



## Evaluation of treatment of effluents contaminated with rifampicin by Fenton, electrochemical and associated processes



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### ABSTRACT

Concerns about the preservation of aquatic ecosystems are growing, drugs that are recalcitrant to conventional treatments can be accumulated in public water supplies and contaminate groundwater. Many technologies, including the Fenton reaction and electrooxidation processes, have been evaluated to remove drugs from water, in the last years. However, the association of different approaches can be a suitable solution when only one technology is not enough. In this frame, this study compares the use of the Fenton reaction, the electrochemical process and coupled process to treat a synthetic effluent containing a potential pollutant, rifampicin. Regarding the electrode materials studied herein, efficiency of rifampicin degradation decreased in the following order: Boron-doped diamond (BDD) > > Ti/Pt > Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> (DSA, Dimensionally stable anode). The better performance of BDD was associated to the species BDD(·OH), which degrades organic compounds more efficiently than the species RuO<sub>(x+1)</sub> and PtO<sub>(x+1)</sub>. The electrochemical reaction employing BDD was as efficient as the Fenton reaction where 80% of chemical oxygen demand (COD) was removed. However, the Fenton reaction was faster. Results also clearly showed that, when both technologies were associated, no significant improvements were achieved. Nevertheless, when hydrogen peroxide was added to the electrochemical process, a remarkable enhancement of the reaction efficiency was attained, especially in the case of BDD, requiring less energy for treatment this kind of effluent.

### 1. Introduction

The presence of residual drugs in domestic sewage and in natural waters has been reported since the 1970s [1,2] and these residual substances have been classified as emerging pollutants. Every year, the Brazilian pharmaceutical industry produces tons of drugs for use in human and veterinary medicine. After administration of the drug, the organism excretes a significant part of the non-metabolized pharmaceutical, which reaches the environment through domestic sewage. Upon contact with the aquatic environment, the drug may be biologically degraded. However, many of these substances persist in nature and remain unaltered for long periods [3,4]. Among the residual drugs, the antibiotics have been shown a great significance because their metabolites in environment could cause chronic toxicity and endocrine disruption to aquatic life and human beings, and increased bacterial resistance [5,6].

Recent studies have indicated that conventional treatment of

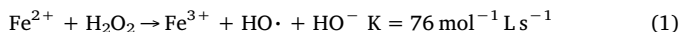
wastewater and sewage fails to remove residual drugs completely. This is a matter of such concern that authoritative publications have putted in evidence the toxicological properties and environmental occurrence of pharmaceuticals as well as with the efficiency of wastewater treatment plants (WWTPs) in removing these substances from effluents [3,4,7]. Besides the potential ecotoxicity and deleterious effects of drugs on the quality of human life, there is particular concern about pharmaceuticals with antibiotic action: low doses of these substances in aquatic environments can generate more resistant microorganism strains [8–10]. In this context, several technologies have been developed to treat effluents more effectively. These can be used alone, or these can be associated with WWTPs in order to remove satisfactorily the organic pollutants [11–17], giving the insights to be applied for depolluting effluents from pharmaceutical industries, preventing contaminants from reaching water resources.

Among the new technologies that are currently being developed to treat wastewater and sewage, advanced oxidative processes (AOPs)

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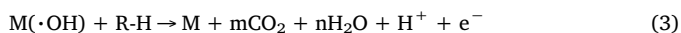
have received great attention because they can cheaply and efficiently degrade compounds that are recalcitrant to conventional treatments [11,12,15–18]. Fenton reaction is one of the most promising AOPs because it has high oxidizing power and is easy to operate and maintain, which makes it an attractive process to degrade drugs in effluents [19–22]. The classic mechanism of the Fenton reaction comprises a simple redox reaction in which  $\text{Fe}^{2+}$  ions are oxidized to  $\text{Fe}^{3+}$ , and  $\text{H}_2\text{O}_2$  is reduced to a hydroxyl ion and to a hydroxyl radical:



0

2  
2

On the other hand, hydroxyl radicals can also be generated by using electrochemical processes. According to Comninellis and De Battisti [23], in this case the organic compound is oxidized through the action of hydroxyl radicals, physically ( $\text{M}(\cdot\text{OH})$ ) or chemically ( $\text{MO}_{x+1}$ ), adsorbed on the anode surface. The production of both species depends on the nature of electrocatalytic material, which are classified as non-active and active anodes, based on the power to produce  $\text{M}(\cdot\text{OH})$  or  $\text{MO}_{x+1}$  (commonly named, higher oxides), respectively [24,25]. It is important to remark that, both species  $\text{M}(\cdot\text{OH})$  and  $\text{MO}_{x+1}$  oxidize organic compounds, but  $\text{MO}_{x+1}$  is more selective and favors partial oxidation Eq. (2), whereas  $\text{OH}$  is more reactive promoting complete mineralization of the pollutant Eq. (3).



Nevertheless, the combination of heterogeneous (electrochemical) and homogeneous (Fenton reactions) hydroxyl radicals production has shown to be more efficient to eliminate organic pollutants from water [37]. Therefore, in this study, we have evaluated the performance of electrooxidation and Fenton approaches in the treatment of a synthetic effluent contaminated with the rifampicin, used as model drug.  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  and  $\text{Ti}/\text{Pt}$ , classified as active anodes, and BDD, a non-active electrode; were used as electrocatalytic materials by electrooxidation. Meanwhile, Fenton reaction was also employed to degrade rifampicin in order to understand its efficacy in terms of organic removal and time of treatment. After that, the association of both processes (Fenton reaction + electrooxidation) was achieved to evaluate the synergic effect as well as to assess the hydrogen peroxide effect on the efficacy of the electrooxidation. Rifampicin was chosen as model substrate because this drug is widely employed in the treatment of tuberculosis and it is used by the government health program as an adjuvant in the treatment of immunosuppressed patients [26]. This is classified in the World Health Organization's list as an essential medicine because it is considered the most important medications needed in a basic health system. Rifampicin (Fig. 1) is an antibiotic belonging to the class of rifamycins, which act on the  $\beta$  subunit of RNA polymerase. After its use, rifampicin is transformed in the body, but the excess is released by the humans via urine, and according to few studies, it was already found in effluents treated in WWTPs because treatment systems fail to eliminate this kind of compound [4,27].

The rifampicin degradation was recently studied by using AOPs [28,29]. Gao and co-workers [28] reported that the photocatalytic degradation of five antibiotics, including rifampicin, using  $\text{ZnIn}_2\text{S}_4$  under visible light irradiation was efficiently achieved, after 90 min, involving the participation of superoxide radical ( $\text{O}_2^{\cdot-}$ ) during the treatment. Meanwhile, Stets and coworkers [29] investigated the degradation of rifampicin (RIF) by applying  $\text{TiO}_2$  and  $\text{ZnO}$  heterogeneous photocatalysis and homogeneous and heterogeneous UV-A photo-Fenton processes. By using  $\text{ZnO}$ -mediated photocatalysis and

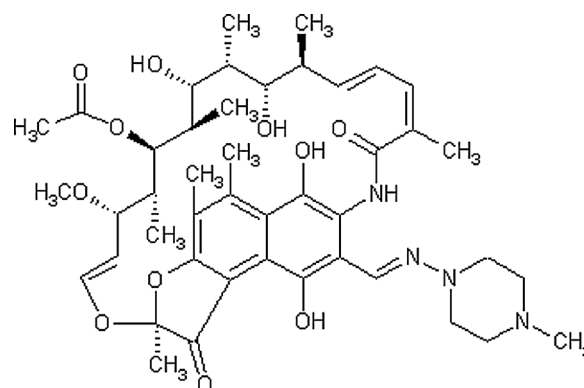


Fig. 1. Chemical structure of rifampicin.

heterogeneous photo-Fenton processes, lower degradation efficiencies were achieved. Conversely, UV-A radiation in  $\text{TiO}_2$ -mediated photocatalysis removed approximately 60% of drug, while photo-Fenton process with iron-immobilized in chitosan beads promoted 80% of elimination after 60 min.

In this context, the recent results about the degradation of rifampicin [28,29] by using POAS encouraged to extend the research for evaluating the efficiency of new technologies in the degradation of this drug, such as Fenton reaction and electrooxidation approaches.

## 2. Experimental

### 2.1. Chemicals and materials

All the reagents were commercially available. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 50% m/m), ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), sulfuric acid, and sodium chloride were purchased from Vetec. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was acquired from ChemCruz. All the reagents were analytical grade and were used without purification. MilliQ water was employed to prepare the different solutions employed in this study. For the electrochemical process,  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  ( $3.0 \times 2.5$  cm),  $\text{Ti}/\text{Pt}$  ( $3.0 \times 2.5$  cm), or BDD ( $3.0 \times 2.5$  cm) electrodes were used as anodes, and the  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  ( $4.0 \times 4.0$  cm) electrode was used as cathode. Pt-supported on Ti and  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  electrodes were supplied by Industry De Nora S.p.A. (Milan, Italy) and (Sorocaba/SP, Brazil), respectively.

### 2.2. Electrochemical experiments

The electrochemical oxidation experiments were performed in a 250-mL undivided open cell equipped with magnetic stirring, under galvanostatic conditions provided by Power Supply EMG18134, at 30 °C. To assess the role of the applied current density (30, 60, and 90  $\text{mA cm}^{-2}$ ) and of the temperature of the effluent (30 and 60 °C) on the oxidation/degradation of rifampicin, an aqueous solution containing 0.2  $\text{g L}^{-1}$  rifampicin (synthetic effluent) was employed.  $\text{Na}_2\text{SO}_4$  0.5  $\text{mol L}^{-1}$  was used as supporting electrolyte. The efficiency regarding the association of processes (electrooxidation + hydrogen peroxide, and electrooxidation + Fenton reaction) was evaluated for the three investigated electrode materials. All electrochemical experiments were conducted under pH-controlled conditions ( $\approx \text{pH } 3$ ) by using sulfuric acid.

### 2.3. Fenton reaction experiments

In this study, a batch reactor containing 250 mL of a synthetic effluent with 0.2  $\text{g L}^{-1}$  rifampicin was employed. A known amount of  $\text{Fe}^{2+}$  (0.1  $\text{mmol L}^{-1}$ ) was added to the effluent, adjusting the pH to 3.0 by adding sulfuric acid.  $\text{H}_2\text{O}_2$  was also added to the effluent in different

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