



# 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<sub>2</sub>O<sub>2</sub> 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 ( $\bullet$ OH) formed from Fenton's reaction between added Fe<sup>2+</sup> and electrogenerated H<sub>2</sub>O<sub>2</sub>. The PEF treatment in Pt/ADE–Pt/CF system yields almost total mineralization because  $\bullet$ OH production is enhanced by Fe<sup>2+</sup> regeneration from Fe<sup>3+</sup> 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<sup>2+</sup> 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<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions are released to the medium. A reaction sequence for propranolol hydrochloride mineralization is proposed.

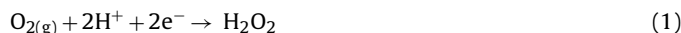
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## 1. Introduction

A large variety of pharmaceutical drugs have been recently detected in surface, ground and drinking waters at low contents of  $\mu\text{g L}^{-1}$  [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 ( $\bullet$ OH) [13,14], which can react with POPs until total mineralization (conversion into CO<sub>2</sub>, water and inorganic ions). The most common EAOP based on Fenton chemistry is the electro-Fenton (EF) process in which H<sub>2</sub>O<sub>2</sub> is continuously supplied to the contaminated solution from the two-electron reduction of injected O<sub>2</sub> at the cathode from reaction (1) [14], while Fe<sup>2+</sup> is added to the medium as catalyst, usually at the optimum pH 3.0, to react with electrogenerated H<sub>2</sub>O<sub>2</sub> producing  $\bullet$ OH and Fe<sup>3+</sup> from Fenton's reaction (2) [15]:



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<sub>2</sub> or air) diffusion electrodes [17,24–28] and boron-doped diamond (BDD) films [29]. In EF, reaction (2) can be propagated from Fe<sup>2+</sup> regenerated by Fe<sup>3+</sup> reduction at the cathode [17,30,31]:



The rate of reaction (3) depends on the cathodic material and its ability to electrogenerate H<sub>2</sub>O<sub>2</sub> from reaction (1). For electrodes

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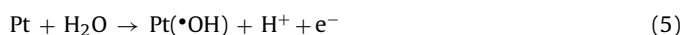
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with low H<sub>2</sub>O<sub>2</sub> production as CF, Fe<sup>3+</sup> reduction is so fast that a large proportion of Fe<sup>2+</sup> remains in the solution, whereas for gas diffusion electrodes where reaction (1) predominates, Fe<sup>3+</sup> is 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<sup>2+</sup> regeneration by photolysis of Fe(OH)<sup>2+</sup>, the predominant Fe<sup>3+</sup> species at pH 3.0 [15]:



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]:



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<sub>2</sub>O<sub>2</sub> electrogeneration at the ADE cathode from reaction (1) and large regeneration of Fe<sup>2+</sup> 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-naphthoxy)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<sup>-1</sup> 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<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> [38], radiolysis [39], UV/H<sub>2</sub>O<sub>2</sub> [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<sup>-1</sup> 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<sup>2</sup>. 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<sup>-1</sup> of air for H<sub>2</sub>O<sub>2</sub> 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<sup>-1</sup> propranolol hydrochloride (100 mg L<sup>-1</sup> TOC) in 0.05 M Na<sub>2</sub>SO<sub>4</sub> as background electrolyte were electrolyzed by EF and PEF after regulation at pH 3.0 with concentrated H<sub>2</sub>SO<sub>4</sub> and addition of 0.5 mM Fe<sup>2+</sup> 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<sub>max</sub> = 360 nm, placed at the top of the open cell at 5 cm above the solution (photoionization energy input of 1.4 W m<sup>-2</sup>).

### 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<sup>-1</sup> sodium dodecyl sulfate at pH 3.0) mixture at 1.5 mL min<sup>-1</sup> 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<sub>2</sub>SO<sub>4</sub> at 0.6 mL min<sup>-1</sup> as mobile phase. Ionic chromatography was performed with a Shimadzu 10 Avp HPLC coupled with a Shimadzu CDD 10 Avp conductivity detector. NH<sub>4</sub><sup>+</sup> 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<sup>-1</sup>. NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> 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<sup>-1</sup> as mobile phase.

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