



Research article

Coupling of acrylic dyeing wastewater treatment by heterogeneous Fenton oxidation in a continuous stirred tank reactor with biological degradation in a sequential batch reactor



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ABSTRACT

This work deals with the treatment of a recalcitrant effluent, from the dyeing stage of acrylic fibres, by combination of the heterogeneous Fenton's process in a continuous stirred tank reactor (CSTR) with biological degradation in a sequential batch reactor (SBR). Three different catalysts (a commercial Fe/ZSM-5 zeolite and two distinct Fe-containing activated carbons – ACs – prepared by wet impregnation of iron acetate and iron nitrate) were employed on the Fenton's process, and afterwards a parametric study was carried out to determine the effect of the main operating conditions, namely the hydrogen peroxide feed concentration, temperature and contact time. Under the best operating conditions found, using the activated carbon impregnated with iron nitrate, 62.7% of discolouration and 39.9% of total organic carbon (TOC) reduction were achieved, at steady-state. Furthermore, a considerable increase in the effluent's biodegradability was attained (BOD₅:COD ratio increased from <0.001 to 0.27 and SOUR – specific oxygen uptake rate – from <0.2 to 11.1 mg O₂/(g_{VSS}·h)), alongside a major decrease in its toxicity (from 92.1 to 94.0% of *Vibrio fischeri* inhibition down to 6.9–9.9%). This allowed the application of the subsequent biological degradation stage. The combination of the two processes provided a treated effluent that clearly complies with the legislated discharge limits. It was also found that the iron leaching from the three catalysts tested was very small in all runs, a crucial factor for the stability and long-term use of such materials.

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1. Introduction

Effluents produced by dye-houses are usually characterized by high pH and temperature, intense colour (resulting from incomplete fixation of dyes), low biodegradability (BOD₅:COD ratio <0.1) and considerable values of chemical oxygen demand (COD) (Kim et al., 2004). Therefore, the discharge of such effluents without any treatment is responsible for several negative environmental impacts, as favourable conditions for eutrophication, low re-oxygenation rates and reduction of solar light penetration are promoted (Shi et al., 2007). Public health may also be at risk as

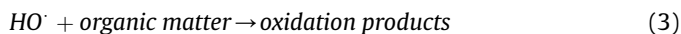
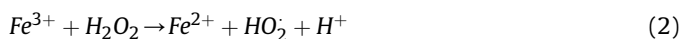
many of the dyes used in this industrial sector have toxic and/or carcinogenic properties (Pinheiro et al., 2004). Therefore, efficient processes are required for the treatment of such effluents.

The advanced oxidation processes (AOPs), based on the generation of highly reactive and non-selective hydroxyl radicals (HO[•]), are among the most promising techniques for the removal of recalcitrant organics. While conventional biological processes (e.g. activated sludge) are usually inefficient as regards the degradation of some complex/toxic compounds present in textile dyeing wastewaters and physical/chemical processes (e.g. adsorption, coagulation/flocculation, membrane separation) only transfer the pollutants from one phase to the other (Zhou et al., 2009), AOPs allow for the effective oxidation of many organics, in some cases up to H₂O and CO₂ (i.e., with complete mineralization).

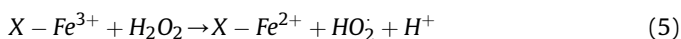
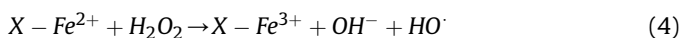
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The homogeneous Fenton's process is one of the most interesting AOPs due to the low investment cost, the easiness of implementation, the low toxicity of reagents and the absence of mass transfer limitations (Tunc et al., 2012, 2013); the generation of hydroxyl radicals is achieved by the decomposition of hydrogen peroxide catalysed by ferrous ions, in acid environment, under mild conditions of pressure and temperature, as described by the simplified Eqs. (1)–(3) (Walling, 1975):



However, the homogeneous Fenton's process entails some disadvantages such as the need of high concentrations of iron in solution (typically 50–80 ppm) and the subsequent effluent treatment for catalyst recovery before discharge. Furthermore, processing of the generated sludge (rich in iron hydroxides) requires large amounts of chemicals and man power, making the process laborious and economically unattractive (Idel-aouad et al., 2011; Soon and Hameed, 2011). To minimize these disadvantages several studies were conducted in the heterogeneous phase, where the iron species are attached to a solid porous matrix (e.g. zeolite, activated carbon, clay) preventing their loss to the effluent (Hassan and Hameed, 2011; Duarte et al., 2013a; Rache et al., 2014). Although the process is globally complex due to simultaneous adsorption and catalysis phenomena, Eqs. (4) and (5) briefly describe the main reactions involved:



where X represents the surface of the solid matrix.

Literature shows several studies where the heterogeneous Fenton's process has been applied for dye removal and textile effluent treatment in either batch (Ramirez et al., 2007; Idel-aouad et al., 2011; Karthikeyan et al., 2011; Yao et al., 2013; Chen et al., 2014) or continuous mode (packed-bed or column reactors) (Su et al., 2011; Mesquita et al., 2012; Duarte et al., 2013a). The first configuration has clear disadvantages for industrial implementation as the reactor operates discontinuously, with the need of a subsequent stage (e.g. filtration) for catalyst recovery, while the latter commonly presents problems of mass transfer, due mainly to the formation of gas bubbles (O_2 and/or CO_2) that are caught in the catalyst particles (as observed in the work of Mesquita et al. (2012)); such problems should not occur in a configuration like a continuous stirred tank reactor (CSTR). The CSTR configuration was recently applied for dye removal (Ramirez et al., 2009), olive-oil mill wastewater (Hodaifa et al., 2013) and landfill leachate (Zhang et al., 2006) treatment by the Fenton's process. However, to the best of our knowledge, only one recent study reported the use of the heterogeneous Fenton's process in a CSTR (Queirós et al., 2015).

Fenton's oxidation is commonly used as a pre-treatment whenever the aim is to partially degrade organic compounds, increase biodegradability and/or reduce toxicity of wastewaters, usually being followed by a biological unit (Reife and Freeman, 1996), making the combined overall process economically attractive. In particular, the use of a sequential batch reactor (SBR) is desirable and has been often the choice of several authors. Simplicity in the implementation, flexibility, low cost and increased resistance to fluctuations in the wastewater characteristics are

among some of the advantages of SBRs, when compared to other conventional biological treatments (Suresh et al., 2011). Additionally, the stages of equalization, reaction and clarification occur in the same reactor (U.S. EPA, 1999).

This work deals with the combination of the heterogeneous Fenton reaction in a CSTR, followed by a biological process in a SBR, for the treatment of an acrylic dyeing effluent, an approach which was found by the authors to be unique in the literature. The main goal is to obtain a treated effluent that accomplishes the maximum allowable limits imposed by Portuguese legislation for discharge into the aquatic environment.

2. Materials and methods

2.1. Synthetic wastewater preparation

As the characteristics of real wastewaters from dye-houses change dramatically from day to day (or even from hour to hour), a synthetic acrylic effluent was prepared and used for this study in accordance with the information presented in a previous work (Rodrigues et al., 2014a). Briefly, the amount of dye (Astrazon Blue FGGL 300% 03 – see the chemical structure in Fig. S1 of the Supporting Information section) and auxiliary products used in the industrial dyeing baths were taken into account, as well as the percentage of these products unfixed by the fibres (rejection percentage) – cf. Table S1 of Supporting Information. Such information was kindly supplied by the dye-house Erfoc – Acabamentos Têxteis S.A. (Famalicão, Portugal) and by DyStar Anilinas Têxteis Unip. Ltd. (Portugal), allowing estimating the concentration of each species in the synthetic acrylic effluent.

2.2. Catalysts and their characterization

For this study, different Fe-based catalysts were chosen: a commercial zeolite – Alsi Penta Fe/ZSM-5 (ref. FE-SH-27, 5 wt.% of Fe) – and two Fe/C catalysts synthesized by impregnation of activated carbon (Norit RX3). In both cases, zeolite and activated carbon were milled and sieved from the commercial pellets ($d_p > 5$ mm), until the fraction of $0.8 < d_p < 1.6$ mm; this particle size was selected based on the work of Duarte et al. (2012). Two portions of AC sieved to this grain size were impregnated with saturated solutions of two different iron precursors (AC1 – iron acetate ($\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$) with 95% of purity from Aldrich, and AC2 – iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) with 97% of purity from Riedel-de Haen). The iron solutions were prepared by dissolving the required amount of each salt precursor in the minimum volume of distilled water (according to the salt solubility), at room temperature and using magnetic stirring, so that the Fe/C catalysts contained the same amount of Fe (5 wt.%) as the commercial zeolite for comparison purposes. The impregnation was carried out by adding the precursor solution dropwise and uniformly to the carbon under stirring for a homogeneous wetting of the particles and avoiding the excess of solution. Finally, after drying for 24 h in an oven at 100 °C, the impregnated samples were treated in a He inert atmosphere at 350 °C for 2 h, for the iron salt decomposition.

Textural characterization of the samples was performed in a Autosorb1 apparatus, from Quantachrome. Before measuring the N_2 adsorption isotherms (at –196 °C), samples were degassed overnight (at 110 °C) under high vacuum (6–10 mbar). The BET equation was applied to the adsorption isotherm data (for $P/P_0 < 0.10$) to provide the specific surface area (S_{BET}) of each catalyst, while their microporosity was characterized by the Dubinin–Radushkevich equation (Bansal et al., 1998):

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