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Electro-Fenton and photoelectro-Fenton degradations of the drug beta-blocker propranolol using a Pt anode: Identification and evolution of oxidation products

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ABSTRACT

The beta-blocker propranolol hydrochloride has been degraded by electrochemical advanced oxidation processes like electro-Fenton (EF) and photoelectro-Fenton (PEF) using a single cell with a Pt anode and an air diffusion cathode (ADE) for H_2O_2 electrogeneration and a combined system containing the above Pt/ADE pair coupled in parallel to a Pt/carbon-felt (CF) cell. Organics are mainly oxidized with hydroxyl radical (•OH) formed from Fenton's reaction between added Fe^{2+} and electrogenerated H_2O_2. The PEF treatment in Pt/ADE–Pt/CF system yields almost total mineralization because •OH production is enhanced by Fe^{2+} regeneration from Fe^{3+} reduction at the CF cathode and Fe(III) complexes with generated carboxylic acids are rapidly photodecarboxylated under UVA irradiation. Lower mineralization degree is found for PEF in Pt/ADE cell due to the little influence of UVA light on Fe^{2+} regeneration. The homologous EF processes are much less potent as a result of the persistence of Fe(III)–carboxylate complexes. Aromatic intermediates such as 1-naphthol, 1,4-naphthoquinone and phthalic acid and generated carboxylic acids such as pyruvic, glycolic, malonic, maleic, oxamic, oxalic and formic are identified. While chloride ion remains stable, NH_4^+ and NO_3^- ions are released to the medium. A reaction sequence for propranolol hydrochloride mineralization is proposed.

1. Introduction

A large variety of pharmaceutical drugs have been recently detected in surface, ground and drinking waters at low contents of $\mu g\,L^{-1}$ [1–8]. This pollution is originated from emission from production sites, direct disposal of overplus drugs in households, excretion after drug administration to humans and animals and treatments throughout the water in fish and other animal farms [2]. Drugs accumulation is due to their inefficient destruction from conventional methods in sewage treatment plants (STPs). Although the interaction of low contents of drugs with living beings in the environment is not well documented, beta-blockers affect the endocrine system of fishes and exert toxic effects on algae and invertebrates [5,9–12]. To avoid the dangerous health effects of such pollutants, potent oxidation methods are needed to remove drugs and their metabolites from wastewaters.

In the last years, an increasing number of papers have been published dealing with the destruction of low concentrations of persistent organic pollutants (POPs) in waters by electrochemical advanced oxidation processes (EAOPs). These eco-friendly methods are based on the in situ generation of hydroxyl radical (•OH) [13,14], which can react with POPs until total mineralization (conversion into CO_2, water and inorganic ions). The most common EAOP based on Fenton chemistry is the electro-Fenton (EF) process in which H_2O_2 is continuously supplied to the contaminated solution from the two-electron reduction of injected O_2 at the cathode from reaction (1) [14], while Fe^{2+} is added to the medium as catalyst, usually at the optimum pH 3.0, to react with electrogenerated H_2O_2 producing •OH and Fe^{3+} from Fenton's reaction (2) [15]:

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (2)$$

Reaction (1) takes place at carbonaceous cathodes like carbon felt (CF) [16–19], reticulated vitreous carbon [20], graphite [21,22], carbon fiber [23], gas (O_2 or air) diffusion electrodes [17,24–28] and boron-doped diamond (BDD) films [29]. In EF, reaction (2) can be propagated from Fe^{2+} regenerated by Fe^{3+} reduction at the cathode [17,30,31]:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

The rate of reaction (3) depends on the cathodic material and its ability to electrogenerate H_2O_2 from reaction (1). For electrodes

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with low H_2O_2 production as CF, Fe^{3+} reduction is so fast that a large proportion of Fe^{2+} remains in the solution, whereas for gas diffusion electrodes where reaction (1) predominates, Fe^{3+} is largely formed [14,17,19]. EF with a gas diffusion cathode yields poor decontamination of aromatics because complexes of Fe(III) with generated carboxylic acids cannot be destroyed with •OH [32–36]. The degradation process can be enhanced by the photoelectro-Fenton (PEF) method [14,25,27,32–36] in which the solution treated under EF conditions is irradiated with UVA light to originate higher •OH generation and Fe^{2+} regeneration by photolysis of $Fe(OH)^{2+}$, the predominant Fe^{3+} species at pH 3.0 [15]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (4)$$

Additionally, UVA light photodecomposes Fe(III)–carboxylate complexes, strongly increasing the degradation rate of POPs [14,25,27].

When EF and PEF treatments are performed in an undivided cell with Pt, heterogeneous hydroxyl radical (Pt(•OH)) is formed from water oxidation at its surface[13]:

$$Pt + H_2O \rightarrow Pt({}^{\bullet}OH) + H^+ + e^- \quad (5)$$

POPs can thus be oxidized by •OH in the bulk and Pt(•OH) at the anode [27,32,35,36].

In our laboratory, we have checked the above EAOPs in a single two-electrode cell containing a Pt anode and a carbon-polytetrafluoroethylene (PTFE) gas diffusion cathode to degrade acidic solutions of antimicrobials, analgesics, biocides, non-steroidal anti-inflammatory drugs (NSAIDs) and a beta-blocker such as atenolol with a benzene ring as aromatic moiety [27,32–36]. To treat the latter compound, a novel cell configuration composed of two systems in parallel, a Pt/air diffusion electrode (ADE) cell and a Pt/CF cell [27] was proposed, to ensure high H_2O_2 electrogeneration at the ADE cathode from reaction (1) and large regeneration of Fe^{2+} at the CF cathode from reaction (3). An important point to ensure the possible application of such combined Pt/ADE–Pt/CF cell in practice is to know its ability to destroy a large number of aromatics with different structure because a mixture of drugs are usually detected in pharmaceutical wastewaters. To test if this combined cell can destroy more efficiently drugs with other structures by EF and PEF, we have studied the oxidation route of propranolol (1-(isopropylamino)-3-(1-naphthyloxy)propan-2-ol). This compound is a beta-blocker with a naphthalene ring, an aromatic structure whose degradation and reaction sequence by •OH attack has not been previously established. This drug is supplied as propranolol hydrochloride and used to treat the hypertension. Since it is partially metabolized by the liver, it is excreted in urine and accumulated in the environment, being found up to 2 μg L^{-1} in SWT effluent discharges [1,3,4,6,8] and surface waters [3,5]. A reduced number of papers have explored its oxidation by advanced oxidation processes like ozonation in neutral and alkaline media [37,38], O_3/H_2O_2 [38], radiolysis [39], UV/H_2O_2 [40] and a biological Fenton-like system mediated by the white-rot fungus *Trametes versicolor* [41]. Mineralization for a mixture of 0.15 mM beta-blockers including propranolol has been described by Sirés et al. [42] using EF with a single Pt/CF cell, but without identification of intermediates.

This paper presents the comparative EF and PEF degradations of propranolol hydrochloride in single Pt/ADE and combined Pt/ADE–Pt/CF cells to ascertain their oxidation power. A drug concentration equivalent to 100 mg L^{-1} of total organic carbon (TOC) was treated to clarify the degradation action of generated hydroxyl radicals and UVA light, as well as to detect the oxidation products by gas chromatography–mass spectrometry (GC–MS) and chromatographic techniques.

2. Experimental

2.1. Chemicals

Propranolol hydrochloride (99% purity) was supplied by the pharmaceutical AstraZeneca España. 1-Naphthol was reactive reagent from BDH Chemical Ltd. and phthalic acid was analytical reagent from Aldrich. Maleic, acetic, oxamic, oxalic and formic 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 resistivity >18 MΩ cm at 25 °C.

2.2. Electrolytic systems

All electrolyses were conducted in an open, cylindrical and undivided tank reactor with a double-jacket for circulation of external thermostated water. The anodes were Pt sheets (99.99% purity) and the cathodes were a carbon-PTFE ADE from E-TEK and/or a CF from Sofacel. The active area of all electrodes was 3 cm^2. Two configurations with monopolar connection, a Pt/ADE or Pt/ADE–Pt/CF cell, were employed [27]. The gas diffusion cathode was fed with 20 mL min^{-1} of air for H_2O_2 electrogeneration from reaction (1). A constant current was applied to each pair of electrodes with an Amel 2053 potentiostat–galvanostat and/or an EG&G P.A.R. 363 potentiostat–galvanostat.

Solutions of 100 mL containing 154 mg L^{-1} propranolol hydrochloride (100 mg L^{-1} TOC) in 0.05 M Na_2SO_4 as background electrolyte were electrolyzed by EF and PEF after regulation at pH 3.0 with concentrated H_2SO_4 and addition of 0.5 mM Fe^{2+} as catalyst. These conditions were chosen because they were optimal for treating other aromatics [27,32–36]. The solution was vigorously stirred with a magnetic bar at 800 rpm and its temperature was kept at 35 °C. In PEF, the solution was irradiated with a Philips TL/6W/08 fluorescent black light blue tube of λ_{max} = 360 nm, placed at the top of the open cell at 5 cm above the solution (photoionization energy input of 1.4 W m^{-2}).

2.3. Apparatus and analysis procedures

The solution pH was determined with a Crison GLP 22 pH-meter. Samples withdrawn from electrolyzed solutions were filtered with 0.45 μm PTFE filters from Whatman before analysis. Solution TOC was obtained with a Shimadzu VCSN analyzer. The evolution of aromatics was followed by reversed-phase HPLC using a Waters 600 chromatograph coupled with a Waters 996 photodiode array detector selected at λ = 291.2 nm for propranolol, λ = 296.0 nm for 1-naphthol and λ = 233.5 nm for phthalic acid. The chromatograph was fitted with a Spherisorb ODS2 5 μm, 150 mm × 4.6 mm (i.d.), column at 35 °C and a 36:36:28 (v/v/v) acetonitrile/methanol/water (with 2 g L^{-1} sodium dodecyl sulfate at pH 3.0) mixture at 1.5 mL min^{-1} circulated as mobile phase. Carboxylic acids were detected by ion-exclusion HPLC using the same chromatograph fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at 35 °C, the photodiode array selected at 210 nm and 4 mM H_2SO_4 at 0.6 mL min^{-1} as mobile phase. Ionic chromatography was performed with a Shimadzu 10 Avp HPLC coupled with a Shimadzu CDD 10 Avp conductivity detector. NH_4^+ concentration was measured using a Shodex IC YK-421, 125 mm × 4.6 mm (i.d.), cation column at 40 °C and a mobile phase of 5.0 mM tartaric acid, 2.0 mM dipicolinic acid, 24.2 mM boric acid and 15.0 mM corona ether at 1.0 mL min^{-1}. NO_3^- and Cl^- contents were obtained with a Shim-Pack IC-A1S, 100 mm × 4.6 mm (i.d.), anion column at 40 °C and 1.0 mM *p*-hydroxybenzoic acid and 1.1 mM *N*,*N*-diethylethanolamine solution at 1.5 mL min^{-1} as mobile phase.

Several EF treatments were made in a Pt/ADE cell at 30 mA for 60 min to identify aromatic intermediates by GC–MS using a HP 5890 Series II gas chromatograph coupled with a HP 5989A mass spectrophotometer operating in EI mode at 70 eV. A non-polar J&W DB-5MS 0.25 μm, 30 m × 0.25 mm (i.d.), column was employed with a temperature ramp of 50 °C for 3 min, 10 °C min^{-1} up to 300 °C and hold time 5 min. Mass spectra were analyzed with a NIFT05 data library. The following trials were made: (i) the organic components of the treated solution were extracted with 30 mL of CH_2Cl_2. The resulting organic solution was dried over Na_2SO_4, filtered and rotavaporated up to 1.5 mL to be analyzed by GC–MS; (ii) 15 mL of the electrolyzed solution were lyophilized and the remaining solid was eluted in 5 mL of CH_2Cl_2. This solution was filtered, concentrated to 1.5 mL and analyzed by GC–MS; and (iii) other lyophilized sample was eluted with 2 mL of ethyl acetate and treated with 100 μL of *N*,*O*-bis-(trimethylsilyl)acetamide under stirring at 70 °C for 10 min to obtain trimethylsilylated derivatives analyzed by GC–MS. Primary generated carboxylic acids formed after 60 min of the same EF treatment were identified after concentration of the solution to 2 mL at low pressure, followed by addition of 5 mL of ethanol, filtration and concentration to 1.5 mL by heating at 40 °C to form ethyl esters.

3. Results and discussion

3.1. Comparative oxidation power of the cells in EF and PEF

The EF and PEF treatments of 100 mL of a 154 mg L^{-1} propranolol hydrochloride solution with 0.5 mM Fe^{2+} of pH 3.0 were comparatively studied in the Pt/ADE and Pt/ADE–Pt/CF cells. A current between 50 and 200 mA was applied to each Pt/ADE pair, while 12 mA were imposed to the Pt/CF cell, which was found optimal in previous work [27]. A gradual TOC decay was always observed by prolonging electrolysis time to 420 min, where almost overall mineralization was only achieved for the Pt/ADE–Pt/CF cell in PEF at currents ≥120 mA of the former pair. A similar degradation degree was found for atenolol using the same system but at lower current of 50–12 mA for 360 min [27], indicating that the naphthalene ring of propranolol is more slowly mineralized than the benzene ring of atenolol.

Fig. 1a shows the TOC-time plots obtained for both EAOPs using the single Pt/ADE cell at 120 mA and the combined Pt/ADE–Pt/CF cell operating at 120–12 mA. In these trials, the pH dropped slowly to 2.6–2.7 due to the production of acidic byproducts [14]. Fig. 1a depicts that EF is much less potent than PEF. About 50% mineralization is achieved for EF in single cell, as expected by the low oxidation ability of Pt(•OH) formed from reaction (5) and the small amounts of •OH produced from Fenton's reaction (2). The latter reaction is strongly enhanced when Fe^{2+} regeneration increases from Fe^{3+} reduction at the CF cathode by reaction (3) using EF with the combined Pt/ADE–Pt/CF cell, since TOC is reduced by 72% in 420 min. However, the PEF process in Pt/ADE cell yields much faster degradation with 91% mineralization. This is related to two synergistic effects: (i) the production of more amounts of Fe^{2+} and •OH from the photolytic reaction (4) and (ii) the photolysis of complexes of Fe(III) with some final carboxylic acids [14]. The PEF treatment becomes much more potent using the combined Pt/ADE–Pt/CF cell, where the additional Fe^{2+} regeneration at the CF cathode allows almost total mineralization with 97% TOC removal (Fig. 1a). The same relative oxidation power for these EAOPs was found for atenolol degradation [27], thus confirming the role of the different catalytic processes taking place in them.

The combined action of H_2O_2 electrogeneration at the ADE cathode, Fe^{2+} regeneration at the CF cathode and UVA irradiation in the Pt/ADE–Pt/CF cell is beneficial to decontaminate wastewaters with propranolol hydrochloride. The higher oxidation power of this

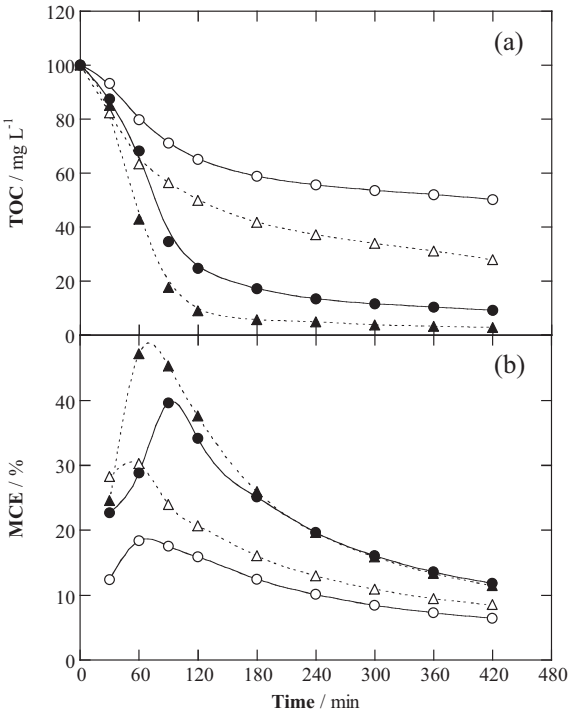


Fig. 1. (a) TOC removal and (b) mineralization current efficiency calculated from Eq. (7) versus electrolysis time for the degradation of 100 mL of a solution containing 154 mg L^{-1} of propranolol hydrochloride in 0.05 M Na_2SO_4 with 0.5 mM Fe^{2+} at pH 3.0 and 35 °C. (○) Electro-Fenton (EF) in Pt/air diffusion electrode (ADE) cell at 120 mA, (△) EF in combined Pt/ADE–Pt/carbon felt (CF) cell at 120–12 mA, (●) photoelectro-Fenton (PEF) in Pt/ADE cell at 120 mA with a 6 W UVA light of λ_{max} = 360 nm and (▲) PEF in combined Pt/ADE–Pt/CF cell at 120–12 mA.

process can be better analyzed considering that drug mineralization follows reaction (6) with formation of ammonium ion and remaining unchanged the chloride ion, as discussed below:

$$C_{16}H_{22}NO_2{}^+Cl^- + 30H_2O \rightarrow 16CO_2 + NH_4{}^+ + Cl^- + 78H^+ + 78e^- \quad (6)$$

and determining the mineralization current efficiency (MCE, in %) for the above trials at a given time t (h) as follows [34,35]:

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

where n is the number of electrons consumed per molecule mineralized (78), F is the Faraday constant (96487 C mol^{-1}), V_s is the solution volume (L), $\Delta(TOC)_{exp}$ is the experimental TOC decay (mg L^{-1}), 4.32×10^7 is a homogenization factor (3600 s h^{-1} × 12,000 mg mol^{-1}), m is the number of carbon atoms of propranolol (16) and I is the applied total current (0.120 A for Pt/ADE cell or 0.132 A for Pt/ADE–Pt/CF cell).

As can be seen in Fig. 1b, the efficiency for both PEF processes is much greater than that of homologous EF ones, being superior for the combined system. Maximum MCE values of 18% for EF in Pt/ADE cell, 30% for EF in Pt/ADE–Pt/CF cell, 40% for PEF in Pt/ADE cell and 47% for PEF in Pt/ADE–Pt/CF cell are reached at 60–90 min of electrolysis. This evidences a rapid mineralization of several byproducts at the early stages of all treatments, which rises when more •OH is produced and/or UVA light is irradiated. However, the efficiency decays dramatically for times >90 min by the progressive drop of organic matter and the production of hardly oxidizable species such as carboxylic acids. These findings corroborate that PEF in Pt/ADE–Pt/CF cell is the preferable EAOP tested, yielding almost total mineralization with the higher current efficiency. The same behavior is expected if these EAOPs are applied

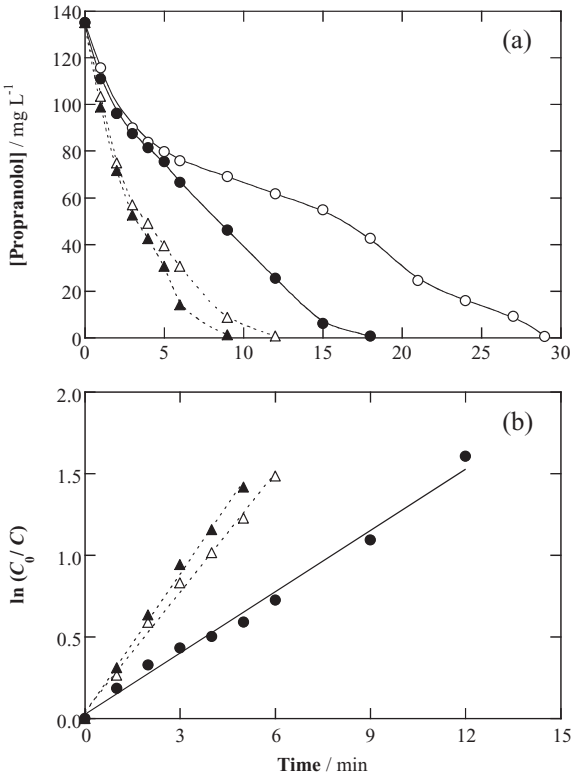


Fig. 2. (a) Decay of propranolol (without HCl) concentration with electrolysis time for the trials of Fig. 1. (b) Kinetic analysis assuming a pseudo first-order reaction for propranolol.

to smaller propranolol contents, even at levels of SWT effluents, although lower currents should be imposed because organics are removed in shorter time, but with lesser efficiency, according to the performance of these systems [14,27].

3.2. Decay kinetics for propranolol

The synergistic action of electrogenerated hydroxyl radicals and UVA light on propranolol destruction was analyzed by measuring its concentration decay by reversed-phase HPLC, where it exhibited a well-defined peak at retention time (t_r) of 6.02 min. Before these trials, it was confirmed that the concentration of 154 mg L^{-1} propranolol hydrochloride at pH 3.0 does not vary in the presence of 20 mM H_2O_2 and/or under UVA irradiation, as expected if in EF and PEF the drug is only destroyed by Pt(•OH) and •OH [14,33], without direct photolysis by UVA light.

The concentration decays determined under the conditions of Fig. 1a (C_0 = 135 mg L^{-1} of pure propranolol, without the HCl molecule) are depicted in Fig. 2a. An exponential abatement can be observed in all cases, except for EF in Pt/ADE cell where propranolol removal is slightly inhibited at times >5 min. This anomalous phenomenon can be ascribed to competition with the destruction of its oxidation products, also attacked by Pt(•OH) and •OH, causing the deceleration of drug decay. This is not observed for the other EAOPs because the additional production of •OH accelerates propranolol removal. Fig. 2a shows that this compound disappears in 29 min for EF in Pt/ADE cell, 18 min for PEF in Pt/ADE cell, 12 min for EF in Pt/ADE–Pt/CF cell and only 9 min for PEF in Pt/ADE–Pt/CF cell. The PEF process in single cell originates less •OH in the bulk than EF in combined cell, as expected if photolytic reaction (4) is much less potent for generating this species than the efficient Fe^{2+} regeneration at the CF cathode from reaction (3). This is opposite to the faster TOC reduction found for PEF in Pt/ADE cell in Fig. 1a, indicating that its higher oxidation power with respect to EF in combined cell is due to the photolysis of intermediates. Results of Fig. 2a also evidences that the maximum •OH generation occurs in PEF using the Pt/ADE–Pt/CF cell, indicating that this EAOP gives the quicker destruction of organics. A similar trend of these systems was found for atenolol decay [27], corroborating that the combined cell accelerates the oxidation of organics by both, EF and PEF because of the greater production of •OH from the Fe^{2+} regeneration at CF.

Fig. 2b presents the kinetic analysis of the concentration decays of Fig. 2a assuming a pseudo first-order reaction for the drug. The excellent linear straights found suggest a constant hydroxyl radical (Pt(•OH) and •OH) concentration formed in these systems while propranolol is removed. Increasing values for the pseudo first-order rate constant (k_1) of 2.1×10^{-3} s^{-1} (square regression coefficient (R^2) = 0.990) for PEF in Pt/ADE cell, 4.0×10^{-3} s^{-1} (R^2 = 0.994) for EF in Pt/ADE–Pt/CF cell and 4.7×10^{-3} s^{-1} (R^2 = 0.995) for PEF in Pt/ADE–Pt/CF cell, are determined, in agreement with the gradual increase in •OH from Fenton's reaction (2) produced by photolytic reaction (4), Fe^{2+} regeneration from reaction (3) and both reactions, respectively. Taking into account that the absolute rate constant for the reaction of propranolol with •OH is $k_2 = 3.4 \times 10^9$ M^{-1} s^{-1} [42], one can estimate a hydroxyl radical concentration ($=k_1/k_2$) of 6.2×10^{-13} M produced by PEF in single cell, which rises twice up to 1.4×10^{-12} M in the combined one. These generated •OH concentrations are of the same magnitude order as determined for the EF treatments of other aromatics [14,42].

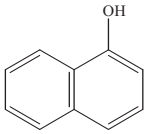
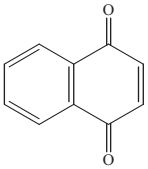
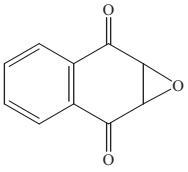
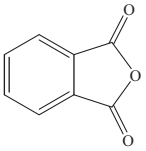
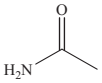
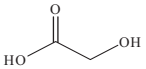
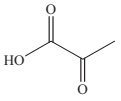
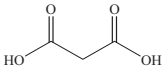
3.3. Identification of aromatic intermediates and generated carboxylic acids

To detect the oxidation products by GC–MS, several 154 mg L^{-1} drug solutions were treated by EF in Pt/ADE cell at a current as low as 30 mA for 60 min. Under these very weak oxidation conditions in which the drug persists for >2 h, the identification of the most stable aromatics and primary carboxylic acids is feasible. Table 1 summarizes the intermediates identified from different procedures, along with their main characteristics. 1-Naphthol, the initial hydroxylated and deaminated naphthalene derivative, was found in most cases, along with its oxidation products 1,4-naphthoquinone, 1a,7a-dihydronaphto[2,3-b]oxirene-2,7-dione and phthalic anhydride. Acetamide as well as the ethylated derivative of glycolic and pyruvic acids and the diethylated derivative of malonic acid were also identified. These byproducts can be produced from the oxidative breaking of the (2-hydroxy-3-isopropylamine)propoxyl radical, the lateral group lost from propranolol when 1-naphthol is formed.

Reversed-phase chromatograms of electrolyzed solutions displayed two defined peaks associated with 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. Note that phthalic anhydride was not detected by this technique because in aqueous medium it is hydrated to the stable phthalic acid [43].

Ion-exclusion chromatograms of treated solutions exhibited peaks related to final short-linear carboxylic acids such as oxalic (t_r = 6.4 min), maleic (t_r = 7.6 min), oxamic (t_r = 9.1 min), formic (t_r = 13.6 min) and acetic (t_r = 14.9 min). While oxamic and acetic acids come from the oxidation of acetamide [32] and pyruvic acid [14], respectively, maleic acid is expected from the cleavage of the aromatic ring of benzenic intermediates such as phthalic acid [24,27,31–36]. Oxamic, oxalic and formic acids are ultimate acids that are directly mineralized to CO_2 [27,32,36]. The two latter acids proceed from longer or less oxidized carboxylic acids [14]. These results agree with those reported by Wang et al. [28], who found that under EF conditions, phthalic acid is oxidized to maleic, malonic, mesoxalic, oxalic and formic acids. The EAOP degradation of

Table 1
Aromatic intermediates and primary carboxylic acids identified by GC–MS during the degradation of propranolol by EF in a Pt/ADE cell.

Compound	Molecular formula	t_r/min	M/g mol^{-1} [a]
1-Naphthol		16.4[b] 16.2[c,e]	218[b] 144[d,e]
1,4-Naphthoquinone		15.0[b,c,d]	158
1a,7a-Dihydronaphto [2,3-b]oxirene-2,7-dione		16.1[d]	174
Phthalic anhydride		13.6[b–e]	148
Acetamide		4.0[b]	59
Glycolic acid		3.9[e]	104
Pyruvic acid		4.4[e]	116
Malonic acid		9.3[e]	160

[a] Molecular mass corresponding to the trimethylsilyl derivative, ethyl derivative or molecular formula according to the analytical technique utilized.
[b] GC–MS analyses were performed after electrolyzing 100 mL of 154 mg L^{-1} propranolol hydrochloride solutions in 0.05 M Na_2SO_4 of pH 3.0 at 30 mA for 60 min, followed by: lyophilization and silylation.
[c] Lyophilization and elution in CH_2Cl_2.
[d] Extraction with CH_2Cl_2.
[e] Ethylation.

naphthalene derivatives then produces the same carboxylic acids as obtained from benzenic compounds. This is feasible because the latter byproducts are generated from the attack of hydroxyl radicals on the naphthalene moiety, as phthalic acid formed from 1-naphthol.

3.4. Time–course of intermediates and evolution of inorganic ions released

Fig. 3a and b shows the evolution of the intermediates 1-naphthol and phthalic acid, respectively, under the same conditions of Fig. 1. Both compounds are accumulated in small extent (<1.5 mg L^{-1}) and persist while the initial drug is being oxidized. These aromatics are then quickly destroyed by •OH formed from

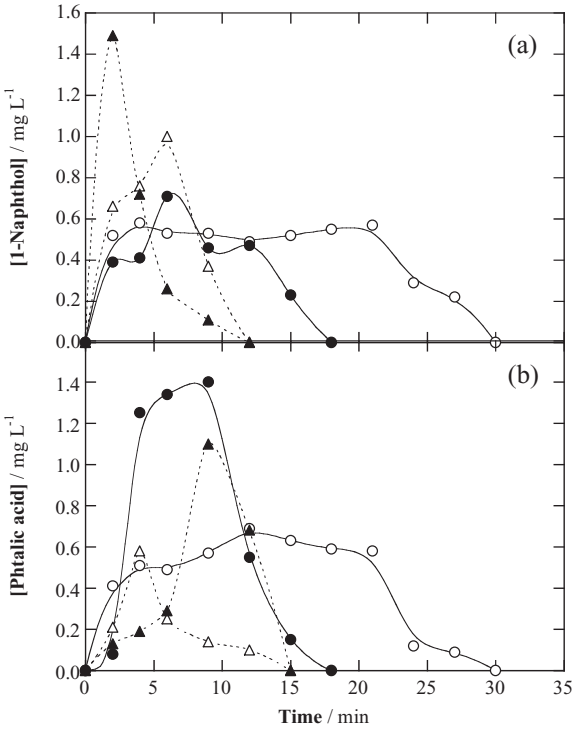


Fig. 3. Evolution of the concentration of (a) 1-naphthol and (b) phthalic acid detected as aromatic intermediates during the degradation of 154 mg L^{-1} of propranolol hydrochloride in the same conditions of Fig. 1.

Fenton's reaction (2), which is accelerated by reaction (4) and in larger extent by reaction (3) depending on the EAOP, without being photolyzed by UVA light.

A different trend can be observed in Fig. 4 for final carboxylic acids since UVA light accelerates their degradation. Formic acid was undetected in EF in Pt/ADE cell because the low oxidizing power of this method does not allow the destruction of its precursors (Fig. 1a). However, Fig. 4a shows that this acid is rapidly formed in the other EAOPs with higher oxidation ability, although its Fe(III) complexes are completely destroyed in 90 min with •OH by EF in Pt/ADE–Pt/CF cell and more quickly photolyzed in 40 min in both PEF treatments. The same behavior can be deduced for maleic acid from Fig. 4b. This acid is accumulated in very small contents (<0.18 mg L^{-1}) and totally removed in 60–90 min by PEF and for times >240 min by EF, as expected if Fe(III)–maleate complexes are more easily photodecomposed than oxidized with •OH. In contrast, Fig. 4c and d shows that oxalic and oxamic acids remain up to the end of electrolysis. In EF treatments, these acids reach a steady state of 55 and 0.85 mg L^{-1} in Pt/ADE cell and 91 and 2 mg L^{-1} in Pt/ADE–Pt/CF system, respectively, as expected if their Fe(III) complexes are hardly oxidized with Pt(•OH) and •OH. The larger formation of both acids in the latter system can be explained by the faster degradation of precedent intermediates by the higher production of •OH by Fe^{2+} regenerated at the CF cathode. Under PEF conditions, both acids are removed at similar rate in both cells (Fig. 4c and d). This evidences that their Fe(III) complexes are photodecomposed, although 1 mg L^{-1} of oxalic acid and 0.2–0.3 mg L^{-1} of oxamic acid, corresponding to <0.5 mg L^{-1} TOC, persist at 420 min. That means that the final solution of the Pt/ADE cell with 9 mg L^{-1} TOC (Fig. 1a) contains other undetected organics, which are reduced to <3 mg L^{-1} TOC by additional •OH formed in the more potent Pt/ADE–Pt/CF cell. The photolysis process detected for Fe(III)–carboxylate complexes by UVA light in PEF is expected to occur via photodecarboxylation such as reaction (8) exemplifies for Fe(III)–oxalate complexes ($Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$

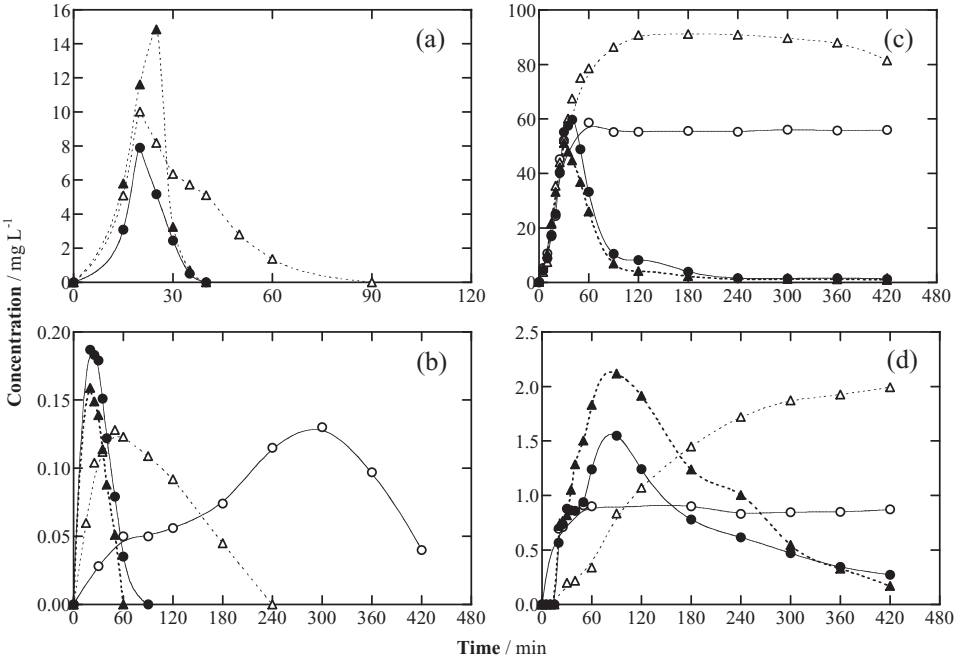


Fig. 4. Time–course of the concentration of (a) formic, (b) maleic, (c) oxalic and (d) oxamic acids generated during the mineralization processes performed in the same conditions as given in Fig. 1.

and $Fe(C_2O_4)_3^{3-}$) [44]:

$$2Fe(C_2O_4)_n^{(3-2n)} + h\nu \rightarrow 2Fe^{2+} + (2n-1)C_2O_4^{2-} + 2CO_2 \quad (8)$$

On the other hand, ionic chromatography revealed that chloride ions (18.5 mg L^{-1}) present in the 154 mg L^{-1} propranolol hydrochloride solution are stable during all treatments. This technique showed the conversion of the nitrogen of the drug (7.3 mg L^{-1}) into ammonium and nitrate ions. A gradual accumulation of both ions, with larger NH_4^+ formation, can be observed for all EAOPs in Fig. 5a and b, respectively. EF yields 5.6 mg L^{-1} of NH_4^+ (60% of initial N) and 1.2 mg L^{-1} of NO_3^- (4% of initial N) in both cells at 360 min, indicating that 64% of nitrogen is mineralized, although part of it is contained in *N*-intermediates like oxamic acid with 7% of initial N as maximum (Fig. 4d). A greater generation of both ions takes place in PEF, primordially using the more potent Pt/ADE–Pt/CF cell since final organic products are more extensively destroyed. For this system, only 77% of initial N is converted in such ions (68% of NH_4^+ and 9% of NO_3^-) at 360 min, when 96% TOC decay is achieved (Fig. 1a) and oxamic acid contains <1% of initial N (Fig. 4d). This suggests the loss of part of N of propranolol as volatile *N*-products, probably NO_x species, during all EAOPs.

3.5. Reaction sequence

The above results allow the proposal of the general reaction pathway of Fig. 6 for the mineralization of propranolol hydrochloride by EF and PEF involving all detected intermediates. The main oxidizing agent is •OH produced from Fenton's reaction (2), although slower oxidation of organics with Pt(•OH) is feasible. Fe(III)–carboxylate complexes are only given for the ultimate oxamic, oxalic and formic acids for simplicity.

The process is initiated by the attack of •OH on the C(1)–O bond of the naphthalene moiety of propranolol hydrochloride giving 1-naphthol and (2-hydroxy-3-isopropylamine)propoxyl radical with release of HCl. 1-Naphthol is oxidized to 1,4-naphthoquinone, which is hydroxylated to 1a,7a-dihydronaphto[2,3-b]oxirene-2,7-dione, followed by its oxidation to phthalic acid. The cleavage of (2-hydroxy-3-isopropylamine)propoxyl radical produces acetamide and carboxylic acids like pyruvic, glycolic and malonic with loss of NH_4^+ along with NO_3^- in smaller extent. Acetamide is subsequently oxidized to oxamic acid, pyruvic acid to acetic acid and phthalic acid to maleic and malonic [28] acids. Glycolic, acetic, maleic and malonic acids are independently transformed into oxalic and formic acids. The ultimate oxamic, oxalic and formic acids react with Fe^{3+} to form Fe(III)–oxamate, Fe(III)–oxalate and Fe(III)–formate complexes. They are photolyzed to CO_2 by UVA

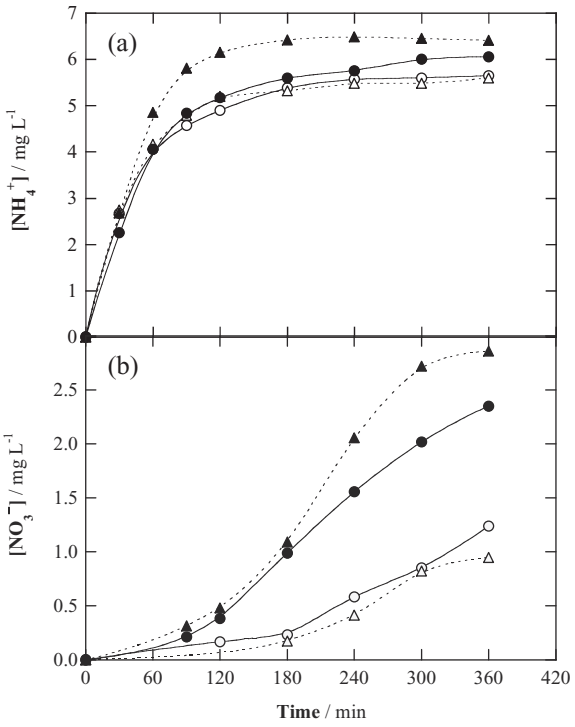


Fig. 5. Concentration of released (a) ammonium and (b) nitrate ions versus electrolysis time for the same experimental conditions as in Fig. 1.

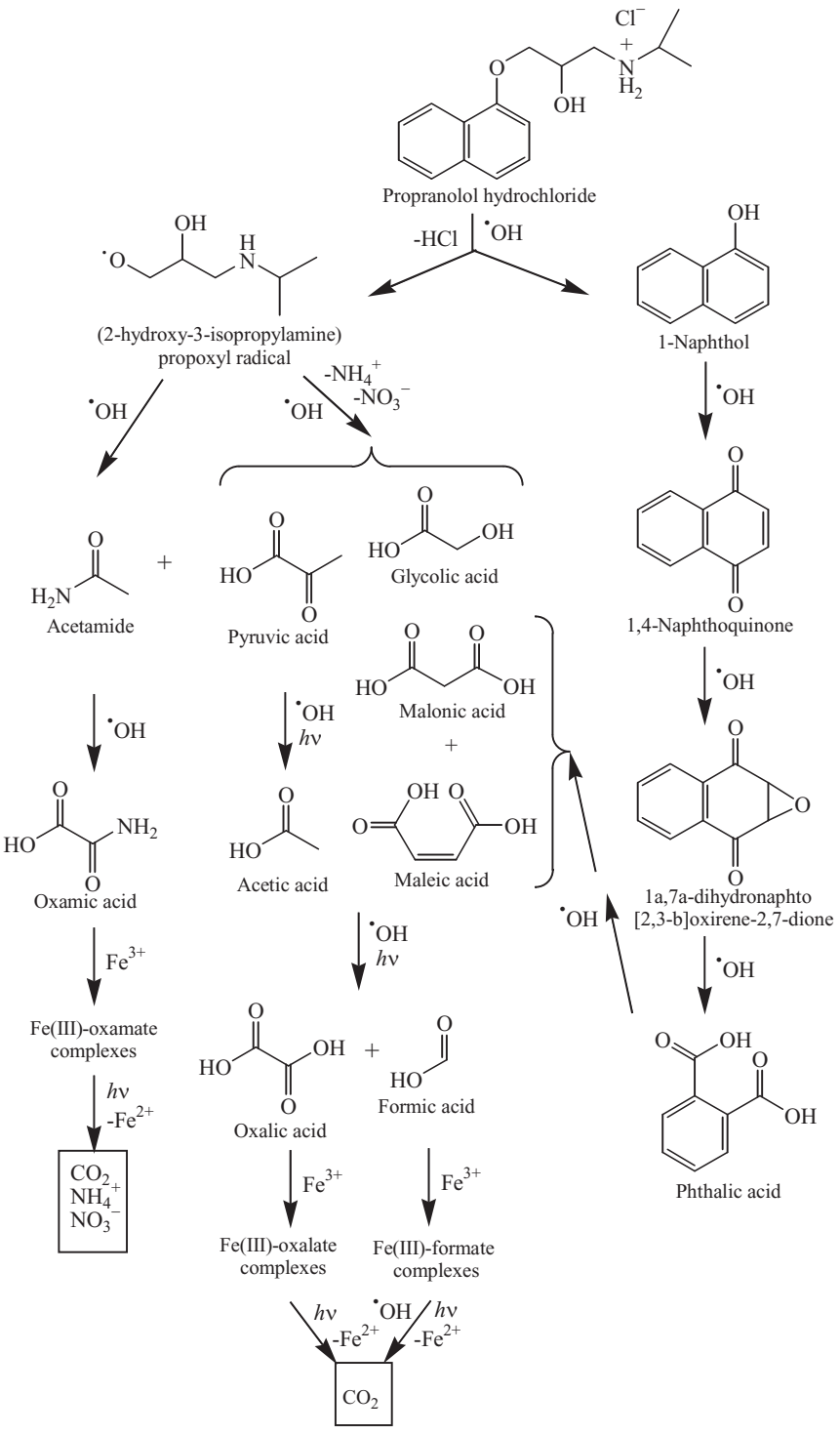


Fig. 6. Proposed reaction sequence for the mineralization of propranolol hydrochloride by EF and PEF using a Pt anode. The main oxidizing agent is hydroxyl radical formed from Fenton's reaction.

light with loss of Fe^{2+}, although only the latter species are also mineralized with •OH. NH_4^+ and NO_3^- ions are released during oxamic acid oxidation.

4. Conclusions

It has been demonstrated that the beta-blocker propranolol hydrochloride with a naphthalene ring is extensively degraded by PEF under the synergistic action of electrogenerated hydroxyl radicals and UVA light. This EAOP leads to almost total mineralization with the higher current efficiency using the combined Pt/ADE–Pt/CF cell in which the •OH production by Fenton's reaction (2) is strongly accelerated by Fe^{2+} regeneration from Fe^{3+} reduction at the CF cathode via reaction (3). This promotes a larger destruction of organics compared with the weaker action of photolytic reaction (4), which yields lower mineralization degree and smaller efficiency in the Pt/ADE cell. The use of this combined cell is then more viable for the treatment of drugs with different aromatic rings. The EF process in both single and combined systems is much less

potent because Fe(III)–oxamate and Fe(III)–oxalate complexes are very stable. The quick photodecarboxylation of these complexes under UVA light explains the faster TOC removal in PEF. For most EAOPs, the drug decay follows a pseudo first-order reaction. Aromatic intermediates and primary short aliphatic derivatives are identified by GC–MS, while final carboxylic acids are detected and quantified by HPLC. The primary 1-naphthol is degraded to phthalic acid, indicating that naphthalene compounds are oxidized to benzene derivatives and then, the same final carboxylic acids such as maleic, oxalic and formic are produced during the destruction of both kinds of aromatics. While chloride ion remains stable, initial N is mineralized to NH_4^+ and NO_3^-.

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