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Bioelectro-Fenton: A sustainable integrated process for removal of organic pollutants from water: Application to mineralization of metoprolol

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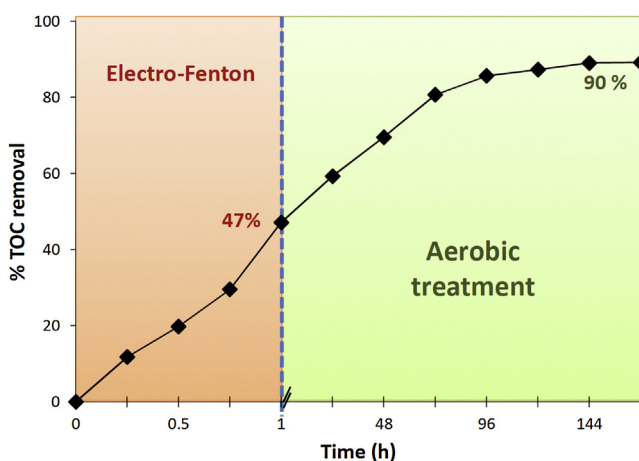
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HIGHLIGHTS

- Electro-Fenton (EF) process was able to quickly mineralize metoprolol aqueous solution.
- Rate constant of metoprolol oxidation by OH was found to be $1.72 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.
- A new coupled process “Bio-EF” was described.
- EF process removed 47% TOC at 1 h treatment increasing significantly biodegradability.
- Mineralization of EF pre-treated solution was then completed in a 4-days aerobic treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

The relevant environmental hazard related to the presence of pharmaceuticals in water sources requires the development of high effective and suitable wastewater treatment technologies. In the present work, a hybrid process coupling electro-Fenton (EF) process and aerobic biological treatment (Bio-EF process) was implemented for the efficient and cost-effective mineralization of beta-blocker metoprolol (MTPL) aqueous solutions. Firstly, operating factors influencing EF process were assessed. MTPL solutions were completely mineralized after 4 h-electrolysis under optimal operating conditions and BDD anode demonstrated its oxidation superiority. The absolute rate constant of MTPL oxidation by $\bullet\text{OH}$ (k_{MTPL}) was determined by the competition kinetics method and found to be $(1.72 \pm 0.04) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. A reaction pathway for the mineralization of the drug was proposed based on the identification of oxidation by-products. Secondly, EF process was used as pre-treatment. An increase of BOD₅/COD ratio from 0.012 to 0.44 was obtained after 1 h EF treatment, along with 47% TOC removal and a significant decrease of

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toxicity, demonstrating the feasibility of a post-biological treatment. Finally, biological treatment successfully oxidized 43% of the total TOC content. An overall 90% mineralization of MPTL solutions was achieved by the Bio-EF process, demonstrating its potentiality for treating wastewater containing pharmaceutical residues.

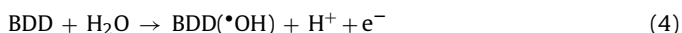
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1. Introduction

The increasingly alarming environmental problem represented by the occurrence of human pharmaceuticals in wastewater and surface water has been extensively reported [1,2]. Conventional methods are generally inefficient in the treatment of these biorefractory contaminants. Consequently, advanced oxidation processes (AOPs) arose as a potent alternative [3,4]. Among these technologies, Electrochemical AOPs (EAOPs) have shown their substantial oxidation/mineralization capacity for the destruction of persistent organic pollutants (POPs) [5–7]. EAOPs are based on the in-situ production of the strong oxidizing agent, hydroxyl radical ($\bullet\text{OH}$), which is able to oxidize any organic compound until its transformation to CO_2 , water and inorganic ions [8–11]. These environmentally friendly technologies possess numerous advantages, mainly their ability to prescind from the manipulation of dangerous chemicals, as well as their operability at mild conditions [6].

Electro-Fenton (EF) process is one of the most applied EAOPs for wastewater treatment [5,6,8–12]. During this process, homogeneous $\bullet\text{OH}$ are generated in the bulk solution from Fenton's Reaction (1), which is promoted by the reaction between the in situ electrogenerated H_2O_2 at a carbonaceous cathode (Reaction (2)), and a catalytic amount of externally added Fe(II) salt [13]. Ferrous ions are then electro-regenerated at the cathode according to Reaction (3), creating a catalytic cycle and whence enhancing the mineralization process [4,8,9,11,14].

Boron doped diamond electrode (BDD) is shown as the better anode in EF process because of its high O_2 -overpotential, which promotes the generation of heterogeneous BDD ($\bullet\text{OH}$) from water oxidation (Reaction (4)), significantly contributing to the oxidation of organics [15–18].



In spite of the their high oxidation power, AOPs present important drawbacks, mostly high costs associated with the important consumption of chemicals, as well as the elevated energetic needs resulting from the long treatment times required for mineralization experiments. With the aim of reducing these disadvantages, coupled technologies, combining the main advantages of individual processes, emerged as potential alternatives [19,20]. Thereby, AOPs have been successfully coupled to biological methods for the degradation of a variety of pollutants [21,22], evidencing the potentiality of this integrated technology for high-efficiently and cost-effectively removing persistent contaminants [23]. Among the AOPs used as a first step prior to a biological treatment, ozonation is the most employed, followed by photo-Fenton and photocatalysis. However, more recently some approaches have been reported describing the application of integrated EAOPs-biological technologies [24]. In this sense, EF treatment proved to increase biodegradability of solutions containing recalcitrant organics, permitting further application of a biological treatment to remove the remaining by-products,

hence completing the mineralization process [25–27]. Nevertheless, considering the very few reports about the combined electro-oxidation–biological technology, further research is imperative for optimization purposes and feasibility evaluation, aiming to implement these integrated techniques in response to the urgent necessity of eliminating emerging pollutants with concomitant consideration of economic issues related to wastewater treatment.

Metoprolol (MTPL) is a beta-blocker highly prescribed for the treatment of diverse cardiovascular diseases such as hypertension, heart rhythm disturbances and coronary artery disease [28]. It is among the 20 most encountered pharmaceuticals in European wastewater and surface waters [29,30] on account of its extensive utilization and its often incomplete metabolism [31]. Some reports have described its potential ecotoxicity towards different species [28,32]. Moreover, metabolites and transformation products of pharmaceuticals are of great importance, as they can importantly contribute to the overall toxicity [28,33].

Low elimination rates of MTPL are usually reported in activated sludge treatment (up to 31% removal), due to the formation of persistent metabolites, which remain in the solution as they are refractory to microorganisms [34,35]. On the other hand, several studies have also reported the destruction of MTPL by different AOPs [36–38], all of them being effective for its degradation. However, photocatalysis and electrochemical technologies resulted to be the more efficient methods for its mineralization [39–41].

Considering the numerous reports concerning both, the ineffective biological and the advantageous electrochemical degradation of MTPL, this drug was chosen as a model for assessing the application of a hybrid “bio-EF” process as a potential alternative for the suitable and cost-effective treatment of wastewater containing pharmaceuticals. In the first part of the present study, the electrochemical oxidation of MTPL or mineralization of its aqueous solution by EF process was thoroughly assessed, evaluating the influence of different parameters affecting the process. In the second stage, biodegradability and toxicity tests were conducted with the purpose of evaluating applicability of a biological post-step. The last phase consisted on the application of an aerobic treatment of electro-Fenton pre-treated solutions in order to complete the mineralization of the drug.

2. Materials and methods

2.1. Chemicals

Metoprolol tartrate (purity > 98%) was of reagent grade supplied by Sigma–Aldrich and used as received. Anhydride sodium sulfate (background electrolyte) and heptahydrated iron(II) sulfate, (catalyst), were of analytical grade purchased from Acros Organics. All solutions were prepared with high-purity water from a Millipore Milli-Q system with resistivity > 18 $\text{M}\Omega\text{ cm}$. All the other chemicals were either of HPLC or analytical grade purchased from Prolabo, Fluka and Acros Organics.

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