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Enhancement of a solar photo-Fenton reaction by using ferrioxalate complexes for the treatment of a synthetic cotton-textile dyeing wastewater

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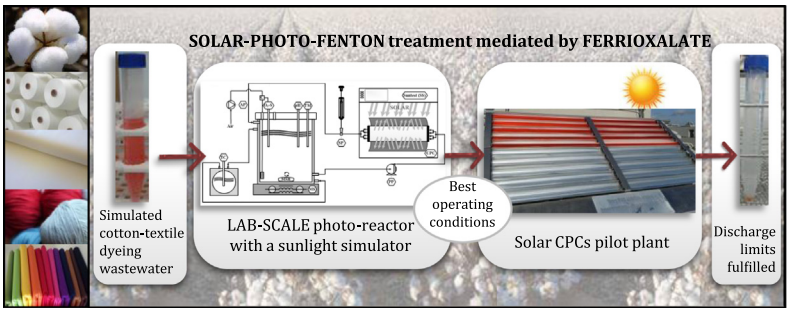
HIGHLIGHTS

- Strategies for the treatment of a cotton-textile dyeing wastewater are examined.
- Photo Fenton (PF) treatment leads to insoluble ferric–organic complexes.
- PF/Ferrioxalate remarkably improves wastewater mineralization rate.
- The suitability of combining biological and PF/Ferrioxalate processes is evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

Biological, photo-Fenton (PF) and photo-Fenton mediated by ferrioxalate complexes (PF/Ferrioxalate) processes were examined for the degradation of a synthetic cotton-textile dyeing wastewater. Aerobic biological treatment had a negligible effect on discolouration whereas total organic content decreased mainly due to the biodegradation of acetic acid initially present in the wastewater. PF process yielded a fast and pronounced dissolved organic carbon concentration decay, mostly associated to the abrupt precipitation of Fe(III)–organic complexes. The addition of oxalic acid limited iron precipitation, allowing mineralization of most organic contaminants. The influence of the different dyes and main dyeing auxiliary constituents of the synthetic textile wastewater on the PF and the PF/Ferrioxalate efficiency was systematically analysed. The suitability of combining PF/Ferrioxalate with conventional biological processes as a pre and/or post treatment was evaluated.

This study highlights the potential of PF/Ferrioxalate reaction to mineralize the synthetic cotton-textile wastewater under appropriate experimental conditions, the best being: $[Fe^{3+}] = 40\ mg\ L^{-1}$, iron/oxalate molar ratio = 1:3, pH = 4.0 and $[H_2O_2] = 50–100\ (1.5–2.9)\ mg\ L^{-1}$ ($mmol\ L^{-1}$). At these conditions, the PF/Ferrioxalate treatment was carried out under natural sunlight in a pilot plant equipped with compound parabolic collectors.

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1. Introduction

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater [1]. Textile wastewater is heavily coloured and exhibit high salts content and biological recalcitrant character [2,3]. Therefore, development of robust and complete textile wastewater treatment methods is imperative for preserving the environment. Many chemical and physical processes have been proposed for the removal of dyes from wastewater, such as adsorption, coagulation, activated sludge treatment and oxidation by ozone or hypochlorite. These methods can be expensive and, in some cases, they may not eliminate the colour completely [4].

Recently, Advanced Oxidation Processes (AOPs) have emerged as an effective alternative to conventional methods. AOPs are characterized by the production of highly reactive radicals ($HO^{\cdot}$), which are able to degrade most of the recalcitrant organic pollutants due to their high oxidative capacity. Among the AOPs, the photo-Fenton (PF) process carried out under solar radiation as UV–Vis photon source for enhancing the $HO^{\cdot}$ generation is a potentially low cost technique [5,6]. However, application of this process for treating textile wastewater presents some drawbacks: (i) the coloured compounds reduce light penetration; (ii) textile wastewater is generally alkaline and PF works efficiently under acid conditions, to avoid iron precipitation and promote the pre-eminence of the photoactive ferric ion–water complex ($FeOH^{2+}$) species in solution [7]; (iii) ferric–organics complexes can be formed, limiting the photo-reduction of Fe^{3+} and thus decreasing the generation of radicals; (iv) the high content of inorganic ions (Cl^{-}, SO_4^{2-}, CO_3^{-}) induces the hydroxyl radicals scavenger reactions and the formation of inorganic ion–ferric complexes, which again decreases the rate of hydroxyl radicals generation [8–10].

To overcome these drawbacks, the addition of oxalic acid to PF treatment has been proposed [7,11,12]. PF mediated by ferrioxalate (PF/Ferrioxalate) offers further advantages over the conventional PF process. Ferrioxalate complexes provide much higher quantum yields, accelerating the regeneration of ferrous iron and therefore producing a higher amount of $HO^{\cdot}$ radicals; then, solar light is more efficiently used [13]. Ferrioxalate complexes reduce the formation of stable complexes between ferric ions and organic species present in wastewater. Moreover, in the presence of ferrioxalate, iron precipitation is inhibited even at near neutral pH (5–6) [7,14].

The application of a solar photo-Fenton reaction mediated by ferrioxalate complexes to different contaminants and wastewaters from various industrial sources has been recently reported. This treatment showed to be effective in the degradation of pure aqueous solutions contaminated with diclofenac [15], sulfamethoxazole and trimethoprim [16] at low iron concentrations and near neutral pH conditions. Monteagudo et al. [17] also showed the effectiveness of the photo-Fenton reaction mediated by ferrioxalate on the treatment of a real winery wastewater generated during the cleaning of winemaking facilities and equipment. Duran et al. [18] demonstrated that under certain conditions, the synergism between the photo-Fenton process and the ferrioxalate photochemistry was 22.9%, considering the treatment of a wastewater from a beverage industry. Recently, Soares et al. [19] evaluated different photo-Fenton-iron(III)–organic ligands complexes systems in the treatment of a synthetic acrylic-textile wastewater (mainly composed of a basic azo dye, and commercial auxiliary products such as, an Sera®Con N-VS, Sera® Tard A-AS, sodium sulphate, Sera®Sperce M-IW, Sera®Lube M-CF). The best results were obtained with the photo-Fenton reaction mediated by ferrioxalate. It is important to remark that the presence of specific auxiliary products, characterizing different types of textile wastewater, significantly and distinctly affect the applied Fenton and photo-Fenton processes. In this work, their influence is disclosed by comparing the process performance when applied to the synthetic cotton-dyeing wastewater and to isolated dyes and auxiliary products solutions. Moreover, the precipitation of Fe(III)–organic matter complexes generated in the photo-Fenton treatment is particularly examined.

Operating costs of the PF/Ferrioxalate process, mainly related to energy and reagents consumption, are higher than those of biological treatments. From an economic point of view, an effective treatment of recalcitrant wastewater may require a combination of processes, such as biological and advanced oxidation processes [6,20–23]. Refractory wastewater can be chemically pre-treated to increase biodegradability before being subjected to a conventional biological treatment. Alternatively, a biological pre-treatment can remove the biodegradable pollutants, therefore reducing the required amount of reagents in the subsequent oxidation process [6,21].

This research focuses on defining the best treatment strategy for a simulated/synthetic cotton-textile dyeing wastewater to accomplish the discharge limits established by Portuguese regulations. The viability of the PF and the PF/Ferrioxalate treatments using a photocatalytic tubular reactor irradiated with simulated solar radiation was particularly evaluated. The efficiency of the PF/Ferrioxalate process was evaluated under different iron concentrations, pH values and H_2O_2 availability. Operating conditions leading to the best performance were selected to carry out a solar-photo-Fenton/Ferrioxalate assay in a pilot plant equipped with compound parabolic collectors (CPCs). The extent of oxidation was assessed by analysing colour, organic matter content in terms of dissolved organic carbon (DOC), chemical oxygen demand (COD), 5 days biochemical oxygen demand (BOD_5), and biodegradability (Zahn Wellens test, BOD_5/COD ratio, carbon oxidation state (COS) and low-molecular-weight carboxylic acids content). Finally, the suitability of coupling biological with advanced oxidation processes was evaluated and discussed.

2. Experimental methodology

2.1. Preparation of the synthetic wastewater

The simulated cotton-textile wastewater was prepared by mixing the dyes (Procion Deep Red H-EXL gran and Procion Yellow H-EXL gran) and the auxiliary products, according to the information provided by the textile dyeing company Erfoc-Acabamentos Têxteis S.A. (Famalicão, Portugal). The concentration of each component in the final effluent was estimated taking into account the percentage of fixation of each compound on cotton fibres. This wastewater is assumed to be representative of the liquid effluent taken from the supernatant of a sedimentation tank. Samples of dyes and dyeing auxiliary products were kindly supplied by the above mentioned company and by DyStar Anilinas Têxteis, Unip Ltd (Porto, Portugal). Table 1 lists the dyes and auxiliary products used, their function and its contribution to DOC content on final wastewater. The biodegradable acetic acid (HAc) represents 40% of the total DOC content.

The characteristics of the simulated cotton textile dyeing wastewater are provided in Table 2. The synthetic wastewater has a low-moderate organic load. It presents a basic pH of 11.5 and a red-orange colour with a maximum absorbance peak at 478 nm. When acidified, the wastewater acquires a defined red colour, and the peak shifts to 518 nm. Wastewater colour remains visible after a dilution 1:40. The BOD_5/COD ratio of the synthetic effluent is relatively high (0.43); the Zahn–Wellens test indicates 56% of biodegradability after 28 days.