Degradation of the beta-blocker propranolol by electrochemical advanced oxidation processes based on Fenton's reaction chemistry using a boron-doped diamond anode

Eloy Isarain-Chávez, Rosa María Rodríguez, José Antonio Garrido, Conchita Arias, Francesc Centellas, Pere Lluís Cabot [1], Enric Brillas [*,1]

Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

ABSTRACT

The electro-Fenton (EF) and photoelectro-Fenton (PEF) degradation of solutions of the beta-blocker propranolol hydrochloride with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 has been studied using a single cell with a boron-doped diamond (BDD) anode and an air diffusion cathode (ADE) for H$_2$O$_2$ electrogeneration and a combined cell containing the above BDD/ADE pair coupled in parallel to a Pt/carbon felt (CF) cell. This naphthalene derivative can be mineralized by both methods with a BDD anode. Almost overall mineralization is attained for the PEF treatments, more rapidly with the combined system due to the generation of higher amounts of hydroxyl radical from Fenton's reaction by the continuous Fe^{2+} regeneration at the CF cathode, accelerating the oxidation of organics to Fe(III)–carboxylate complexes that are more quickly photolyzed by UVA light. The homologous EF processes are less potent giving partial mineralization. The effect of current density, pH and Fe^{2+} and drug concentrations on the oxidation power of PEF process in combined cell is examined. Propranolol decay follows a pseudo first-order reaction in most cases. Aromatic intermediates such as 1-naphthol and phthalic acid and generated carboxylic acids such as maleic, formic, oxalic and oxamic are detected and quantified by high-performance liquid chromatography. The chloride ions present in the starting solution are slowly oxidized at the BDD anode. In PEF treatments, all initial N of propranolol is completely transformed into inorganic ions, with predominance of NH$_4^+$ over NO$_3^-$ ion.

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1. Introduction

Electrochemical advanced oxidation processes based on Fenton's reaction chemistry such as electro-Fenton (EF) and photoelectro-Fenton (PEF) are environmentally friendly methods in which organic pollutants are destroyed in acidic medium by homogeneous hydroxyl radical ($^\bullet$OH) formed from the Fenton's reaction between Fe^{2+} ion and hydrogen peroxide [1,2]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{1}$$
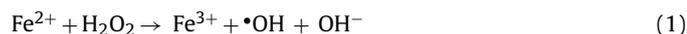
$^\bullet$OH radical is a strong oxidant with so high standard reduction potential ($E°(^\bullet OH/H_2O) = 2.80$ V vs SHE) that can yield overall mineralization of organics, i.e. their total conversion into CO$_2$, water and inorganic ions. A main characteristic of these methods is the continuous supply of H$_2$O$_2$ to the contaminated solution from the two-electron reduction of O$_2$ gas [2]:

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

Reaction (2) is very efficient using cathodes of carbon felt (CF) [3–10], gas (O$_2$ or air) diffusion electrodes [5,11–20], graphite [21,22], reticulated vitreous carbon [23], carbon fiber [24] and boron-doped diamond (BDD) [25]. In the EF process, a small quantity of added Fe^{2+} reacts with generated H$_2$O$_2$ by Fenton's reaction (1) and Fe^{2+} can be regenerated by Fe^{3+} reduction at the cathode [2–5]:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$
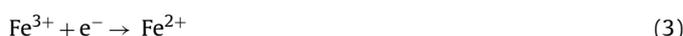
When a high O$_2$ overpotential anode such as BDD is used, heterogeneous hydroxyl radical (BDD($^\bullet$OH)) is formed as intermediate from water oxidation at its surface [26,27]:

$$BDD + H_2O \rightarrow BDD(^\bullet OH) + H^+ + e^- \tag{4}$$
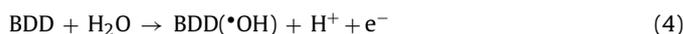
and it is also able to completely degrade organic pollutants by anodic oxidation [26–29]. The oxidation by BDD($^\bullet$OH) is accelerated in EF if an undivided cell with a BDD anode is combined with

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an O_2 diffusion cathode since organics are also removed with $^\bullet OH$ in the bulk [15,17,19].

The PEF process involves the irradiation with UVA light of an acidic solution treated under EF conditions yielding: (i) higher amounts of $^\bullet OH$ and quicker Fe^{2+} regeneration from photolysis of $Fe(OH)^{2+}$, the predominant Fe^{3+} species at pH near 3 [1,30]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \qquad (5)$$

and (ii) the photolysis of complexes of Fe(III) with generated carboxylic acids [31]. These reactions accelerate the decontamination process and lower currents can then be applied in PEF than in EF and anodic oxidation for organic destruction.

Recent studies have reported the detection of a high number of pharmaceutical drugs in surface, ground and even drinking waters [32–38]. Some drugs like beta-blockers affect the endocrine system of fishes and exert toxic effects on algae and invertebrates [35,39–41] and then, it is needed their efficient removal from wastewaters. In this way, we have tested that the EF and PEF treatments with single BDD/gas diffusion cells can be useful to degrade pharmaceuticals containing benzene rings as aromatic moiety [5,13,15,17,19,20]. A novel configuration with two cells combined in parallel, a BDD/air diffusion electrode (ADE) and a Pt/CF pair, has been recently proposed by us to accelerate these processes, a requirement for its possible viability for wastewater remediation [20]. To better clarify the oxidation characteristics of this novel BDD/ADE–Pt/CF system, we have undertaken a study on the degradation of propranolol (1-(isopropylamino)-3-(1-naphthyloxy)propan-2-ol). This beta-blocker has been chosen because it contains a naphthalene ring, a kind of aromatic that has not been previously treated by EF and PEF with BDD anode. Several papers described the destruction of this drug by ozonation in neutral and alkaline media [42,43], O_3/H_2O_2 [43], radiolysis [44], UV/H_2O_2 [45] and a biological Fenton-like system mediated by the white-rot fungus *Trametes versicolor* [46]. Recently, Sirés et al. [10] reported that the mineralization of a mixture of beta-blockers including propranolol is feasible by means of EF using a single Pt/CF cell at pH 3 and high current.

This paper presents the comparative degradation of propranolol hydrochloride by EF and PEF in single BDD/ADE and combined BDD/ADE–Pt/CF cells. The influence of the main experimental variables was explored to clarify the oxidation power of PEF in the latter cell. The decay kinetics of the drug and the evolution of aromatic products, generated carboxylic acids and released inorganic ions were determined to explain the degradation processes.

2. Experimental

2.1. Chemicals

Propranolol hydrochloride of 99% purity was supplied by the pharmaceutical AstraZeneca España (Madrid, Spain). 1-Naphthol was reactive reagent from BDH Chemical Ltd. and phthalic acid was analytical reagent from Aldrich. Oxamic and oxalic acids were analytical grade from Panreac. Sulfuric acid, anhydrous sodium sulfate and ferrous sulfate heptahydrate were analytical grade from Merck and Fluka. Solutions were prepared with pure water obtained from a Millipore Milli-Q system with TOC content < 1 $\mu g\,dm^{-3}$ and resistivity > 18 $M\Omega\,cm$ at 25 °C. Organic solvents and other chemicals used were either HPLC or analytical grade from Merck, Fluka, Panreac and Aldrich.

2.2. Electrolytic systems

Electrolytic experiments were conducted in open, thermostated, cylindrical and undivided tank reactors with two or four electrodes containing 100 cm^3 solutions. The anodes were a Pt

sheet of 99.99% purity from SEMPSA (Barcelona, Spain) and/or a BDD thin film from Adamant Technologies (La Chaux-de-Fonds, Switzerland), while the cathodes were a carbon-PTFE ADE from E-TEK (Somerset, NJ, USA) and a CF from Sofacel (Sant Feliu de Llobregat, Spain). Cells were mounted with monopolar connection, as described elsewhere [20]. The geometric area of all electrodes was 3 cm^2. An air flow rate of 20 $cm^3\,min^{-1}$ was injected into the ADE cathode to generate H_2O_2 from reaction (2). An independent current density was applied to each pair of electrodes using an Amel 2053 potentiostat–galvanostat and/or an EG&G P.A.R. 363 potentiostat–galvanostat. Prior to the use of the BDD/ADE pairs, they were polarized in a 0.05 $mol\,dm^{-3}$ Na_2SO_4 solution at 100 $mA\,cm^{-2}$ for 60 min to remove the impurities from the BDD surfaces and to activate the gas diffusion electrodes.

Solutions with 154 $mg\,dm^{-3}$ of propranolol hydrochloride (corresponding to 100 $mg\,dm^{-3}$ TOC) in 0.05 $mol\,dm^{-3}$ Na_2SO_4 were initially electrolyzed at pH 3.0 and 35 °C. A sulfate electrolyte was used for this synthetic solution to analyze the removal of inorganic ions from the drug. The effect of current density, solution pH and Fe^{2+} and drug concentrations on the oxidation power of PEF treatment in combined cell was also studied. In each assay, the solution was vigorously stirred with a magnetic bar at 800 rpm to transport the reactants toward/from the electrodes and to ensure their homogenization. For PEF, a Philips TL/6W/08 fluorescent black light blue tube of UVA light with $\lambda_{max} = 360$ nm was placed at the top of the open cell at 5 cm above the solution surface for irradiation. A mirror was placed under the cell to better collect the incident UVA light with a photoionization energy input of 1.4 $W\,m^{-2}$, detected with a NRC 820 laser power meter.

2.3. Apparatus and analysis procedures

The solution pH was determined with a Crison GLP 22 pH-meter. Before analysis, samples withdrawn from treated solutions were filtered with 0.45 μm PTFE filters from Whatman. Total organic carbon (TOC) of solutions was obtained using a Shimadzu VCSN analyzer, with an accuracy of ±1% by injecting 50 μl aliquots into the analyzer. From these data, the mineralization current efficiency (MCE, in %) for the above trials at a given time t (h) was calculated as follows [15,17]:

$$MCE = \frac{nFV_s\Delta(TOC)_{exp}}{4.32 \times 10^7 mIt} \times 100 \qquad (6)$$

where F is the Faraday constant (96487 $C\,mol^{-1}$), V_s is the solution volume (dm^3), $\Delta(TOC)_{exp}$ is the experimental TOC decay ($mg\,dm^{-3}$), 4.32×10^7 is a conversion factor to homogenize units (3600 $s\,h^{-1} \times 12000\,mg\,mol^{-1}$), m is the number of carbon atoms of propranolol (16 carbon atoms) and I is the applied total current. The number of electrons (n) consumed per molecule mineralized was taken as 78 assuming the following overall reaction for the mineralization of propranolol hydrochloride:

$$C_{16}H_{22}NO_2^+Cl^- + 30H_2O \rightarrow 16CO_2 + NH_4^+ + Cl^- + 78H^+ + 78e^- \qquad (7)$$

where the initial nitrogen is mainly converted into ammonium ion, as discussed below.

The propranolol decay and the evolution of its aromatic products were monitored by reversed-phase HPLC using a Waters 600 liquid chromatograph coupled with a Waters 996 photodiode array detector selected at the maximum wavelength found for the UV spectrum of each compound. This analysis was made with a Spherisorb ODS2 5 μm, 150 mm × 4.6 mm (i.d.), column at 35 °C, under circulation of a mobile phase composed of a 36:36:28 (v/v/v) acetonitrile/methanol/water (with 2 $g\,dm^{-3}$ sodium dodecyl sulfate and 0.15 $mol\,dm^{-3}$ phosphoric acid at pH 3.0) mixture at 1.5 $cm^3\,min^{-1}$. To quantify the generated carboxylic acids by ion-exclusion HPLC, the above chromatograph fitted with a Bio-Rad

Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at 35 °C, along with the photodiode array detector selected at $\lambda = 210$ nm, were used. A 4 mmol dm^{-3} H$_2$SO$_4$ solution at 0.6 cm^3 min^{-1} circulated as mobile phase. In all HPLC measurements, 20 μl samples were injected into the liquid chromatograph.

Ionic chromatographic analyses were performed by injecting 25 μl aliquots into a Shimadzu 10 Avp HPLC coupled with a Shimadzu CDD 10 Avp conductivity detector. Cl$^-$ and NO$_3^-$ concentrations were obtained with a Shim-Pack IC-A1S, 100 mm × 4.6 mm (i.d.), anion column at 40 °C and a 1.0 mmol dm^{-3} p-hydroxybenzoic acid and 1.1 mmol dm^{-3} N,N-diethylethanolamine solution at 1.5 cm^3 min^{-1} as mobile phase. The NH$_4^+$ concentration was determined using a Shodex IC YK-421, 125 mm × 4.6 mm (i.d.), cation column at 40 °C and an aqueous mobile phase of 5.0 mmol dm^{-3} tartaric acid, 2.0 mmol dm^{-3} dipicolinic acid, 24.2 mmol dm^{-3} boric acid and 15.0 mmol dm^{-3} corona ether at 1.0 cm^3 min^{-1}.

3. Results and discussion

3.1. Comparative total organic carbon removal and mineralization current efficiency

The relative oxidation power of EF and PEF degradations in BDD/ADE and BDD/ADE–Pt/CF cells was studied by electrolyzing a 154 mg dm^{-3} propranolol hydrochloride solution with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 and 35 °C. A current density of 40 mA cm^{-2} was imposed to the BDD/ADE pairs, whereas 4 mA cm^{-2} were applied to the Pt/CF pair of the combined cell [20]. For these trials, the pH decayed slowly by the formation of acidic byproducts, reaching values of 2.6–2.7 after 420 min of treatment.

Fig. 1a shows that the PEF treatments have much greater oxidation ability than the EF processes. EF in single cell leads to 85% mineralization in 420 min by the oxidation of organics with $^\bullet$OH formed from Fenton's reaction (1) and BDD($^\bullet$OH) generated from reaction (4). For EF in combined cell, TOC decays more rapidly during the initial 120 min, but it attains a similar 88% reduction at 420 min. This evidences the formation of greater amounts of oxidant $^\bullet$OH in the combined system from Fe^{2+} regenerated at the CF cathode by reaction (3), although this radical becomes less efficient at long times when hardly oxidizable byproducts like Fe(III)–carboxylate complexes are formed [2,15,19]. In contrast, the drug solution attains almost total mineralization (96% TOC removal) by applying PEF for 240 min in single cell and 180 min in combined cell. This large effect of UVA irradiation can be related to the fast photolysis of Fe(III)–carboxylate complexes formed [2,31], rather than $^\bullet$OH production via reaction (5). The enhancement in the formation of these complexes due to the generation of more $^\bullet$OH from Fe^{2+} regenerated at the CF cathode, along with their quicker photolysis by UVA light, explain the slightly greater oxidation ability of PEF in combined cell.

The MCE values for the trials of Fig. 1a are presented in Fig. 1b. As expected, the efficiencies for both PEF treatments are much higher than those of EF ones. The use of the combined system increases the efficiency of both methods, primordially at the beginning of the degradation processes. Maximum efficiencies of 24% and 36% for EF and 62% and 65% for PEF in the corresponding single and combined cells are reached between 60 and 120 min of treatments.

From the above considerations, one can conclude that the use of the BDD/ADE–Pt/CF cell is more beneficial for the first stages of the EF and PEF degradations, where organics are mainly oxidized with $^\bullet$OH formed from Fenton's reaction (1). At long times, the performance of this cell is more similar to that of the single one, although it always yields fast mineralization.
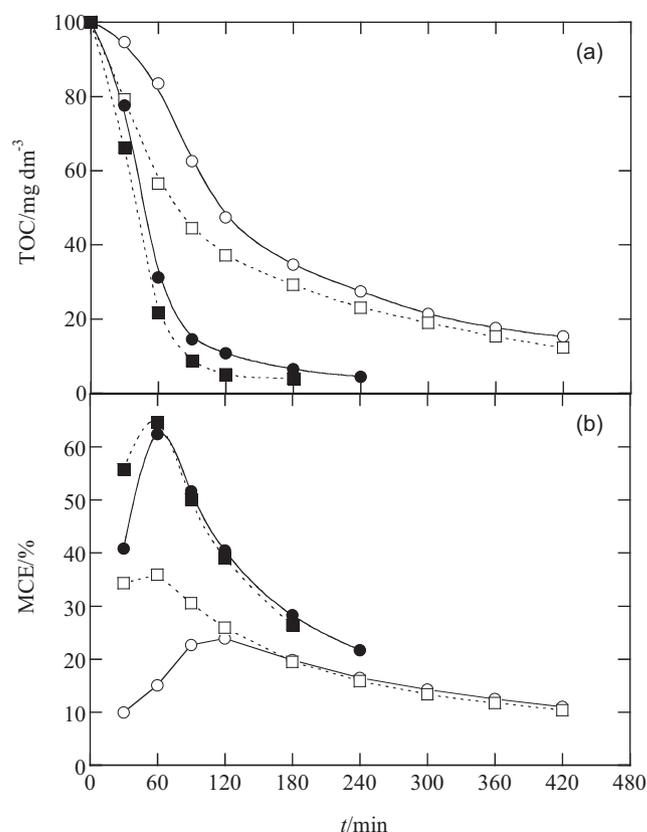
Fig. 1. Variation of (a) TOC and (b) mineralization current efficiency calculated from Eq. (6) with electrolysis time for the treatment of 100 cm^3 of a 154 mg dm^{-3} propranolol hydrochloride solution with 0.05 mol dm^{-3} Na$_2$SO$_4$ and 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 and 35 °C. (○) Electro-Fenton (EF) in a boron-doped diamond (BDD)/air diffusion electrode (ADE) cell at 40 mA cm^{-2}, (□) EF in a combined BDD/ADE–Pt/carbon felt (CF) cell at 40–4 mA cm^{-2}, (●) photoelectro-Fenton (PEF) under a 6 W UVA irradiation of $\lambda_{max} = 360$ nm in single BDD/ADE cell at 40 mA cm^{-2} and (■) PEF in combined BDD/ADE–Pt/CF cell at 40–4 mA cm^{-2}.

3.2. Influence of current density on electro-Fenton and photoelectro-Fenton processes

For the EF process in BDD/ADE cell, Fig. 2a shows a faster TOC decay of the above drug solution with increasing current density, attaining final values of 78%, 80%, 85%, 88% and 91% at 10, 20, 40, 60 and 80 mA cm^{-2}, respectively. This trend is attributable to the production of higher amounts of: (i) $^\bullet$OH from Fenton's reaction (1) due to the quicker generation of H$_2$O$_2$ at the ADE cathode and (ii) BDD($^\bullet$OH) by increasing the rate of reaction (4) [19,20,26]. However, the opposite tendency can be observed for their efficiency in the inset panel of Fig. 2a, reaching maximum MCE values of 75%, 47%, 24%, 16% and 11% at 90–120 min of 10, 20, 40, 60 and 80 mA cm^{-2}, respectively. The increase in current density then causes the acceleration of parasite reactions of hydroxyl radicals ($^\bullet$OH and BDD($^\bullet$OH)) giving a relatively lower quantity of organic oxidation events with the consequent loss in efficiency. These waste reactions involve the oxidation of BDD($^\bullet$OH) to O$_2$ by reaction (8), as well as the dimerization of $^\bullet$OH to H$_2$O$_2$ by reaction (9) or its destruction with H$_2$O$_2$ and Fe^{2+} by reactions (10) and (11), respectively [1,2,26]:

$$2BDD(^\bullet OH) \rightarrow 2BDD + O_{2(g)} + 2H^+ + 2e^- \tag{8}$$

$$2^\bullet OH \rightarrow H_2O_2 \tag{9}$$

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2{}^\bullet + H_2O \tag{10}$$

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \tag{11}$$
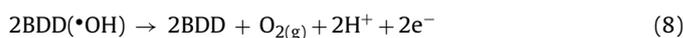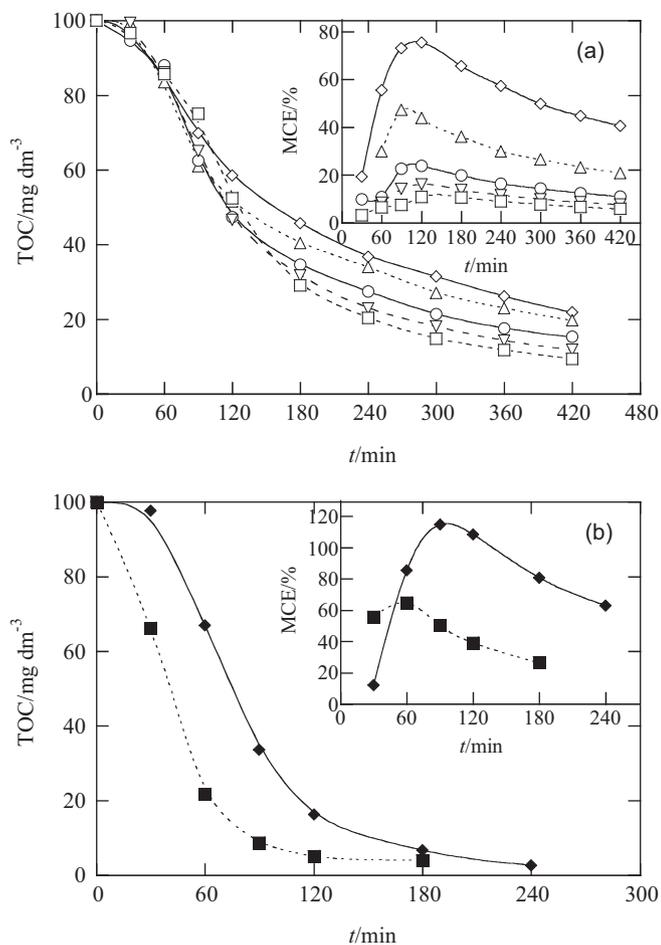
Fig. 2. Influence of current density on TOC abatement of 100 cm^3 of 154 mg dm^{-3} of propranolol hydrochloride with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 and 35 °C. (a) EF in single BDD/ADE cell at: (◇) 10, (△) 20, (○) 40, (▽) 60 and (□) 80 mA cm^{-2}. (b) PEF in combined BDD/ADE–Pt/CF at: (◆) 10–4 and (■) 40–4 mA cm^{-2}. The inset panels give the mineralization current efficiency for the corresponding processes.

Moreover, the relative proportion of generated BDD($^\bullet$OH) can also be reduced by the formation of weaker oxidants such as S$_2$O$_8^{2-}$ by reaction (12) and ozone by reaction (13) [26]:

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (12)$$

$$3H_2O \rightarrow O_{3(g)} + 6H^+ + 6e^- \qquad (13)$$
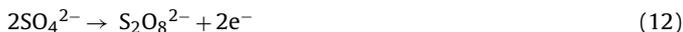
Similar effects of current density were found for the other treatments. Fig. 2b shows that almost total mineralization with 96–97% TOC decay is attained after 240 and 180 min of PEF treatment in combined cell at 10–4 and 40–4 mA cm^{-2}, respectively. The influence of UVA light in the PEF process is so significant that even allows the rapid removal of organics operating at low current densities, making the process highly efficient. The inset panel of Fig. 2b shows a maximum MCE value of 114% at 10–4 mA cm^{-2}, which drops to 65% at 40–4 mA cm^{-2} due to the larger enhancement of waste reactions, e.g. reactions (8)–(13).

3.3. Influence of other experimental variables on the photoelectro-Fenton process in combined cell

The Fe^{2+} content and pH for the more potent PEF treatment in BDD/ADE–Pt/CF cell were optimized. Fig. 3a shows the TOC–time plots for a 154 mg dm^{-3} drug solution with Fe^{2+} concentration between 0.1 and 5.0 mmol dm^{-3} at 10–4 mA cm^{-2}. The faster degradation is reached for an optimum content of 0.5 mmol dm^{-3}
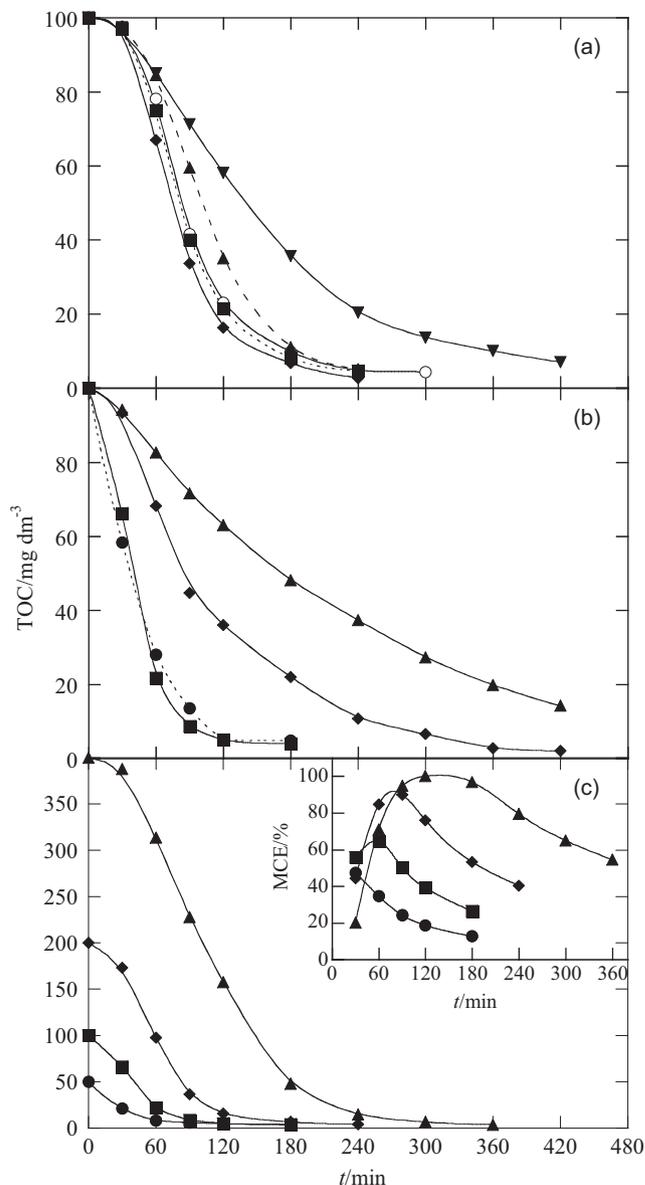
Fig. 3. Effect of experimental parameters on TOC abatement of 100 cm^3 of propranolol hydrochloride solutions in 0.05 mol dm^{-3} Na$_2$SO$_4$ at 35 °C using PEF in combined BDD/ADE–Pt/CF cell. (a) 154 mg dm^{-3} of propranolol hydrochloride with: (○) 0.1, (■) 0.25, (◆) 0.5, (▲) 2.5 and (▼) 5.0 mmol dm^{-3} Fe^{2+} at pH 3.0 by applying 10–4 mA cm^{-2}. (b) 154 mg dm^{-3} of propranolol hydrochloride with 0.5 mmol dm^{-3} Fe^{2+} at pH: (●) 2.0, (■) 3.0, (◆) 4.0 and (▲) 6.0 electrolyzed at 40–4 mA cm^{-2}. (c) (●) 77, (■) 154, (▲) 308 and (▼) 616 mg dm^{-3} of propranolol hydrochloride with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 treated at 40–4 mA cm^{-2}. The mineralization current efficiency for the corresponding processes is depicted in the inset panel.

Fe^{2+} where 97% mineralization is attained in 240 min. At this time, similar TOC removal is also obtained for the slower degradations with 0.1 and 0.25 mmol dm^{-3} Fe^{2+}. However, the process is strongly decelerated using a Fe^{2+} content as high as 5.0 mmol dm^{-3} Fe^{2+}, where TOC is only reduced by 93% in 420 min, as expected by the loss of generated $^\bullet$OH from reaction (11) with the excess of Fe^{2+} [2,4]. Fig. 3b depicts the influence of pH in the range 2.0–6.0 on TOC removal of 154 mg dm^{-3} propranolol hydrochloride with 0.5 mmol dm^{-3} Fe^{2+} operating at 40–4 mA cm^{-2}. For the trials of pH 4.0 and 6.0, the pH decayed rapidly and it was continuously regulated to its initial value by adding small volumes of 0.5 mol dm^{-3} NaOH. Although TOC undergoes a similar decay for pH 2.0 and 3.0, attaining almost overall mineralization in 180 min, the degradation rate at pH 3.0 is slightly higher. In contrast, the process becomes

slower at pH 4.0 and much slower at pH 6.0. These findings corroborate that pH 3.0 is optimal for PEF in combined cell, a value close to the optimum pH of 2.8 for Fenton's reaction (1) [1]. This evidences the main destruction of organics with $^\bullet OH$ radical formed from this reaction, since the production of BDD($^\bullet OH$) from reaction (4) is pH-independent [26].

The PEF oxidation of different drug concentrations under the optimum conditions of 0.5 mmol dm^{-3} Fe^{2+} and pH 3.0 operating at 40–4 mA cm^{-2} was also examined. Fig. 3c shows that longer electrolysis time is needed for achieving >96% TOC decay when more amount of drug is present in solution. This trend is not surprising because more time is necessary to destroy greater quantities of organic matter. Nevertheless, the efficiency rises gradually shifting its maximum at higher time, as can be seen in the inset panel of Fig. 3c. Maximum MCE values of 47% at 30 min, 65% at 60 min, 90% at 90 min and 100% at 120 min are determined for increasing drug contents of 77, 154, 308 and 616 mg dm^{-3}, respectively. This suggests the removal of greater contents of organics with higher amounts of BDD($^\bullet OH$) and $^\bullet OH$, thereby decreasing the rate of their parasite reactions (8)–(11).

3.4. Decay kinetics for propranolol

The decay of propranolol concentration under the same conditions of Fig. 1a was determined by reversed-phase HPLC, where the drug displayed a well-defined absorption peak at a retention time (t_r) of 6.02 min. No change in drug content was previously observed for the treatment of a 154 mg dm^{-3} propranolol hydrochloride (corresponding to 135 mg dm^{-3} of pure propranolol) solution with 20 mmol dm^{-3} H$_2$O$_2$ of pH 3.0 in the presence and absence of UVA light, as expected if it does not react with H$_2$O$_2$ and is not directly photolyzed by UVA light.

Fig. 4a evidences the existence of a slight inhibition in drug removal by EF in single cell, disappearing in 29 min. This can be associated with a low generation of $^\bullet OH$ and BDD($^\bullet OH$), which attack competitively to propranolol and its oxidation products giving a gradual deceleration of the destruction of the former as more byproducts are being formed. This phenomenon is not observed for the other treatments that produce additional $^\bullet OH$ maintaining BDD($^\bullet OH$) electrogeneration. Thus, propranolol disappears in only 15 min by EF in combined cell, indicating a large enhancement of
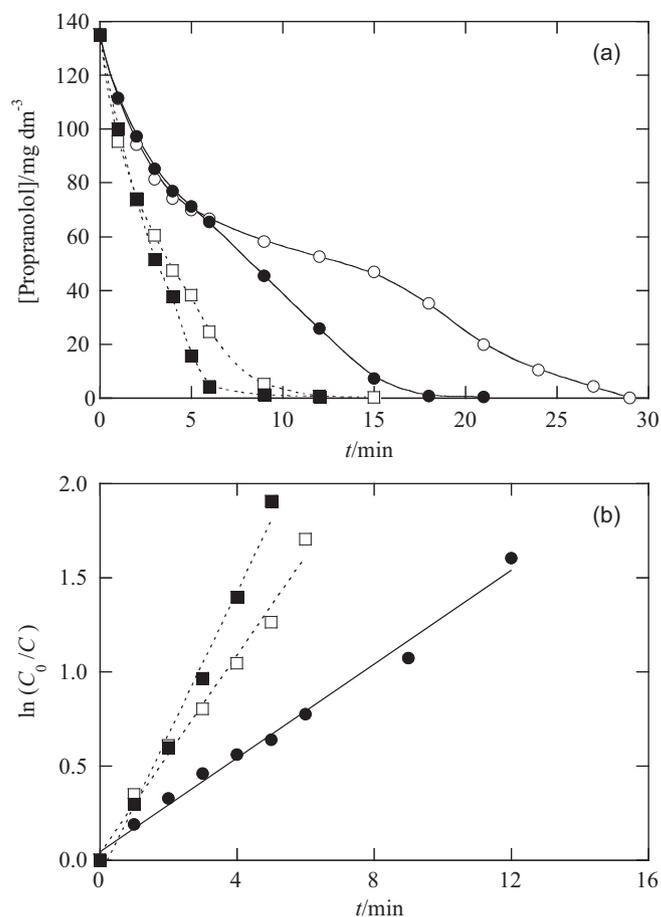
Fig. 4. (a) Decay of pure propranolol concentration with electrolysis time under the conditions given in Fig. 1 (initial concentration (C_0): 135 mg dm^{-3}). (b) Kinetic analysis considering that the drug follows a pseudo first-order reaction.

Fenton's reaction (1) from the continuous Fe^{2+} regeneration by Fe^{3+} reduction at the CF cathode. In contrast, PEF in single cell yields smaller $^\bullet OH$ production via reaction (5) and propranolol persists up to 21 min. The superiority of EF in combined cell compared with PEF
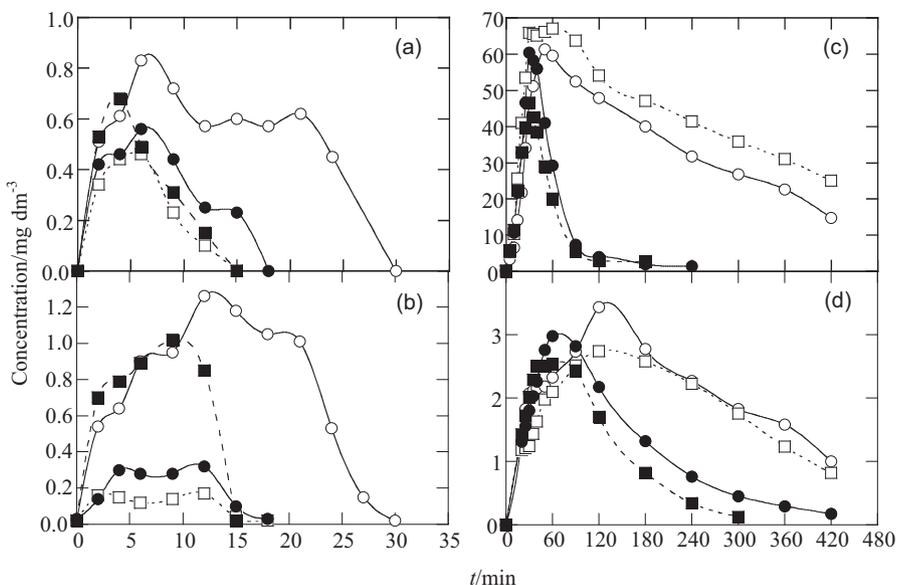
Fig. 5. Evolution of the concentration of (a) 1-naphthol, (b) phthalic acid, (c) oxalic acid and (d) oxamic acid detected as oxidation products during the degradation of 154 mg dm^{-3} of propranolol hydrochloride in 0.05 mol dm^{-3} Na$_2$SO$_4$ with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 and 35 °C. (○) EF in single BDD/ADE cell at 40 mA cm^{-2}, (□) EF in combined BDD/ADE–Pt/CF cell at 40–4 mA cm^{-2}, (●) PEF in BDD/ADE cell at 40 mA cm^{-2} and (■) PEF in BDD/ADE–Pt/CF cell at 40–4 mA cm^{-2}.

in single cell to generate $^{\bullet}$OH does not agree with the much quicker TOC reduction obtained for the latter system (Fig. 1a) due to the parallel photolysis of intermediates like Fe(III)–carboxylate complexes. The faster propranolol decay, with total removal in 12 min, takes place using PEF in combined cell, corroborating that this system generates greater amounts of $^{\bullet}$OH from the combination of the above reactions.

The concentration decays of Fig. 4a, except for EF in single cell, were well shifted to a pseudo first-order reaction, as can be seen in Fig. 4b. From this analysis, increasing pseudo first-order rate constant (k_1) values of 2.1×10^{-3} s^{-1} (square regression coefficient (R^2) = 0.990) for PEF in BDD/ADE cell, 4.4×10^{-3} s^{-1} (R^2 = 0.989) for EF in BDD/ADE–Pt/CF cell and 5.8×10^{-3} s^{-1} (R^2 = 0.989) for PEF in BDD/ADE–Pt/CF cell are determined. This behavior presupposes the attack of the drug with constant $^{\bullet}$OH and BDD($^{\bullet}$OH) concentrations, although rising $^{\bullet}$OH content is formed in such systems.

3.5. Evolution of oxidation products and inorganic ions

It is known that the C–O bond of phenoxy derivatives is broken under the attack of hydroxyl radicals yielding the corresponding phenol with release of the lateral group [12]. On this basis, 1-naphthol may be expected from an analogous reaction of propranolol. Further oxidation of this primary byproduct can give phthalic acid [47]. These assumptions were confirmed from the reversed-phase HPLC of electrolyzed solutions that displayed two absorption peaks related to 1-naphthol (t_r = 1.89 min) and phthalic acid (t_r = 1.12 min), which were unequivocally identified by comparing their retention times and UV–vis spectra, measured on the photodiode array detector, with those of pure compounds. The evolution of these compounds under the conditions of Fig. 1a is presented in Fig. 5a and b, respectively, where contents <0.9 mg dm^{-3} for 1-naphthol and <1.3 mg dm^{-3} for phthalic acid can be observed. Both aromatics are completely removed in 30 min by EF in BDD/ADE cell and in 15–18 min by the other treatments, i.e. at similar times to the disappearance of propranolol in the same processes (Fig. 4a). Their rapid formation and destruction while the drug persists in the medium suggests that they are oxidized with hydroxyl radicals, without direct photolysis by UVA irradiation.

Ion-exclusion chromatograms of treated solutions exhibited two well-defined absorption peaks corresponding to ultimate oxalic (t_r = 6.4 min) and oxamic (t_r = 9.1 min) acids that are directly mineralized to CO$_2$ [2,6,11]. Small contents (<0.2 mg dm^{-3}) of other short-linear carboxylic acids such as maleic (t_r = 7.6 min) and formic (t_r = 13.6 min) were also detected at short times. While oxamic acid is produced from the oxidation of the lateral group of propranolol, the other acids can proceed from the cleavage of the aromatic ring of precedent products [6,11,13].

Fig. 5c and d evidence that oxalic and oxamic acids persist up to the end of each treatment, since they form Fe(III) complexes that are not removed with $^{\bullet}$OH in the bulk [2,19,20]. Oxalic acid is largely accumulated up to ca. 65 mg dm^{-3} after 45–60 min of EF in both cells, whereupon it decays progressively to reach between 15 and 25 mg dm^{-3} in 420 min. A similar behavior is found for oxamic acid in the same EF processes, although only 3 mg dm^{-3} are obtained as maximum at 120 min and 1 mg dm^{-3} at 420 min. The gradual destruction of Fe(III)–oxalate and Fe(III)–oxamate complexes in these methods can then be ascribed to their oxidation with BDD($^{\bullet}$OH) formed from reaction (4). At the end of these treatments, the remaining oxalic and oxamic acids give 7 mg dm^{-3} of TOC as maximum, a value lower than 12–15 mg dm^{-3} of TOC present in the electrolyzed solutions (Fig. 1a), indicating that they contain >5 mg dm^{-3} of TOC of other undetected organic components. Under UVA irradiation, Fe(III)–oxalate complexes are more rapidly and completely photodecomposed in 240 and 180 min in the single and combined cells, respectively, explaining the slightly greater
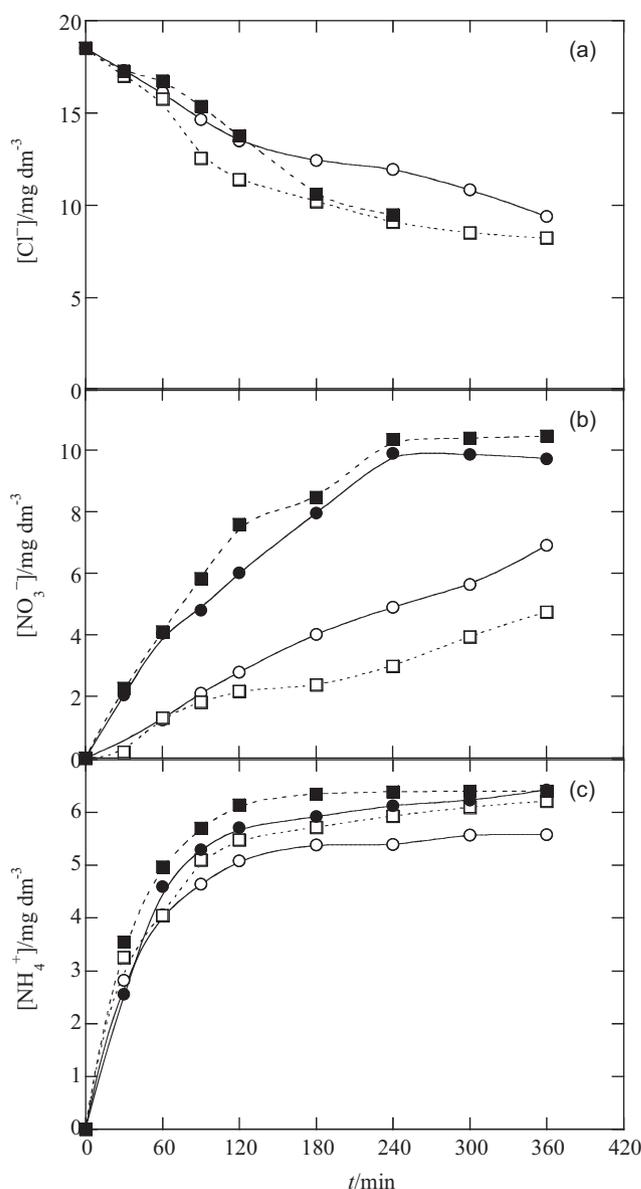
Fig. 6. Time-course of the concentration of (a) chloride, (b) nitrate and (c) ammonium ions accumulated in the medium during the mineralization of 154 mg dm^{-3} of propranolol hydrochloride in 0.05 mol dm^{-3} Na$_2$SO$_4$ with 0.5 mmol dm^{-3} Fe^{2+} at pH 3.0 and 35 °C under the same conditions as given in Fig. 5.

oxidizing power of the latter system. This is also observed for the Fe(III)–oxamate complexes, which are photolyzed more slowly disappearing in 420 min in the single cell and more quickly, in 300 min, in the combined cell. Since almost total mineralization is attained for both PEF treatments when oxalic acid is destroyed (Figs. 1a and 5c), one can infer that UVA light helps to remove the species remaining at the end of EF methods. Note that the photolytic process of Fe(III)–carboxylate complexes by UVA light in PEF involves their photodecarboxylation such as exemplified by reaction (14) for Fe(III)–oxalate complexes (Fe(C$_2$O$_4$)$^+$, Fe(C$_2$O$_4$)$_2$$^-$ and Fe(C$_2$O$_4$)$_3$$^{3-}$) [31]:

$$2Fe(C_2O_4)_n^{(3-2n)} + h\nu \rightarrow 2Fe^{2+} + (2n-1)C_2O_4^{2-} + 2CO_2 \quad (14)$$
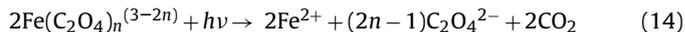
Inorganic ions such as Cl$^-$, NO$_3$$^-$ and NH$_4$$^+$ were detected in treated solutions and quantified by ionic chromatography. Fig. 6a reveals that the 18.5 mg dm^{-3} of Cl$^-$ ion present in the 154 mg dm^{-3} propranolol hydrochloride solution are slowly reduced in all cases, as expected if it is oxidized to Cl$_2$ with BDD($^{\bullet}$OH) at the anode sur-

face [26]. That means that organics could also react with generated chlorine in very small extent in view of the low content of Cl^- removed ($10\,mg\,dm^{-3}$ in 420 min). On the other hand, NO_3^- and NH_4^+ ions formed from the initial N of the drug ($7.3\,mg\,dm^{-3}$) are gradually accumulated, as shown Fig. 6b and c, respectively. Steady states of about $10\,mg\,dm^{-3}$ of NO_3^- (31% of initial N) at 240 min and $6.4\,mg\,dm^{-3}$ of NH_4^+ (68% of initial N) at 120 min are obtained for PEF in single and combined cells, indicating that all organic nitrogen is mineralized with preponderance of NH_4^+. For the less potent EF processes, NO_3^- concentration rises much more slowly and NH_4^+ ion follows the same tendency as for the PEF methods. After 360 min of EF, 81% of the initial N is converted into inorganic ions in both cells, suggesting that the remaining species in solution are composed of a large proportion of N-derivatives, which mainly yield NO_3^- when they are destroyed by UVA light in the homologous PEF treatments.

4. Conclusions

It has been demonstrated that EF and PEF treatments with BDD anode are able to mineralize naphthalene derivatives such as the beta-blocker propranolol. The use of a combined BDD/ADE-Pt/CF cell enhances the degradation processes compared with a single BDD/ADE one because more oxidant •OH is formed from Fe^{2+} regeneration at the CF cathode. The PEF treatments lead to almost overall mineralization due to the photolysis of Fe(III)–carboxylate complexes by UVA light, which are hardly oxidized with hydroxyl radicals in the less potent EF processes. The oxidation power of all methods increases with increasing current density. The PEF process is optimal with $0.5\,mmol\,dm^{-3}$ Fe^{2+} at pH 3.0 and is more viable at lower current density and higher drug content. Propranolol decay follows a pseudo first-order kinetics in most cases, mainly being attacked by •OH. 1-Naphthol and phthalic acid are detected as aromatic products while the drug persists and are also mainly destroyed with •OH. Final Fe(III)–oxalate and Fe(III)–oxamate complexes are slowly oxidized with BDD(•OH) in EF and more rapidly photodecarboxylated by UVA light in PEF. The initial Cl^- is slowly oxidized by BDD(•OH). NH_4^+ and in smaller proportion NO_3^- are lost during all degradations.

Acknowledgements

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