



# Electro-Fenton degradation of anti-inflammatory drug ibuprofen in hydroorganic medium



Silvia Loaiza-Ambuludi<sup>a</sup>, Marco Panizza<sup>b</sup>, Nihal Oturan<sup>a</sup>, Ali Özcan<sup>c</sup>, Mehmet A. Oturan<sup>a,\*</sup>

<sup>a</sup> Université Paris-Est Marne-la-Vallée, Laboratoire Géomatériaux et Environnement, 5 boulevard Descartes, Champs-sur-Marne, 77454 Marne-la-Vallée Cedex 02, France

<sup>b</sup> Department of Civil, Chemical and Environmental Engineering, University of Genoa, Piazzale Kennedy 1, Genoa 16129, Italy

<sup>c</sup> Anadolu University, Faculty of Science, Department of Chemistry, 26470 Eskişehir, Turkey

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## ABSTRACT

The oxidative degradation of ibuprofen in hydroorganic medium water/acetonitrile has been investigated by electro-Fenton processes. Experiments have been performed in a one-compartment cell with a Pt or BDD anode and a commercial 3D graphite felt cathode. The effect of operating conditions such as applied current, catalyst concentration, and supporting electrolyte nature has been studied. Ibuprofen decay kinetics and the evolution of its aromatic intermediates have been monitored during the electrolysis by HPLC and GC–MS analyses. The experimental results have shown that ibuprofen has been completely removed in all experimental conditions either by homogeneous ·OH formed in the bulk of the solution through electrochemically generated Fenton's reagent (H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>) and heterogeneous BDD(·OH) at the anode surface from water oxidation. The removal rate has been more effective using a Pt anode than a BDD anode because of the greater regeneration of Fe<sup>2+</sup> catalyst on the former. With both the anodes, the decay kinetics of ibuprofen always followed a pseudo-first-order reaction and the oxidation rate largely depends on applied current, Fe<sup>2+</sup> concentration and electrolyte nature. Several aromatic by-products such as 1-(1-hydroxyethyl)-4-isobutylbenzene, 4-isobutylacetophenone, 4-isobutylphenol and benzoquinone has been identified, and a plausible reaction mechanism has been proposed.

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## 1. Introduction

Ibuprofen (2-(4-isobutylphenyl)propionic acid) is a non-steroidal anti-inflammatory drug (NSAID) of the propionic acid. Thanks to its analgesic and antipyretic properties, it is widely employed in the treatment of rheumatoid arthritis, osteoarthritis, but it is also used for the alleviation of mild to moderate pain, inflammation and fever caused by many and diverse diseases. Because of its widespread use and persistence, concentration of ibuprofen below 10 µg dm<sup>-3</sup> has been detected in river waters [1–3]. It is also considered to be one of the most important pharmaceutical contaminants in sewage treatment plant (STP) influents [4]. Since ibuprofen, like most of pharmaceutically active compounds, is poorly biodegradable and it affects significantly the growth of several bacterial and fungal species [5,6], an efficient destruction of ibuprofen and that of its degradation by-products needs powerful oxidation methods for achieving its complete removal from wastewaters.

The abatement of ibuprofen from aqueous solutions has been studied under applications of different water treatment technologies such as ozonation [7], advanced oxidation processes (AOPs) [8,9] and electrochemical oxidation [10–12]. For example, Zwiener

and Frimmel [13] reported that simple ozonation was ineffective to remove ibuprofen (i.e. 12% of degradation efficiency) while the application of AOP O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> almost quantitatively degraded the drugs (i.e. 99.4%). In a previous paper [14] we reported that using boron-doped diamond (BDD) anode, ibuprofen has been completely destroyed under all the conditions tested, following pseudo first-order kinetics. Almost complete mineralization (i.e. TOC removal higher than 96%) of ibuprofen was also obtained in 8 h of electrolysis. Similar results were also obtained by Ciriaco et al. [10].

Recently, there is an increasing interest in the use of electrochemical Advanced Oxidation Processes (EAOPs) such as electro-Fenton (EF) process for wastewater remediation. In the EF process, the highly powerful oxidizing agent, hydroxyl radicals (·OH) are produced in the bulk of the polluted solution using the Fenton reaction (Eq. (2)) through electrogenerated Fenton's reagent (mixture of H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>) [15–17]. H<sub>2</sub>O<sub>2</sub> is supplied by in situ electrogeneration from the two-electron reduction of O<sub>2</sub> (Eq. (1)) and Fe<sup>2+</sup> is continually regenerated from Fe<sup>3+</sup> reduction (Eq. (3)). The process needs thus the introduction of a catalytic amount of an iron (III) salts to the solution.



\* Corresponding author. Tel.: +33 1 49 32 90 65.

E-mail address: [mehmet.oturan@univ-paris-est.fr](mailto:mehmet.oturan@univ-paris-est.fr) (M.A. Oturan).



These reactions occur with high yield and satisfactory rate only at gas diffusion cathodes (GDE) [18–20] and three-dimensional carbon-based cathodes, such as graphite felt [21–26]. This process has been efficiently applied for the treatment of some phenols and polyphenols, dyes and pesticides enabling the complete mineralization of the wastewater [27–32].

Using an undivided electrolytic cell for the EF process, the organic compounds can be also destroyed by heterogeneous hydroxyl radicals ( $\text{M}(\cdot\text{OH})$ ) produced at the anode surface (M) from water oxidation following the Eq. (4), thus accelerating the mineralization rate of the pollutants [33–38]:



In this field, the degradation of ibuprofen solution has been comparatively studied by Skoumal and co-workers [12] using different methods such as electro-Fenton and solar photoelectro-Fenton using an  $\text{O}_2$ -diffusion cathode and a Pt or boron-doped diamond (BDD) anode. Higher mineralization was attained using BDD instead of Pt, because the former produces greater quantity of  $\cdot\text{OH}$  enhancing the oxidation of pollutants. The mineralization rate also increased under solar irradiation by the rapid photodecomposition of complexes of Fe(III) with acidic intermediates. The most potent method was solar photoelectro-Fenton with BDD anode giving 92% mineralization.

The solubility of ibuprofen in water is low (about  $45 \text{ mg L}^{-1}$  at pH 3.0 and  $25^\circ\text{C}$ ) [39], while it has large solubility in many organic solvents. In the present paper, we report a detailed study on the performance of the electro-Fenton process for the degradation of ibuprofen in a hydroorganic medium containing 20% acetonitrile. Hydroorganic medium was chosen for a technical reason (see experimental part). The experiments were carried out in an undivided cell using commercial graphite felt cathode and a Pt or BDD anode. The effect of some operating parameters such as applied current, catalyst dose, electrolyte nature and anode material on the removal rate was investigated. Aromatic intermediates were identified by gas chromatography-mass spectrometry (GC-MS), and, based on identified reaction intermediates, a plausible reaction scheme was also proposed for the oxidative degradation of ibuprofen.

## 2. Experimental

### 2.1. Chemicals

Ibuprofen, 2-(4-(2-methylpropyl)phenyl)propanoic acid ( $\text{C}_{13}\text{H}_{18}\text{O}_2$ ) was obtained from Sigma-Aldrich and used without further purification. Anhydrous sodium sulfate, sodium chloride, hexahydrated ammonium iron(II) sulfate (Mohr's salt),  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , as ferrous ion (catalyst) source and pentahydrated ferric sulfate used as ferric iron ions (catalyst) source were analytical grade from Fluka. Deionized water used for the preparation of solutions and HPLC eluents was obtained from a Millipore Milli RO6 system, with resistivity  $>18 \text{ M}\Omega \text{ cm}$ . Methanol (chromanorm grade) used as organic solvent for the liquid chromatography mobile phase and sulfuric acid used for pH adjustment were supplied by VWR International.

### 2.2. Electrochemical cell

The electrolyses were performed in a small, open, cylindrical, one-compartment electrochemical cell of 6-cm diameter and 230 mL capacity, stirred by a magnetic PTFE follower during the treatment to enhance the mass transport towards electrodes. Either a cylindrical Pt mesh or a  $25 \text{ cm}^2$  boron-doped diamond (BDD) electrode (BDD thin-film deposited on a niobium substrate

from CONDIAS, Germany) was used as the anode, and a large surface area graphite felt ( $14 \text{ cm} \times 5 \text{ cm}$  each side, 0.5 cm in width, from Carbone-Lorraine, France) as the cathode. In all cases, the anode was centred in the electrochemical cell and surrounded by the cathode, which covered the inner wall of the cell.

Experiments were carried out in hydroorganic medium containing 20% acetonitrile with 0.05 M  $\text{Na}_2\text{SO}_4$  or 0.100 M NaCl as supporting electrolyte and were investigated at room temperature ( $23 \pm 2^\circ\text{C}$ ) by applying a constant current in the range 50–500 mA.

The solution pH was fixed to 3, since much higher pH values hamper the development of Fenton-based systems due to the  $\text{Fe}(\text{OH})_3$  precipitation, which lead to both the decrease of dissolved iron ion [16].

Continuous saturation of the solution by  $\text{O}_2$  gas at atmospheric pressure was ensured by bubbling compressed air having passed through a frit at about  $1 \text{ L min}^{-1}$  in the solution to be treated, starting 10 min before electrolysis to reach a stationary  $\text{O}_2$  concentration. The electrolyses were performed with a Hameg HM8040 triple power supply at constant current. This instrument displayed the cell voltage along the treatments as well. The solution pH was measured with a CyberScan pH 1500 pH-meter from Eutech Instruments.

### 2.3. Analytical procedures

Ibuprofen solutions were prepared in water-acetonitrile (80:20 (v/v)) medium because the experiments conducted in aqueous solution did not yield reproducible results in electro-Fenton degradation over a relatively long time. We observed that the bubbling of compressed air or  $\text{O}_2$  through the solution leads to a decrease of the concentration of ibuprofen even if it was completely disappear over a long treatment time. Preliminary experiments, with and without Fe(II), with and without compressed air bubbling, bubbling with  $\text{O}_2$  or  $\text{N}_2$ , were carried out for monitoring the concentration of the ibuprofen by HPLC. When the solution was bubbled with pure  $\text{O}_2$  and/or compressed air, the decrease in the concentration of ibuprofen was accompanied by the appearance of white crystals on the inner walls of the cell. The nature of this substance is not investigated but it was probably formed by oxidation of the acid group of ibuprofen, leading to the formation of an oxidation product which was less soluble than ibuprofen.

Samples withdrawn from the treated solution at different electrolysis times were microfiltered onto a hydrophilic membrane (Millex-GV Millipore, pore size  $0.22 \mu\text{m}$ ) before analysis.

The time course of the concentration of ibuprofen was followed by reversed-phase HPLC using a Merck Lachrom liquid chromatograph, equipped with a L-7100 pump, fitted with a Purospher RP-18  $5 \mu\text{m}$ ,  $25 \text{ cm} \times 4.6 \text{ mm}$  (i.d.) column at  $40^\circ\text{C}$ , and coupled with a L-7455 photodiode array detector selected at optimum wavelengths of 228 nm for ibuprofen. The analyses of the ibuprofen decay were carried out isocratically with a methanol/water (with 1% phosphoric acid) 68:32 (v/v) mixture as the mobile phase. A flow rate of  $0.5 \text{ mL min}^{-1}$  was always used. The corresponding retention time ( $t_{\text{R}}$ ) for ibuprofen was 11.6 min. In all cases, the identification of intermediates was made by comparison of  $t_{\text{R}}$  and UV spectra with those of pure standards.

GC-MS analysis was performed by using a Thermo Finnigan PolarisQ GC-MS analyzer, equipped with a TRB-5-MS column. The column was held at  $40^\circ\text{C}$  for 2 min, and then a gradient temperature program at  $10^\circ\text{C min}^{-1}$  was applied between 40 and  $280^\circ\text{C}$ . The temperature was held at  $280^\circ\text{C}$  for 2 min. The temperature of the injection part and the MS transfer line was  $250^\circ\text{C}$ . Helium was used a carrier gas at a flow rate of  $1.0 \text{ mL min}^{-1}$ .

## 3. Results and discussion

A set of electrolysis was carried out with 0.2 mM ibuprofen in hydroorganic solutions to determine the influence of the main

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