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Mineralization of clofibric acid by electrochemical advanced oxidation processes using a boron-doped diamond anode and Fe^{2+} and UVA light as catalysts

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Abstract

This work shows that aqueous solutions of clofibric acid (2-(4-chlorophenoxy)-2-methylpropionic acid), the bioactive metabolite of various lipid-regulating drugs, up to saturation at pH 3.0 are efficiently and completely degraded by electrochemical advanced oxidation processes such as electro-Fenton and photoelectro-Fenton with Fe^{2+} and UVA light as catalysts using an undivided electrolytic cell with a boron-doped diamond (BDD) anode and an O_2-diffusion cathode able to electrogenerate H_2O_2. This is feasible in these environmentally friendly methods by the production of oxidant hydroxyl radical at the BDD surface from water oxidation and in the medium from Fenton's reaction between Fe^{2+} and electrogenerated H_2O_2. The degradation process is accelerated in photoelectro-Fenton by additional photolysis of Fe^{3+} complexes under UVA irradiation. Comparative treatments by anodic oxidation with electrogenerated H_2O_2, but without Fe^{2+}, yield much slower decontamination. Chloride ion is released and totally oxidized to chlorine at the BDD surface in all treatments. The decay kinetics of clofibric acid always follows a pseudo-first-order reaction. 4-Chlorophenol, 4-chlorocatechol, hydroquinone, *p*-benzoquinone and 2-hydroxyisobutyric, tartronic, maleic, fumaric, formic and oxalic acids, are detected as intermediates. The ultimate product is oxalic acid, which is slowly but progressively oxidized on BDD in anodic oxidation. In electro-Fenton this acid forms Fe^{3+}–oxalato complexes that can also be totally destroyed at the BDD anode, whereas in photoelectro-Fenton the mineralization rate of these complexes is enhanced by its parallel photodecarboxylation with UVA light.

Keywords: Boron-doped diamond anode; Catalysis; Electro-Fenton; Photoelectro-Fenton; Drug mineralization

1. Introduction

The detection of a large variety of pharmaceutical drugs and metabolites including analgesics, anti-inflammatories, anti-microbials, antiepileptics, beta-blockers, estrogens and lipid regulators as emerging pollutants in waters at concentrations from nanograms to micrograms per litre has been recently documented [1–10]. The main sources of this contamination include emission from production sites, direct disposal of overplus drugs in households, excretion after drug administration to humans and animals, treatments throughout the water in fish and other animal farms and inadequate treatment of manufacturing waste [8]. To avoid the potential adverse health effects of these pollutants on living beings, research efforts are underway to develop efficient oxidation techniques for achieving their total mineralization, i.e. their complete conversion into CO_2.

Clofibric acid (2-(4-chlorophenoxy)-2-methylpropionic acid) is the bioactive metabolite of drugs such as clofibrate, etofibrate and etofyllineclofibrate, widely used as blood lipid regulators because they decrease the plasmatic content of cholesterol and triglycerides [9]. This compound has an estimated environmental persistence of 21 days [10] and has been found up to 10 $\mu g\ l^{-1}$ in sewage treatment plant effluents, rivers, lakes, North Sea, ground waters and drinking waters [1,2,6]. However, it is poorly degraded by ozonation [5,11], H_2O_2/UV [11], sunlight and UV photolysis [7] and TiO_2/UV [12], as well as after application of biological and physico-chemical methods in sewage treatment

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plants [9]. In previous work [13] we have explored the electrochemical degradation of clofibric acid solutions in the pH range 2.0–12.0 by means of the classical method of anodic oxidation with a cell containing either a Pt or boron-doped diamond (BDD) anode and a stainless steel cathode. Under these conditions, the metabolite solutions were poorly decontaminated with a Pt anode, whereas the alternative use of BDD yielded their complete mineralization, but with very low degradation rate and current efficiency. The greater oxidizing power of BDD compared to Pt is ascribed to its higher O_2-overpotential, which allows the generation of more amount of the strong oxidant hydroxyl radical (BDD($^\bullet$OH)) adsorbed on its surface from water oxidation [14–18]:

$$BDD(H_2O) \rightarrow BDD(^\bullet OH) + H^+ + e^- \quad (1)$$

Under these conditions, other weaker oxidants such as peroxodisulfate ion, H_2O_2 and O_3 at the BDD anode are also produced [18]. Anodic oxidation with a BDD anode seems a viable technique to mineralize clofibric acid, but its very low oxidation power prevents its possible application to the treatment of industrial wastewaters containing this compound. This makes necessary the search of other potent technologies with higher ability to remove this pollutant from waters.

Recently, powerful indirect electrooxidation methods such as electro-Fenton and photoelectro-Fenton are being developed for water remediation [19–31]. These electrochemical advanced oxidation processes (AEOPs) are environmentally friendly technologies based on the continuous supply of H_2O_2 to an acidic contaminated solution from the two-electron reduction of injected O_2:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

Reticulated vitreous carbon [19,20], carbon-felt [21,22,24,27,30], activated carbon fibre [28] and O_2-diffusion [23,25,26,29,31] cathodes are usually employed to reduce efficiently O_2 from reaction (2). In the electro-Fenton process the oxidizing ability of electrogenerated H_2O_2 is strongly enhanced by adding to the solution a small quantity of Fe^{2+} to produce hydroxyl radical ($^\bullet$OH) and Fe^{3+} from the classical Fenton's reaction [32]:

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

An advantage of this method is that the Fe^{3+}/Fe^{2+} system is catalytic and reaction (3) is propagated from Fe^{2+} regeneration, mainly by reduction of Fe^{3+} at the cathode [21]. However, a part of generated $^\bullet$OH is wasted by non-oxidizing reactions, for example, with Fe^{2+} and H_2O_2 or its direct recombination to hydrogen peroxide [32,33]:

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \quad (5)$$

$$2{}^\bullet OH \rightarrow H_2O_2 \quad (6)$$

In the photoelectro-Fenton process, the treated solution is illuminated with UV light, which can also act as catalyst to favor: (i) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids [23,25,30,34] and/or (ii) the regeneration of more Fe^{2+} with additional production of $^\bullet$OH from photoreduction of $Fe(OH)^{2+}$, the predominant Fe^{3+} species in acid medium [32]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \quad (7)$$

This paper reports a comparative study on the degradation of clofibric acid by electro-Fenton and photoelectro-Fenton using an undivided electrolytic cell with a BDD anode and an O_2-diffusion cathode to electrogenerate continuously H_2O_2 from reaction (2). Both AEOPs were tested with metabolite solutions containing a low content of 0.05 M Na_2SO_4 as background electrolyte and 1.0 mM Fe^{2+} as catalyst at pH 3.0, near the optimum pH of 2.8 for Fenton's reaction (3) [32]. For these methods, organic pollutants are expected to be mainly oxidized by BDD($^\bullet$OH) and $^\bullet$OH formed from reactions (1) and (3), respectively, although parallel reactions with weaker oxidants such as electrogenerated H_2O_2, as well as peroxodisulfate ion [18], ozone [18] and ferrate ion [35] also produced at the BDD anode, are possible in much less extent. Photoelectro-Fenton was performed by irradiating the solution with UVA light. Comparative treatments by anodic oxidation without and with UVA irradiation were also made to assess the higher oxidation power of electro-Fenton and photoelectro-Fenton. The influence of current density and metabolite concentration on the degradation rate and mineralization current efficiency of these AEOPs was investigated. The decay kinetics of clofibric acid in each method was determined. The evolution of identified aromatic products and carboxylic acids was followed by chromatographic techniques to clarify their pathways in the different oxidation processes.

2. Experimental

Clofibric acid, 4-chlorophenol, hydroquinone, *p*-benzoquinone, 2-hydroxyisobutyric acid, tartronic acid, maleic acid, fumaric acid, formic acid and oxalic acid were either reagent or analytical grade from Sigma–Aldrich, Merck, Panreac and Avocado. 4-Chlorocatechol was synthesized by chlorination of pyrocatechol with SO_2Cl_2 [23]. Anhydrous sodium sulfate and heptahydrated ferrous sulfate were analytical grade from Fluka. Solutions were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity >18 MΩ cm at 25 °C) and their pH was adjusted to 3.0 with analytical grade sulfuric acid from Merck. Other chemicals and organic solvents were either HPLC or analytical grade from Panreac.

The solution pH was determined with a Crison 2000 pH-meter. Aliquots withdrawn from treated solutions were filtered with Whatman 0.45 μm PTFE filters before analysis. The degradation of clofibric acid solutions was monitored from the removal of their total organic carbon (TOC), measured on a Shimadzu VCSN TOC analyzer. Reproducible values were obtained using the standard non-purgeable organic carbon method. From these results, the mineralization current efficiency (MCE) for each treated solution at a given