than BDD [17,18,19]. However, little research on these ceramic materials has been conducted so far.  $TiO_2$  based materials are another type of electrodes commonly used in photoelectrocatalytic EAOPs, in which the photocatalytic oxidative properties of  $TiO_2$  are enhanced by the application of an external bias potential [20].

Because of its numerous advantages, electro Fenton (EF) has received especial attention among the IEO techniques and several studies have evidenced its potentiality [21–25]. The EF process is characterized by the *in situ* cathodic production of the Fenton’s reagent:  $H_2O_2$  is formed through the  $2e^-$  reduction reaction of soluble  $O_2$  at a suitable electrode material (Eq. (2)), while  $Fe^{2+}$  is constantly regenerated via Eq. (4). In this way,  $\cdot OH$  are continuously formed in the bulk solution via the Fenton’s reaction (Eq. (3)). The efficiency of the process is highly dependent on the properties of the cathode material [6,21] and generally, carbonaceous electrodes have been used in EF, including gas diffusion electrodes (GDE), carbon felt (CF), graphite, carbon nanotubes (CNT), reticulated carbon vitreous (RCV), carbon fibers, graphene, etc. [6,9,21,26–28]. Additionally, the performance of EF can be enhanced when powerful anodes promoting the generation of  $M(\cdot OH)$  (Eq. (1)) like the BDD are utilized in the same system [29,30].



On the other hand, single water treatment methods encounter several difficulties, mostly related to technical unavailability and in complete removal of target pollutants. Therefore, combined or integrated technologies have been increasingly applied over the last years, in which the main advantages of individual processes are enhanced by the beneficial effects of their counterpart, while their downsides are overcome [4,7,31]. In this way, a great variety of coupled systems have been proposed, in which AOPs (including electrochemical methods) have been privileged for the partial or total destruction of organic pollutants during pre or post treatment stages [4,32,33].

In this scenario, Membrane technology (MT) AOPs systems have been applied for the treatment of different organic pollutants with satisfactory results, as recently reviewed by Ganiyu et al. [33]. AOPs as pre treatment have been usually applied with the goal of removing fouling agents, while highly charged concentrates can be efficiently post treated by AOPs/EAOPs [34]. The utilization of anti fouling photocatalytic membranes ( $TiO_2$  based) has become an attractive alternative since physical separation and chemical oxidation can occur in a single unit during “one step” treatments [33,35]. The use of electrocatalytic membranes in integrated MT EAOPs systems has been proposed in more recent works, where the membrane acts as both, separation barrier for filtration and electrode material for the oxidation of organics [36]. Different materials have been used as reactive electrochemical membranes:  $Ti$ /BDD [37,38], carbon based membranes [39–42] and sub stoichiometric  $Ti_4O_7$  [43,44]. Nonetheless, the reports available are still scarce and great efforts are needed for improvement.

In precedent investigations, graphite based tubular membranes have been utilized as electrodes for the electrochemical generation of

$H_2O_2$  during EF in dynamic filtration mode, demonstrating the potentiality of this innovative hybrid technique [39]. In fact, carbon based membranes have found a wide range of applications (mainly the separation of gasses and pesticides) because of their high chemical stability and thermal resistance, as well as their good permeability and selectivity [45]. Furthermore, various studies have demonstrated the great potential of carbon membranes as electrodes due to their anti fouling capacity [46]. A recent work reported the use of a membrane with a polymer coating film which promoted the electrochemical formation of  $\cdot OH$  via the EF process. However, the polymer layer was supported on a steel mesh with poor filtration capacity, which was subjected to corrosion issues [47].

In the present study, we thoroughly investigated the application of an electrocatalytic graphite membrane as cathode for the electro production of the Fenton’s reagent during a combined dynamic cross flow EF process (DCF EF) at pre pilot scale. Paracetamol (PCTM), a widely prescribed analgesic and antipyretic drug, whose unequivocal presence in surface, drinking and wastewater has been stated worldwide, was used as model compound. The main parameters affecting the efficiency of the process, named applied current and transmembrane pressure (TMP), were systematically assessed. Furthermore, a “non active”  $Ti_4O_7$  anode was used as the counter electrode during EF in filtration mode for the very first time, which resulted in a significant rise of efficiency. The mechanisms involved in the oxidation of the drug were deeply investigated and a plausible degradation pathway was proposed based on the identification of degradation by products.

## 2. Materials and methods

### 2.1. Membrane characterization

The conductive membrane used as cathode was a graphite based ultrafiltration membrane from Carbone Lorraine, France, with dimensions: 15 cm long, 1 cm outer diameter and 0.8 cm inner diameter. Before utilization, it was washed in deionized water, sonicated, washed with acetone for removal of any organic remnant, overnight in 0.05 M  $H_2SO_4$  and finally immersed in deionized water for hydration (24 h). The extremes were covered with epoxy resin for sealing inside the cell/filtration module (2 and 4 cm each extreme) and the effective inner membrane area was 22.62  $cm^2$ . Membrane porosity was found to be 14.4% according to Hg measurements, while it has a pore diameter of 2.8 and 0.16  $\mu m$ , according to previous study [39].

### 2.2. EF Membrane cross flow electrolyses

The electrochemical filtration pre pilot scale reactor used in this study is depicted in Fig. SM 1. Experiments were conducted in cross flow filtration mode under galvanostatic conditions using a DC 30 V/10 A power supply. The reservoir consisted in a 5 L capacity stainless steel tank, in which aqueous solutions of PCTM (0.1 mM) were introduced and circulated by a centrifugal pump at a flow rate of 3 L  $min^{-1}$ . The tank was equipped with a cooling system for temperature control and a temperature sensor for monitoring. The electrolytic cell/filtration module was a tubular Teflon® container, which held the graphite membrane (cathode). It had an outlet for the permeate, which was not recirculated. The external wall of the membrane was connected to the power supply by a metallic contact. The counter electrode (anode) consisted of a 1 mm diameter, 30 cm long  $Ti/Ti_4O_7$  rod. It was placed in the axis of the carbon membrane and connected to the supply power by the extremity. Transmembrane pressure (TMP), the driving force of MT, was adjusted using compressed air, which also ensured continuous supply of  $O_2$  for saturation of the solution. For all experiments, the electrolysis started after the system had reached a permanent regime and the concentration of PCTM in the permeate was constant (adsorption was negligible). The solution was saturated with  $O_2$  during the stabilization time. All experiments were replicated and the average



values are reported.

### 2.3. $Ti_4O_7$ anode preparation

The preparation of the  $Ti_4O_7$  anode (rod) was made by the method described in a precedent work, where the deposition of  $TiO_x$  particles was effectuated by plasma coating on titanium plates as support [18]. In this case, the plasma coating was made by Saint Gobain Coating Solutions on a 30 cm titanium rod (1 mm diameter) using their Pro Plasma STD plasma torch. X ray Diffraction (XRD) analyses revealed that  $Ti_4O_7$  was the main phase of the plasma coating. Saint Gobain CREE synthesized the  $TiO_x$  particles by electrofusion using a Heroult furnace in which a mixture of  $TiO_2$  and coke (Coke de Brai AO151203 ALTICHEM 98% C) was melt by the electric arc created between graphite electrodes. XRD of the obtained powder revealed a mixture of  $Ti_4O_7$ ,  $Ti_5O_9$ ,  $Ti_6O_{11}$  and  $Ti_3O_5$  phases.

### 2.4. Analytic techniques and instrumentation

HPLC analysis for PCTM quantification were performed in a HPLC UV Agilent 1200 series chromatograph couple to a UV detector set at 240 nm. An Agilent reversed phase C18 column ( $3.5 \mu m \times 100 mm \times 3 mm$ ) was used. The mobile phase consisted of A (0.1% formic acid aqueous solution) and B (0.1% formic acid in acetonitrile). The gradient program used for elution at a flow rate of  $1.2 mL \cdot min^{-1}$  was as follows: 0 3.5 min (isocratic 97.5/2.5), 3.5 6.5 min (gradient up to 20/80), 6.5 7.5 (gradient up to 97.5/2.5) and 7.5 10.5 (isocratic 97.5/2.5). Quantitation of short chain carboxylic acids was made using an HPLC Jasco BS 2000 04 equipped with a UV 2077 detector. An Agilent Hi Plex H column was used ( $7.7 \times 300 mm, 8 \mu m$ ) and elution was performed with  $0.01 M H_2SO_4$  at a flow rate of  $0.4 mL \cdot min^{-1}$  and  $50^\circ C$ . Detection was made at 210 nm. The mineralization rate was assessed in terms of the TOC decay in the treated solutions. TOC analyses were carried out using a Shimadzu VCSH TOC analyser.

HPLC HRMS analyses were performed in a Thermo Fisher instrument (U3000). HPLC separations were carried out at  $40^\circ C$  using a Luna PFP 2 ( $150 \times 2 mm, 3 \mu m$ ) column. The mobile phase was an A (0.1% v/v formic acid)/B (acetonitrile) mixture, while the gradient program at  $200 \mu L \cdot min^{-1}$  was: 0 5 min (100/0), 5 20 min (gradient up to 20/80), 20 25 min (20/80), 25 25.2 min (gradient up to 100/0), 25.2 30 min (100/0). In parallel, analyses were performed using UV detection (UV Vis RSLC VWD 3400 RS detector) at 250 nm. The MS spectrometer is combined with an Orbitrap mass analyser. It is equipped with an HCD collision cell, using electrospray ionization (ESI), which was operated in positive and negative mode. Mass detection was made between 50 and  $600 m/z$ . Biological oxygen demand at 5 days ( $BOD_5$ ) was determined using an OxiTop® system. The samples, in which pH was adjusted to a value between 6.5 and 7.5, were incubated at  $20^\circ C$  in dark conditions during 5 days. KOH pellets were used to trap  $CO_2$ . BOD seed inoculum (PolySeed®, Interlab® Supply) was used as source of microorganisms, while D(+) Glucose  $H_2O$  was the standard control and N allylthiourea was utilized as nitrification inhibitor.  $H_2O_2$  was quantified by spectrophotometry with  $TiCl_4$  at 410 nm using a UV vis Libra S12 Biochrom spectrophotometer [48].

The voltametric studies were performed on an Autolab PGSTAT204 potentiostat/galvanostat at a scan rate of  $50 mV \cdot s^{-1}$  using a Ag/AgCl reference electrode. The electrolytic cell for the batch experiments reported in Section 3.4, was a 200 mL glass tall container equipped with either a  $Ti_4O_7$  rod or a stainless steel rod (316 L stainless steel with excellent corrosion resistance) as anode, while the cathode was a Pt mesh; 21 cm of both electrodes were immersed in the solution (200 mL). The cell for the electrochemical characterization of the graphite membrane, reported in Section 3.1, consisted in a 200 mL capacity reactor, containing a 7 cm long carbon tubular membrane as cathode and a Pt mesh anode (5 cm immersed in the solution, 150 mL).

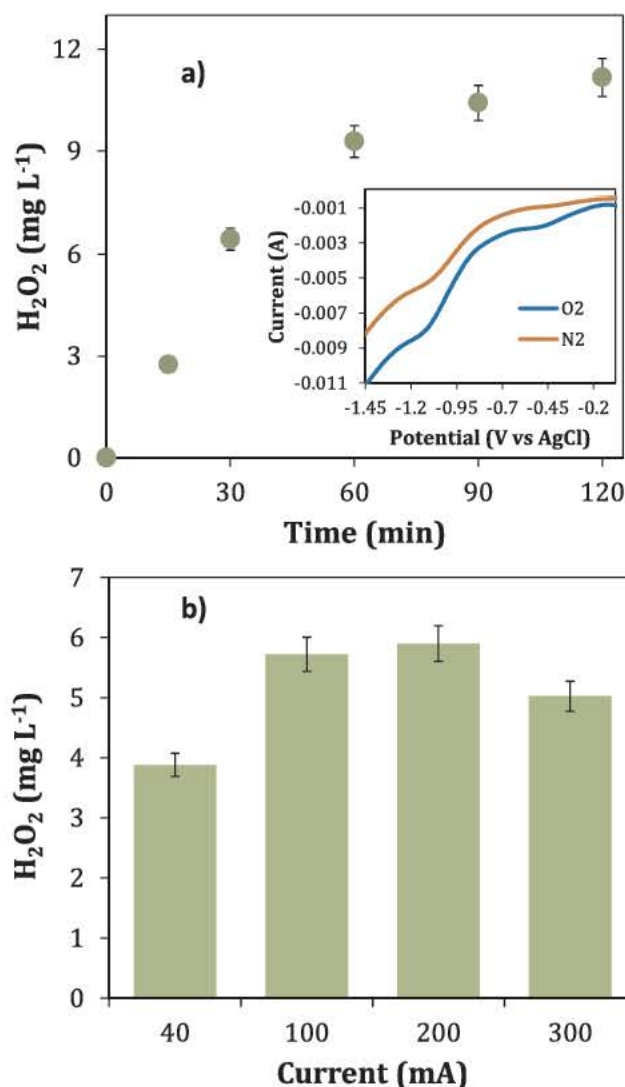


Fig. 1. Effect of applied current on the electrochemical production of  $H_2O_2$ . (a) evolution of  $H_2O_2$  with electrolysis time (at 100 mA). (b) Concentration of  $H_2O_2$  at 30 min-electrolysis under different current values.  $V = 1.5 L$  of  $0.05 M Na_2SO_4$  at pH 3,  $18^\circ C$  and 0.25 bar. Flow =  $3.0 L \cdot min^{-1}$ . The inset panel depicts the linear voltammogram of the electrolyte solution ( $0.05 M Na_2SO_4$  at pH 3) in the presence ( $O_2$ ) and absence ( $N_2$ ).

Before experiments, the solution was saturated with  $O_2$  for 15 min using compressed air. For both cells, the anode and the cathode were installed in parallel in the center of the cell, separated by 1 cm.  $Na_2SO_4$  50 mM at pH 3 was used as a supporting electrolyte.

## 3. Results and discussion

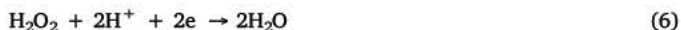
### 3.1. $H_2O_2$ electro generation: effect of TMP and current

TMP and current are the driving forces of this coupled DCF EF process. Accordingly, the effect of both parameters was assessed: first, on the generation of  $H_2O_2$  and second, on PCTM degradation and mineralization efficiencies.

The use of a graphite based membrane ensured the electrochemical production of  $H_2O_2$  from the  $2 e^-$  reduction reaction of dissolved  $O_2$  in the solution. The formation rate of  $H_2O_2$  depends on the structure and properties of the cathode material since  $O_2$  reduction can occur through either the  $2 e^-$  or the  $4 e^-$  reaction pathway (Eqs. (2) and (5), respectively), the latter leading to  $H_2O$  generation [21]. Linear Sweep Voltammetry (LSV) was used to assess the electrochemical reduction



reaction of  $O_2$  in the tubular membrane. The inset panel of Fig. 1 depicts the linear voltammogram of the supporting electrolyte ( $Na_2SO_4$ ) saturated with  $O_2$  at pH 3. Two reduction waves before the evolution of  $H_2$  can be observed at  $-0.47$  V and  $-1.1$  V vs Ag/AgCl, which correspond to the  $2 e^- O_2$  reduction reaction (ORR) (Eq. (2)) and the consecutive  $2 e^-$  reduction of  $H_2O_2$  (Eq. (6)), respectively. These results confirmed the formation of  $H_2O_2$ .



Since current is a crucial parameter for the electro production of  $H_2O_2$  and the generation of  $\cdot OH$  in the presence of  $Fe^{2+}$  ions (Fenton's reaction), its effect on  $H_2O_2$  production was assessed by a series of experiments at different current values, ranging from 40 to 300 mA ( $1.77$  mA  $cm^{-2}$  to  $13.26$  mA  $cm^{-2}$ ). It was found that the concentration of  $H_2O_2$  in the feed increased with time until a plateau was reached, which is illustrated in Fig. 1a. It can be seen that a maximum of  $11$  mg  $L^{-1}$  was obtained after 90 min electrolysis (at 100 mA). Fig. 1b depicts the generation of  $H_2O_2$  as a function of current at 30 min electrolysis. The rate of  $H_2O_2$  production rose with increasing current from 40 to 200 mA, but decreased at higher current values (300 mA). This trend was in agreement with the electrochemical behaviour of the ORR at the cathode membrane (inlet Fig. 1), according to which higher current values (requiring higher potentials) contribute to the progressive decomposition of  $H_2O_2$  into  $H_2O$  (Eq. (5)). The experiments were conducted under constant current since it is known that galvanostatic mode is preferred for large scale applications due to the slow kinetics obtained under potentiostatic conditions [7].

TMP is the other driving force of this coupled process. Accordingly, its effect on the generation of  $H_2O_2$  was also investigated. For this purpose, a series of electrolyses were performed at pressures ranging from 0.5 to 2.0 bars (Fig. 2). It can be seen that TMP has a positive effect on the generation of  $H_2O_2$ . This phenomenon can be explained in terms of the increase in  $O_2$  solubility in water as a function of its partial pressure according to Henry's law. Thereby, a greater amount of  $O_2$  dissolved in the solution increases the mass transport of the gas to the electrode, favouring the generation rate of  $H_2O_2$ . In Fig. 2, the amount of  $H_2O_2$  is presented as a function of TMP and the equivalent amount of dissolved  $O_2$  calculated from Henry's law according to the corresponding  $O_2$  partial pressure. Similarly, in a recent study the electrochemical production of  $H_2O_2$ , as well as the performance of the EF

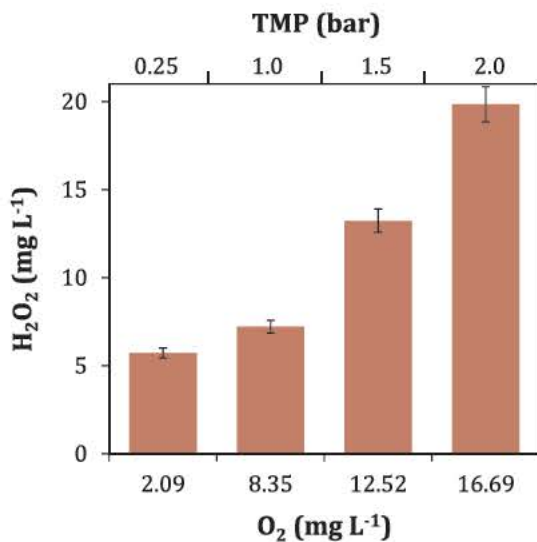


Fig. 2. Effect of TMP (and the corresponding  $O_2$  concentration as a function of its partial pressure) on the electrochemical production of  $H_2O_2$  at 30 min of electrolysis of 1.5 L of 0.05 M  $Na_2SO_4$  at pH 3 and  $18^\circ C$ . Flow =  $3.0$  L  $min^{-1}$ .

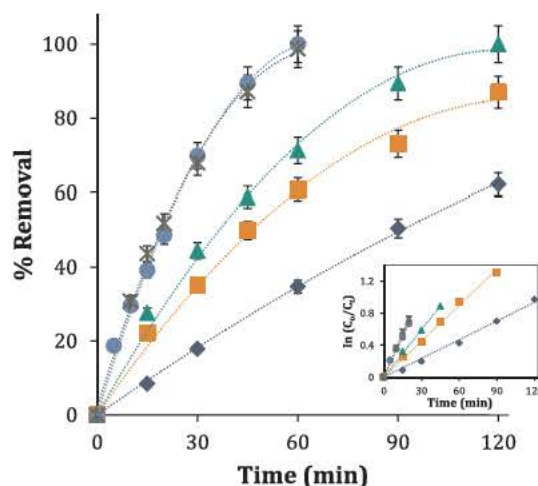


Fig. 3. Effect of TMP on the degradation of PCTM during DCF-EF.  $V = 1.5$  L,  $[PCTM] = 0.1$  mM,  $[Fe^{2+}] = 0.2$  mM,  $I = 100$  mA, with 0.05 M  $Na_2SO_4$  at pH 3 and  $18^\circ C$ . Flow =  $3.0$  L  $min^{-1}$ . (■) 0.25 bar, (▲) 1.0 bar, (●) 2.0 bar, (\*) 3.0 bar, (◆) 0.25 bar in the absence of  $Fe^{2+}$  (AO). The inset panel shows the kinetic analysis assuming a pseudo-first order model.

process, were enhanced by increasing the air pressure in a pressurized electrolytic cell operating in batch mode [49]. This phenomenon is of noticeable importance since it highlights the synergistic effects of EF under pressure driven filtration mode. Therefore, further deposition of ultra or nanofiltration layers on the carbon membrane support, associated with greater TMP values, will be compatible with EF oxidation.

### 3.2. Degradation and mineralization kinetics

#### 3.2.1. Effect of TMP

The effect of TMP and current on the degradation and mineralization of PCTM aqueous solutions under DCF EF conditions was also assessed. Fig. 3 depicts the drug's removal percentage with time at different TMP values. As expected, an increment in TMP resulted in a rise in the degradation kinetics, which is consistent with the greater production of  $H_2O_2$  from the increase of  $O_2$  solubility in solution. Accordingly, larger amounts of  $H_2O_2$  promoted an extensive generation of  $\cdot OH$  from Fenton's reaction (Eq. (3)), which accelerated the oxidation rate of the drug. The removal rate increased with TMP from 0.25 to 2.0 bars, while it did not show any further increase when 3.0 bar were applied. This behaviour can be accounted for by the catalytic capacity of the membrane with regard to the  $2 e^-$  ORR, which limited the formation of  $H_2O_2$  even at higher levels of pressure. A total degradation of the drug was achieved in 60 min for a TMP of 2.0 and 3.0 bar, while PCTM was totally degraded in 90 and 120 min when using 1.0 and 0.25 bar, respectively. In addition, we hypothesize that adsorption of organics on the membrane played an important role on the electrocatalytic activity for  $H_2O_2$  production. In this way, saturation of the membrane conducted to electrode passivation, which accounted for the decrease in the oxidation rates with time.

On the other hand, the degradation kinetic of the drug was found to follow a pseudo first order kinetic model with very good correlation coefficients, as shown in the inset panel of Fig. 3. This behaviour was in agreement with reported kinetic rates of organics with  $\cdot OH$ , in which a quasi stationary state in the concentration of this species has been considered. Table 1 summarizes the calculated pseudo first order rate constants ( $k_{app,PCTM}$ ).

Concerning the mineralization of the drug, it can be seen from Fig. 4 that TMP also had a positive effect on the TOC decay of PCTM solutions. The application of 2.0 and 3.0 bar resulted in up to 44% of mineralization. On the other hand, the contribution of AO on the total mineralization yield is noteworthy. Fig. 4 shows that 19% of TOC decay was achieved in the



**Table 1**

Apparent rate constants for the complete disappearance of 0.1 mM PCTM by means of the DCF-EF process: effect of TMP and current. A pseudo-first order kinetic model was assumed.

Experimental parameters	Values	$k_{app,PCTM}$ (min <sup>-1</sup> )	
TMP (bar)	0.25	0.015	
	( $I = 100$ mA)	1.0	0.020
	2.0	0.034	
	3.0	0.037	
	0.25 (AO) <sup>a</sup>	0.008	
Current (mA)	40	0.005	
	(TMP = 0.25 bar)	100	0.011
	200	0.016	
	300	0.019	

<sup>a</sup> For AO the experiment was conducted in the absence of Fe<sup>2+</sup> ions.

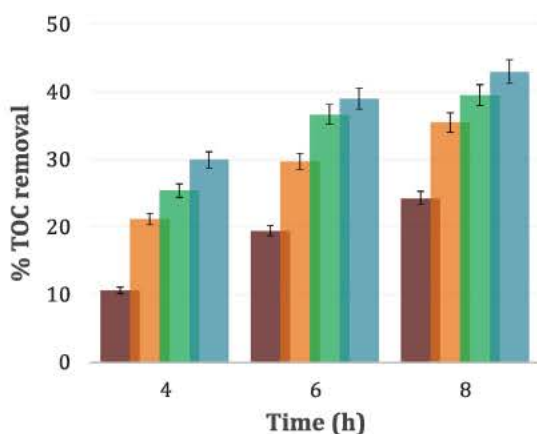
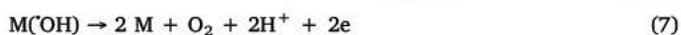


Fig. 4. Effect of TMP on the TOC decay of PCTM solutions during DCF-EF.  $V = 1.5$  L,  $[PCTM] = 0.1$  mM,  $[Fe^{2+}] = 0.2$  mM,  $I = 100$  mA, with  $0.05$  M  $Na_2SO_4$  at pH 3 and  $18$  °C. Flow =  $3.0$  L  $min^{-1}$ . (■) 0.25 bar in the absence of Fe<sup>2+</sup> (AO), (■) 0.25 bar, (■) 1.0 bar, (■) 2.0 bar.

absence of Fe<sup>2+</sup> ions, which evidenced that an important part of PCTM and its degradation by products were mineralized on the anode's surface by means of the M(OH) formed according to Eq. (1). These results highlighted the potential of Ti<sub>4</sub>O<sub>7</sub> anode materials for water remediation. Further discussion is presented in Section 3.4.

### 3.2.2. The effect of current

The effect of current on the performance of DCF EF is depicted in Fig. 5. It can be observed that the concentration decay rose with current from 40 to 200 mA, with a small difference between 100 and 200 mA. Nevertheless, it decreased when 300 mA were applied. The increase in the kinetic rate with current was due to the greater amount of ·OH produced from both the Fenton's reaction (Eq. (3)) and water oxidation (Eq. (1)) as a consequence of a higher energy input. On the contrary, further increment of current entailed progressive acceleration of non oxidizing waste reactions: the heterogeneous electrochemical evolution of O<sub>2</sub> at the anode (Eq. (7)), the reduction of H<sub>2</sub>O<sub>2</sub> at the cathode (Eq. (6)), the homogeneous dimerization of ·OH (Eq. (8)), and ·OH reaction with Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> according to Eqs. (9) and (10), respectively [8,21].



As shown in Fig. 6, TOC decay behaves in a similar way. The mineralization rate increased when rising current from 40 mA to 100 mA, whereas the difference between 100 and 200 mA was not significant

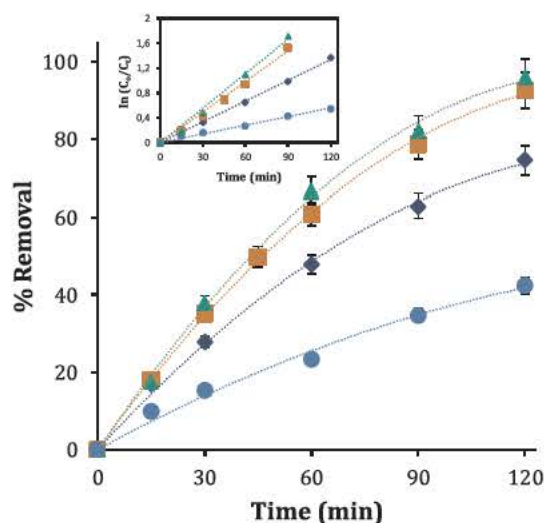


Fig. 5. Effect of current on the degradation of PCTM during DCF-EF.  $V = 1.5$  L,  $[PCTM] = 0.1$  mM,  $[Fe^{2+}] = 0.2$  mM, TMP = 0.25 bar, with  $0.05$  M  $Na_2SO_4$  at pH 3 and  $18$  °C. Flow =  $3.0$  L  $min^{-1}$ . (♦) 40 mA, (■) 100 mA, (▲) 200 mA, (●) 300 mA. The inset panel shows the kinetic analysis assuming a pseudo-first order model.

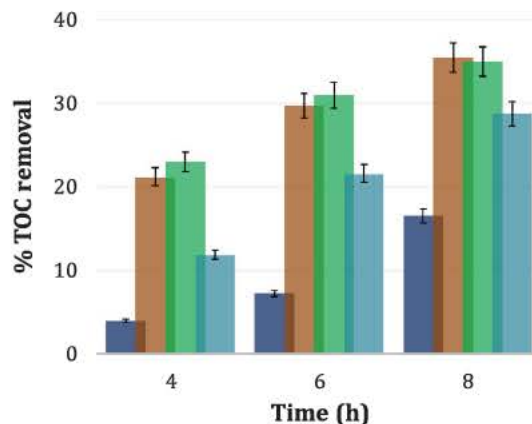


Fig. 6. Effect of current on the TOC decay of PCTM solutions during DCF-EF.  $V = 1.5$  L,  $[PCTM] = 0.1$  mM,  $[Fe^{2+}] = 0.2$  mM, TMP = 0.25 bar, with  $0.05$  M  $Na_2SO_4$  at pH 3 and  $18$  °C. Flow =  $3.0$  L  $min^{-1}$ . (■) 40 mA, (■) 100 mA, (■) 200 mA, (■) 300 mA.

(35% of TOC decay was reached after 8 h of treatment for both, 100 and 200 mA). The application of 300 mA resulted in a significant drop of mineralization efficiency, which can be accounted for by the series of waste reactions depicted in Eqs. (6)–(10), as discussed above.

It can be noted that TOC decay rates decrease with treatment time. For example, for 100 and 200 mA, more than 20% of TOC abatement was reached in 4 h electrolysis, whereas, only around 12% more was achieved during the next 4 h. This trend can be ascribed to the generation of more recalcitrant degradation by products to ·OH, whose reaction rates are significantly slower. These compounds include mostly short chain organic acids. Further discussion is proposed in Section 3.5.

Finally, even though retention was not involved during CF EF, the relevance of these carbonaceous electrocatalytic membranes in EF is to be underlined as the filtration properties can be improved by deposition of ultra and nano filtration layers. Additionally, the efficiency of the membranes towards the  $2 e^-$  O<sub>2</sub> reduction reaction could also be improved by structural modifications with graphene [26,50] or nitrogen based compounds [51] to increase the H<sub>2</sub>O<sub>2</sub> production. For these purposes further research needs to be conducted, which was not the scope of the present investigation.

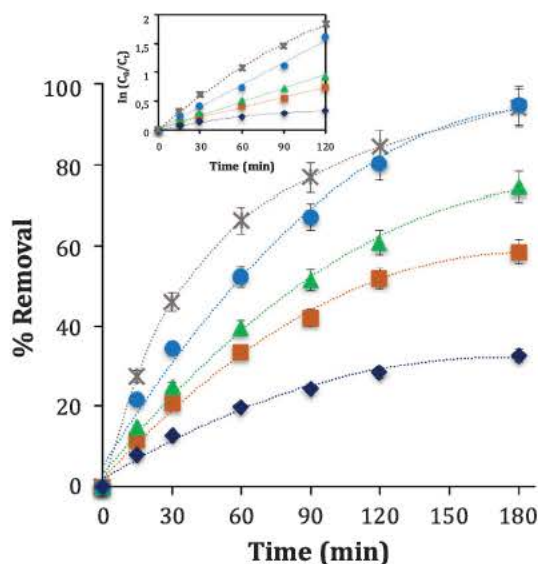


Fig. 7. Effect of current on the degradation of PCTM during AO in batch mode using a  $\text{Ti}_4\text{O}_7$  anode and a Pt cathode.  $V = 0.2$  V,  $[\text{PCTM}] = 0.1$  mM, with  $0.05$  M  $\text{Na}_2\text{SO}_4$  at pH 3 and room temperature. ( $\blacklozenge$ ) 40 mA, ( $\blacksquare$ ) 100 mA, ( $\blacktriangle$ ) 200 mA, ( $\bullet$ ) 300 mA, ( $*$ ) 100 mA using a stainless-steel anode. The inset panel shows the kinetic analysis assuming a pseudo-first order model.

### 3.3. The oxidation power of $\text{TiOx}$

In order to assess the mineralization power of the  $\text{Ti}_4\text{O}_7$  electrode, a series of experiments were conducted in an electrolysis cell operating in batch mode. The cell was equipped with a  $\text{Ti}_4\text{O}_7$  anode and a Pt cathode in either a three or two electrodes configuration. The use of Pt allowed avoiding the cathodic production of  $\text{H}_2\text{O}_2$ . It was found that the concentration decay of the drug followed a pseudo first order kinetic reaction and the degradation rate increased with rising current (Fig. 7), which was consistent with findings obtained in the DCF EF reactor.

When using a stainless steel anode instead of the  $\text{Ti}_4\text{O}_7$  in the same batch cell, the concentration of the drug decreased with time also following a pseudo first order kinetic reaction (Fig. 7). In fact, PCTM was oxidized at the surface of the stainless steel anode by direct electron transfer, which, in acidic medium, lead to the formation and accumulation of p benzoquinone (p BQ), according to Eq. (11) [52]. None theless, according to HPLC analyses (results not presented), p BQ did not suffer further oxidation at prolonged electrolysis time (up to 4 h), which was also reflected in the lack of TOC decrease. In the case of the  $\text{Ti}_4\text{O}_7$  anode, the concentration of p BQ (determined by HPLC and TOC) decreased with electrolysis time, which confirmed that  $\text{M}(\cdot\text{OH})$  mediated oxidation of PCTM occurred at the  $\text{Ti}_4\text{O}_7$  electrode's surface. In deed, p BQ is considered as a probe of  $\cdot\text{OH}$  generation since this compound does not undergo direct electrochemical electron transfer reactions [44]. Thus, the use of PCTM in the present study resulted in an *in situ*  $\text{M}(\cdot\text{OH})$  probe for the anodic oxidation of organics on  $\text{Ti}_4\text{O}_7$  electrodes.

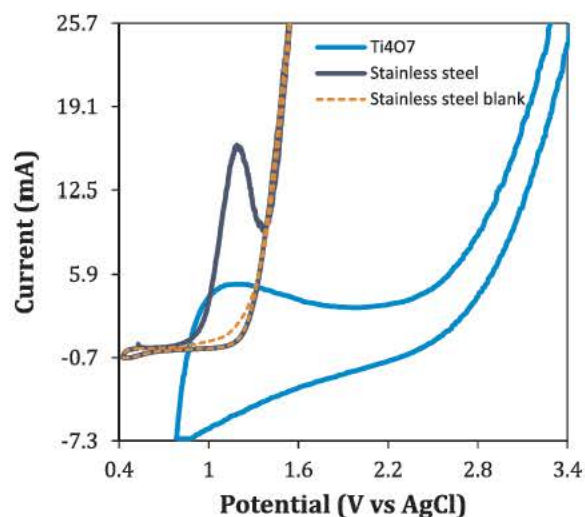
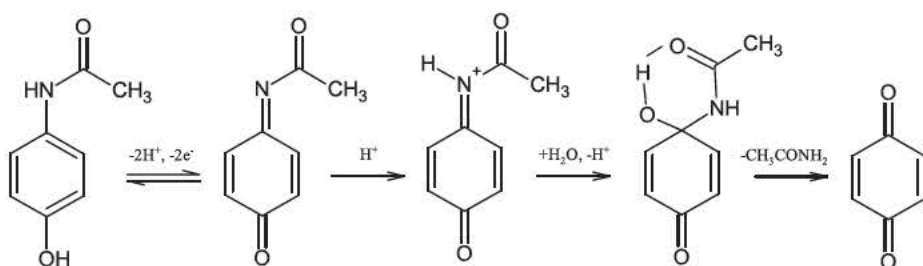


Fig. 8. Cyclic voltammetry of 5 mM PCTM solutions containing  $0.05$  M  $\text{Na}_2\text{SO}_4$  at pH 3 as supporting electrolyte. Stainless-steel or  $\text{Ti}_4\text{O}_7$  were used as anodes with a Pt cathode using a Ag/AgCl reference electrode. The scan rate was  $50$   $\text{mV s}^{-1}$ .

Fig. 8 depicts the cyclic voltammograms of PCTM solutions in  $50$  mM  $\text{Na}_2\text{SO}_4$  at pH 3 using  $\text{Ti}_4\text{O}_7$  and stainless steel anodes. On stainless steel anode, an oxidation wave can be seen at  $+1.18$  V vs Ag/AgCl, which corresponds to the irreversible oxidation of PCTM to p BQ (Eq. (11)). On the contrary, any oxidation wave was observed when utilizing  $\text{Ti}_4\text{O}_7$ , which was in agreement with the slow kinetics of electron transfer reactions reported for this kind of material [14,17]. PCTM was thus oxidized by  $\cdot\text{OH}$  formed in the region of  $\text{O}_2$  evolution ( $+2.7$  V vs Ag/AgCl). The generation of  $\cdot\text{OH}$  in sub stoichiometric  $\text{Ti}_4\text{O}_7$  electrodes (Ebonex $^{\text{®}}$ ) was previously verified by Bejan et al. [17]. Moreover, it is known that Ebonex $^{\text{®}}$  anodes have a very high  $\text{O}_2$  evolution overpotential [14]. Additionally, the electrolysis of a  $0.1$  mM solution of p BQ was performed utilizing a divided cell with a  $\text{Ti}_4\text{O}_7$  anode. Results showed that p BQ was totally degraded in the anodic compartment and up to 20% of mineralization was achieved after 8 h electrolysis at 100 mA, hence confirming the oxidation of p BQ by mediation of heterogeneous  $\text{Ti}_4\text{O}_7(\cdot\text{OH})$ . The slow kinetics for p BQ degradation and mineralization can be explained by: (1) the small surface area of the electrode ( $5.35$   $\text{cm}^2$  for 200 mL of p BQ solution), and (2) the relative less abundance of  $\cdot\text{OH}$  at the  $\text{Ti}_4\text{O}_7$  anode in comparison to those formed at BDD, as suggested in earlier investigations [17].

### 3.4. PCTM oxidation pathway

Aiming at establishing the mechanism reaction through which PCTM is oxidized during DCF EF, the degradation intermediates were identified by means of HPLC and HPLC MS analysis (Table SM 1). Fig. 9 depicts the proposed mechanism pathway. As mention in the previous section, PCTM is oxidized both in the bulk solution with  $\cdot\text{OH}$  formed by





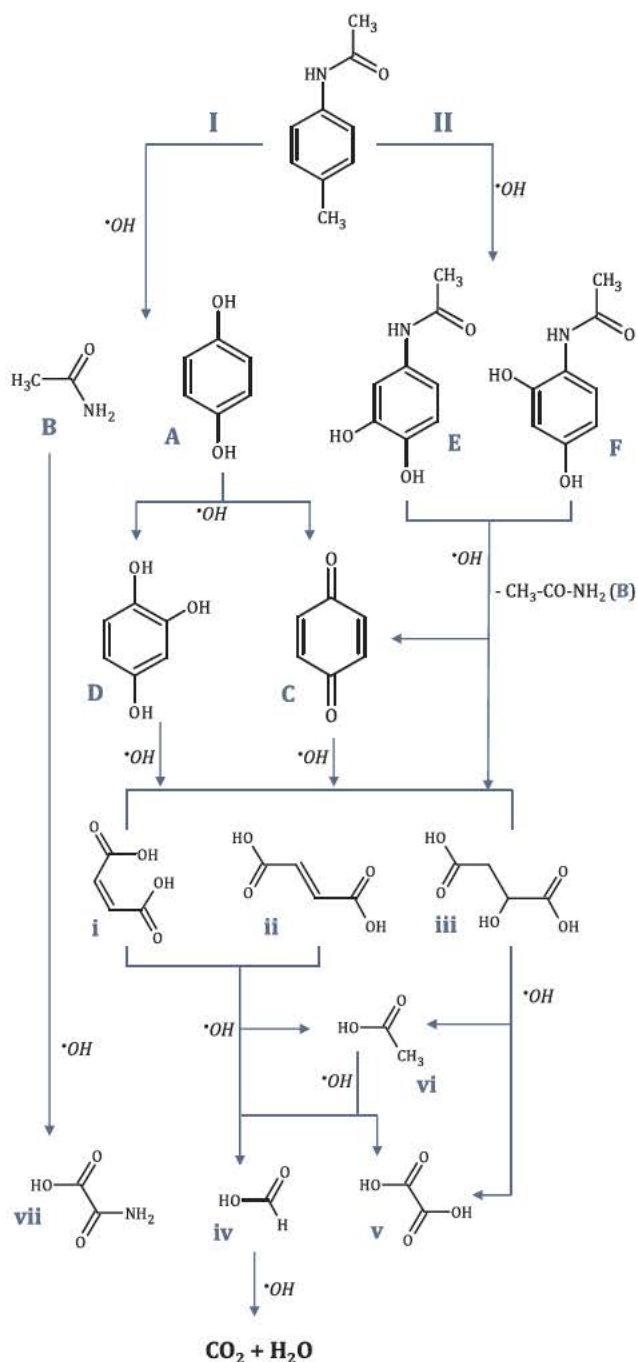


Fig. 9. Proposed mechanisms pathway for the oxidation of PCTM with  $\cdot\text{OH}$  during the DCF-EF process.

Fenton's reaction (Eq. (3)) and at the surface of the anode with  $\text{Ti}_4\text{O}_7(\cdot\text{OH})$  (Eq. (1)). The HPLC chromatograms showed that p BQ was the degradation by product produced in greatest amount, but it was also degraded as the treatment progressed. As depicted in Fig. 9, PCTM oxidation began with hydroxylation at the *p* position with respect to the OH group, which gave first hydroquinone (HQ) (A) and acetamide (B) (route I). Quick subsequent oxidation of HQ generated p BQ (C) as the principal product. However, HQ also underwent further hydroxylation reactions, which was verified by the detection of 1,2,4 trihydroxybenzene (D). On the other hand, formation of 4 acetyl aminocatechol (E) and 4 acetyl aminoresorcinol (F) revealed that hydroxylation reactions at the *o* and *m* positions of PCTM (route II) competed with the first hydroxylation path (route I), but at slower kinetic rates. Further

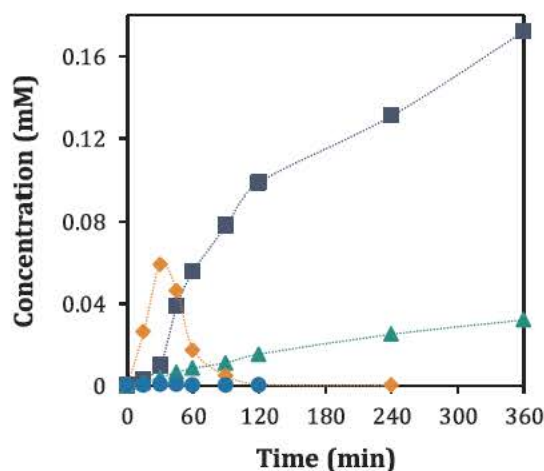


Fig. 10. Evolution of the concentration of the main carboxylic acids formed during the degradation of PCTM by means of DCF-EF.  $V = 1.5\text{L}$ ,  $[\text{PCTM}] = 0.1\text{mM}$ ,  $[\text{Fe}^{2+}] = 0.2\text{mM}$ ,  $\text{TMP} = 1.0\text{bar}$ ,  $I = 100\text{mA}$ , with  $0.05\text{M}$   $\text{Na}_2\text{SO}_4$  at  $\text{pH } 3$  and  $18^\circ\text{C}$ . Flow =  $3.0\text{L}\cdot\text{min}^{-1}$ . (■) oxalic, (●) malic, (▲) oxamic, (◆) formic.

$\cdot\text{OH}$  attack to the aromatic intermediates C, D, E and F provoked their scission leading to short chain organic acids (i to vii). The cleavage of E and F went through progressive hydroxylation reactions giving quinones (like C) by disproportionation of transient semiquinones. The proposed mechanism is in agreement with previous reports dealing with PCTM degradation by anodic oxidation [53], photo Fenton [54] and photocatalytic oxidation [55]. Moreover, Almeida et al. reported that the photoelectron Fenton oxidation of PCTM in a flow plant also went through formation of HQ and p BQ [56]. However, they did not observe either intermediates (E) and (F) formed through the hydroxylation route II or acetamide (B), which can be ascribed to the fast oxidation kinetics of PCTM and its degradation intermediates. Waterston et al. reported that the electrochemical oxidation of PCTM at  $\text{Ti}/\text{IrO}_2$  anodes only conducted to partial degradation to p BQ, since this "active" anode does not promote  $\cdot\text{OH}$  generation [57].

It has been well documented that breakage of aromatic/cyclic by products by the attack of  $\cdot\text{OH}$  during EAOPs leads to short chain carboxylic acids [58,59]. The evolution of the identified carboxylic acids during DCF EF is depicted in Fig. 10. Cleavage of intermediates C, D, E and F, led mainly to C 4 maleic (i), fumaric (ii) and malic acids (iii). These compounds were only detected during the first 60 min of treatment and in very low amounts: malic acid reached a maximum peak ( $7.2 \times 10^{-4}\text{mM}$ ) at 30 min. Their further oxidation conducted to lower molecular weight compounds: maleic and fumaric acids are known to produce formic (iv) and oxalic acid (v), while malic acid yielded mainly oxalic acid (v). It has been reported that acetic acid (vi) can be formed from the oxidation of all the above mentioned C 4 acids. However, only a little amount of it was detected during the first 15 min treatment as it was rapidly oxidized into oxalic and formic acids [58]. Oxalic and formic acids were the species formed in greatest amounts. They were rapidly produced and accumulated in the solution as C 4 acids were oxidized. Both species, along with oxamic acid, are known as the ultimate degradation by products before mineralization to  $\text{CO}_2$  and inorganic ions [21,58,59]. It can be noted in Fig. 10 that formic acid quickly attained a maximum concentration in 15 min and it was oxidized afterwards until undetectable levels. In the case of oxalic acid, it was progressively formed and accumulated in the solution, remaining even after 8 h treatment. Oxamic acid (vii), which resulted principally from the oxidation of acetamide (B), presented a similar trend. In fact, oxalic and oxamic acids are known to be highly resistant to oxidation with  $\cdot\text{OH}$ , presenting slow reaction kinetic rates [59]. Accordingly, they were the main carbon source responsible for the remaining amount of TOC at the end of treatment, which was verified by a simple TOC mass



balance indicating that 86% of the final TOC content of the treated solution corresponded to oxalic and oxamic acids.

### 3.5. Final considerations: the positive impact of the degradation by products

It has been stated that the carboxylic acids formed during electrochemical treatment are biodegradable compounds that can be effectively metabolized by different microorganisms [60,61]. Generally, the subsequent oxidation of these species demands longer treatments times owing to their recalcitrant character towards  $\cdot\text{OH}$ . Prolonged electrolyses are typically accompanied by a significant drop in current efficiency and an increment of energy consumption. Nevertheless, the ability of EAOPs to transform recalcitrant compounds into biodegradable products is indeed one of its most significant features since the striking oxidation power of EAOPs can be capitalized by their combination (as pre or post treatment steps) with conventional biological treatment methods. Thus, the short time partial oxidation of refractory effluents achieved during EAOPs can be completed by implementation of a microbial oxidation stage, which represents considerable technical and economic advantages from a practical perspective [32,62]. In this context, the capability of the DCF EF process to transform refractory pollutants into biodegradable compounds is to be underlined.

In addition, the capacity of DCF EF to degrade p BQ is worthy of note since this intermediate is a hazardous compound much more toxic than PCTM. In fact, Le et al. recently reported that p BQ was the main by product responsible for the significant increase of toxicity (according to the Microtox® method) during the EF treatment of PCTM solutions; 100% of bacteria bioluminescence inhibition even at the lowest detected levels of this compound (0.04 mM) was obtained [26]. They reported that the toxicity decreased with the p BQ degradation and the final carboxylic acids did not show significant toxic effects. The elimination of p BQ during DCF EF is in agreement with these results, which highlights the ability of this coupled approach to degrade toxic contaminants.

## 4. Conclusions

The efficiency and applicability of the one step integrated DCF EF process to the treatment of refractory organic pollutants such as pharmaceuticals has been demonstrated. It was found that the utilization of a graphite based membrane as cathode material was suitable for the electro generation of the Fenton's reagent during electrolysis. TMP and current were the main factors affecting the process efficiency. The results showed that the solubility of  $\text{O}_2$  increased as TMP augmented, which promoted greater production of  $\text{H}_2\text{O}_2$  and a rise of the degradation and mineralization rates. Total degradation of PCTM and up to 44% of mineralization was achieved under optimal conditions (100 mA and 2.0 bar).

The use of a  $\text{Ti}_4\text{O}_7$  ceramic anode during DCF EF was a highlight of this work. It enhanced the performance of the process due to the  $\cdot\text{OH}$  generated on the electrode surface, hence demonstrating the power of  $\text{Ti}_4\text{O}_7$  for the anodic oxidation of organic contaminants. In addition, PCTM was found to be an *in situ* probe for verification of  $\cdot\text{OH}$  formation since its primary oxidation yielded p BQ as the main intermediate, which is known to resist direct electron transfer reactions.

Finally, these findings pointed out the versatility of the EF process, highlighting its capacity to evolve into different directions. Overall, this work opens the door to further investigation for scale up and eventual industrial application of this technology considering the scarce number of reports available to date.

## Acknowledgments

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.seppur.2018.03.063>.

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