



Research article

Treatment of real effluents from the pharmaceutical industry: A comparison between Fenton oxidation and conductive-diamond electro-oxidation



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ABSTRACT

Wastewater produced in pharmaceutical manufacturing plants (PMPs), especially the one coming from organic-synthesis facilities, is characterized by its large variability due to the wide range of solvents and chemical reagents used in the different stages of the production of medicines. Normally, the toxicity of the organic compounds prevent the utilization of biological processes and more powerful treatments are needed becoming advanced oxidation processes (AOPs) a valid alternative. In this work, the efficiency in abatement of pollution by Fenton oxidation (FO) and conductive-diamond electro-oxidation (CDEO) are compared in the treatment of 60 real effluents coming from different processes carried out in a pharmaceutical facility, using standardized tests. In 80% of the samples, CDEO was found to be more efficient than FO and in the remaining 20%, coagulation was found to exhibit a great significance in the COD abatement mechanism during FO, pointing out the effectiveness of the oxidation promoted by the electrochemical technology. Mean oxidation state of carbon was found to be a relevant parameter to understand the behavior of the oxidation technologies. It varied inversely proportional to efficiency in FO and it showed practically no influence in the case of CDEO.

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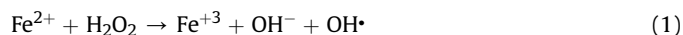
1. Introduction

Wastewater effluents produced in organic-synthesis pharmaceutical industries are complex due to the large variety of solvents and raw chemicals used as well as the complexity of the processes involved in their manufacturing. Those effluents are generally highly toxic and contain wide range of pollutants: organics (unreacted raw chemicals, reaction products and by-products, solvents) and ionic compounds (reagents, acids/bases) resulting in both high COD and salinity levels (EPA, 1991). Moreover, the limited biodegradability of such effluents hinders the application of biological treatment processes (Badawy et al., 2009) and causes the discharge to the environment of persistent organic pollutants, recalcitrant to conventional schemes of municipal wastewater treatment plants (Fernández et al., 2014; Mohapatra et al., 2014; Ribeiro et al., 2016).

Advanced Oxidation Processes (AOPs) are widely considered as an efficient option to treat effluents of low biodegradability (Oller

et al., 2011; Sirés and Brillas, 2012). These processes are based on the production of hydroxyl radical, a highly reactive and non-selective reagent for the oxidation of organic matter (Cominellis et al., 2008). AOPs have been used to confront the treatment of pharmaceutical effluents, including such processes as classic Fenton oxidation (San Sebastián et al., 2003) and Fenton-related processes (Brillas et al., 2009), ozonation (Akmehmet Balçoğlu and Ötker, 2003) or electro-oxidation (Panizza and Cerisola, 2009) especially using boron-doped diamond (BDD) anodes (Urtiaga et al., 2014).

Among these AOPs, Fenton reaction is probably one of the most used to deplete a wide range of refractory organic compounds (Bokare and Choi, 2014; Oturan and Aaron, 2014). The Fenton oxidation is based on the generation of hydroxyl radicals from a mixture of H₂O₂ together with a soluble iron(II) salt, according to Eq. (1) (Ribeiro et al., 2015). It has been described that the attack of hydroxyl radicals to organic matter is usually focused on double bonds, being complex molecules easier to degrade than short-linear chain and more oxidized ones (Munoz et al., 2012; Turan-Ertas and Gurol, 2002).



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Another widely studied AOP is electrochemical oxidation using boron-doped diamond (BDD) anodes, also known as conductive-diamond electro-oxidation (CDEO). In this case, physically adsorbed hydroxyl radicals allow the complete and non-selective degradation of organics (Martínez-Huitle and Brillas, 2009; Martínez-Huitle et al., 2015; Panizza et al., 2001; Sirés et al., 2008). Depending on the supporting electrolyte used, the application of BDD anodes also allows the formation of powerful oxidants as persulfate (Davis et al., 2014; Monteagudo et al., 2016; Serrano et al., 2002), peroxodiphosphate (Cañizares et al., 2005; Sánchez et al., 2013) or perchlorate (Bergmann et al., 2009; Brito et al., 2015; Sánchez-Carretero et al., 2011). Previous studies demonstrated that CDEO overcomes the efficiency of Fenton reaction, especially for the degradation of short-linear chain organics (Cañizares et al., 2008; Turan-Ertas and Gurol, 2002). The role of the generated oxidants, which promotes mediated oxidation pathways that increase the mineralization efficiency of the process, help to explain this dissimilar behavior.

So far, the studies comparing the performance of Fenton and BDD processes in the removal of organic matter are limited to the treatment of synthetic effluents (Cañizares et al., 2007, 2008) or to the treatment of landfill leachates (Vallejo et al., 2013). In the present work, the treatment of approximately 60 real effluents from a pharmaceutical plant was performed by Fenton reaction and BDD electro-oxidation. The influence of chemical organic load (both in terms of chemical oxygen demand (COD) and total organic carbon (TOC)), conductivity and mean carbon oxidation state on the removal efficiency was evaluated for both processes, using standardized tests. It is hoped that this comprehensive study will allow the optimization of the treatment strategy for the removal of organic matter in the pharmaceutical industry.

2. Materials and methods

2.1. Wastewaters characterization

All the samples used in this work are real wastewater effluents coming from an organic-synthesis pharmaceutical manufacturing plant. The sampling time lasted for a year, collecting more than 100 samples from different production processes. A numeric code was used to identify the effluents. The organic load and conductivity values measured in the wastewater generated in the chemical synthesis pharmaceutical industry showed a wide range of variation (100–500,000 mg O₂ dm⁻³ of COD, 0.2–200 mS cm⁻¹ of conductivity). For this work, just effluents with COD lower than the discharge limit (2,000 mg dm⁻³) and higher than 100,000 mg dm⁻³ were not evaluated. A more detailed characterization list can be found in the [supplementary material](#).

2.2. Analytical procedures

The Total Organic Carbon (TOC) concentration was measured using a Multi N/C 3100 Analytik Jena analyser. COD was determined in all the experiments by COD measurement kits (Reference HC550862, recommend for sample up to 50,000 mg dm⁻³ of Chloride) and a Spectroquant Pharo 100 supplied by Merck KGaA (Darmstadt, Germany). In Fenton oxidation experiments, unreacted hydrogen peroxide was measured according to the method described elsewhere (Eisenberg, 1943). After that, COD value was corrected with the value of hydrogen peroxide to obtain the COD associated to the organic pollutants contained in the wastes (Kang et al., 1999). The conductivity was measured using a GLP31 conductimeter and the pH using a GLP 22 pHmeter, both of them supplied by Crison Instruments (Alella, Barcelona).

2.3. Experimental set-ups and procedures

2.3.1. Fenton oxidation

The Fenton oxidation (FO) experiments were performed in laboratory scale borosilicate glass reactors (Pyrex®) of 250 mL placed over a multi-stirrer magnetic plate (MIX 15 Eco, 2 mag, Germany) as described elsewhere (Cañizares et al., 2008). They consisted in evaluating the removal of COD and TOC in a batch reactor in which the dosages under the stoichiometric ratio of hydrogen peroxide were added.

In each experiment, the reactors were filled with 150 mL of wastewater and the FO tests were maintained during 3 h. FeSO₄·7H₂O (iron source) and H₂O₂ (33% w/v) were supplied by Panreac. In a Fenton oxidation process, the key parameters affecting the overall performance of the technology are the pH, the H₂O₂/Fe ratio and the H₂O₂ dosage (Babuponnusami and Muthukumar, 2014). The pH was kept at 3 in all the experiments, since it is widely considered as the optimum value for organics abatement regardless of the target substrate (Babuponnusami and Muthukumar, 2014; Gallard and De Laat, 2000; Rivas et al., 2001). H₂O₂/Fe ratio was previously optimized (data not shown), setting 5:1 (mass units) as the optimum value. Maintaining constant this H₂O₂/Fe ratio, increasing H₂O₂ dosages were added in order to evaluate the effect of this variable in COD abatement.

The stoichiometric H₂O₂ dosage supplied in the oxidation process can be easily estimated by Eq. (2), where OCC (Oxygen-equivalent Chemical-oxidation Capacity) is the parameter proposed in previous works (Cañizares et al., 2007) to quantify the kg of O₂ that are equivalent to the quantity of oxidant reagents used in each advanced oxidation process to treat 1 m³ of wastewater.

COD abatement efficiency was calculated as follows (Eq. (3)):

$$OCC \left(\text{kgO}_2 \text{m}^{-3} \right) = 0.471 \cdot [\text{H}_2\text{O}_2] \left(\text{kgH}_2\text{O}_2 \text{m}^{-3} \right) \quad (2)$$

COD abatement efficiency was calculated by Eq. (3), where COD abatement efficiency (%) is the percentage of hydrogen peroxide effectively used to reduce COD, COD₀ (mgO₂/dm³) is the D value at the beginning of the experiment, COD_f (mgO₂/dm³) is the COD value at the end of the experiment V₀ (mL) is the initial volume of the sample, COD_f (kg O₂/l) is the COD value measured at the end of the experiment, V_f (mL) is the final volume considering pH modifiers, coagulant and hydrogen peroxide volumes added to the initial. V_{H₂O₂,S} (mL) is the volume of hydrogen peroxide added and V_{H₂O₂,T} is the theoretical volume of hydrogen peroxide to completely oxidize the organic matter.

$$COD_{abatement} \text{ efficiency}(\%) = \frac{\left(\frac{COD_0 \cdot V_0 - COD_f V_f}{COD_0 \cdot V_0} \cdot 100 \right)}{\left(\frac{V_{H_2O_2,S}}{V_{H_2O_2,T}} \right)} \quad (3)$$

2.3.2. Conductive-diamond electro-oxidation

Conductive-diamond electro-oxidation (CDEO) experiments were performed in a single compartment electrochemical flow cell working under batch mode described elsewhere (Martín de Vidales et al., 2012). Diamond-base material (p-Si-boron-doped diamond) was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular-shaped (100 mm diameter) resulting in 78 cm² of active area. The gap between electrodes was 9 mm. Boron-doped diamond films were supplied by Adamant Technologies (Switzerland). Test consisted in evaluating the removal of COD and TOC for electric current up to the stoichiometric required

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