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Assessment of a multistage system based on electrocoagulation, solar photo-Fenton and biological oxidation processes for real textile wastewater treatment

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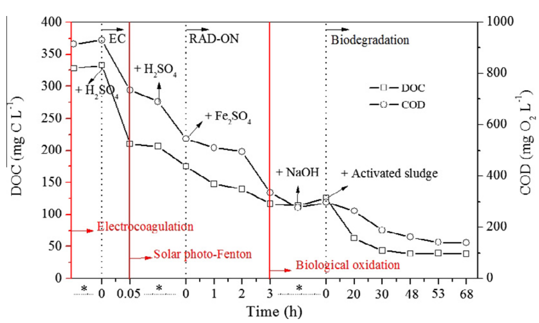
HIGHLIGHTS

- A multistage system was applied on the treatment of a real textile wastewater.
- Optimal operating conditions for each process was assessed and integrated.
- Partial pollutants reduction was achieved by the EC process as a first stage.
- Photo-Fenton oxidations improve the biodegradability index of EC-treated.
- Effluent according to legislation was attained after the biological oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of a multistage treatment system for textile wastewater was investigated in this study. The processes of electrocoagulation (EC), photo-Fenton oxidation, and activated sludge biological degradation were integrated in batch mode. The integrated treatment system performance was assessed according to three response variables: dissolved organic carbon (DOC), chemical oxygen demand (COD) and biodegradability index. Based on preliminary tests, the EC-based wastewater treatment was suitable as the first stage of the integrated treatment system, followed by the photo-Fenton process. A lab photo-reactor was used to assess the influence of photo-Fenton variables on the process performance. Based on the better lab photo-Fenton reactor conditions, the improvement of some biological indicators related to the organics biodegradability of treated wastewater was investigated in a pilot-scale photoreactor. An activated sludge-based biological reactor at lab-scale was used as a final treatment stage, in order to achieve the legislated limits for discharge into water bodies. Partial degradation of the organic pollutants was achieved by the EC process, with a 36% reduction in COD. In the second treatment stage, a 70% biodegradability index was attained by setting the photo-Fenton reaction conditions at 100 mg Fe^{2+} L^{-1}, pH 2.8, 12 mM H_2O_2 and 6.9 kJ L^{-1} accumulated energy. Finally, a residual COD of 139 mg O_2 L^{-1} was achieved at the outlet of the biological process, which is below the maximum limit established by the Portuguese legislation.

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1. Introduction

The textile industry generates large quantities of highly colored wastewaters coming from dyeing/printing processes. In textile-processing steps, many auxiliary chemicals such as metals, salts, surfactants, organic processing assistants, sulfide and formaldehyde are commonly added to improve the final product. In addition, depending on the method and fixation-type to textile fiber, dyes such as acid, basic, direct, dispersed, reactive, azoic and sulphurous are commonly used [1]. Consequently, different recalcitrant dyes and other auxiliary products, with complex organic structures, as well as high alkalinity and inorganic salts concentrations, characterize such wastewaters. The presence of toxic and non-biodegradable components in the textile wastewaters, such as complex aromatic and polymeric structures, as well as their high solubility in water, has become a serious threat for aquatic biota. For this reason, the input of such organic compounds into water bodies without previous treatment or with incomplete treatment must be avoided [2,3].

Several types of treatment systems based on coagulation/flocculation [4–7], adsorption [8–10], membranes [11–14], electrocoagulation [15–18], advanced oxidation (AOPs) [19–23] and biological processes [24–27] have been adopted to remove or degrade textile dyes. It is remarkable that the application of AOPs, which are characterized by the production of highly oxidizing species such as hydroxyl radicals, have the ability to degrade complex organic compounds that are difficult to remove by conventional methods.

Based on their singular characteristics for the treatment of industrial effluents, the AOPs have become in the most promising technology [28]. Among all AOPs, the Fenton and photo-Fenton reactions have been the most widely used techniques [29]. As reported in the literature [20,30], it is expected to improve the biodegradability of textile wastewaters by a solar photo-Fenton oxidation process. The production of highly oxidizing species is enhanced by applying UV–vis light on Fenton reactants, supporting sustained chemical reactions as well as an increase in efficiency compared to other AOP-based methods for the degradation of different recalcitrant pollutants [31]. When a photo-Fenton process is applied to degrade textile dyes, iron-dye and iron-inorganic salt complexes are created, leading to a significant reduction in the process reaction rate [32,33]. Meanwhile, as suggested by Yilmaz et al. [34] and Rosáles et al. [35], an electrocoagulation process-based pre-treatment of textile wastewater, with a partial reduction in organic pollutants, should be performed as the first stage of the photo-Fenton process. In an electrocoagulation (EC) process, when the electric current passes throughout an aqueous medium with high conductivity, the processes of anodic metal dissolution and water electrolysis close to the cathode take place and consequently all pollutants are transformed into amorphous precipitates or hydroxide compounds or low-density flocks [36]. A combination of different treatment processes can improve the wastewater treatment performance and minimize costs, by providing little to no generation of secondary recalcitrant wastes and producing final treated wastewaters with sufficient quality for discharge into receiving water bodies [37].

New strategies based on the integration of processes such as electrochemical, biological and advanced oxidation methods have also been investigated, in order to improve, as a whole, integrated system efficiency [29]. From the literature, an integration of EC and photo-Fenton processes has been investigated for textile [38] and tannery effluent treatment [39,40], while the integration of advanced oxidation and biological processes has been applied to treat cork [41,42], pharmaceutical [43] and leachate wastewaters [44,45].

In this study, a treatment system based on the integration of EC, photo-Fenton and biological processes was applied to degrade recalcitrant organic matter and enhance the biodegradability index of a real textile wastewater. Previously, the EC process, photo-Fenton's oxidation at pilot-plant scale and aerated biological degradation were separately assessed to achieve the best reactor conditions for the organic pollutants removal. By working in the optimal operating conditions for each process, a significant improvement on the final characteristics of the treated wastewater was achieved, complying with the requirements for wastewater discharge into water bodies.

2. Experimental methodology

2.1. Sampling and chemicals

The wastewater sample was collected from an equalization tank of an industrial textile plant located in Vizela (Portugal), showing a dark blue color associated with the mixture of several classes of dyes (Reactive, Direct, Dispersive, Acid and Cuba dyes), as well as other pollutants used in the textile process. Treated and untreated samples were preserved according to the Standard Methods [46]. Analytical grade chemical reagents were used. Hydrogen peroxide (Quimitécnica, 50% w/v, 1.10 g cm^{-3}) and iron (II) sulfate heptahydrate (Panreac) were used as Fenton reagents. Milli-Q ultrapure and deionized water were used to prepare and dilute reagents. A catalase solution (2500 U mg^{-1} from bovine liver) was used to eliminate the remaining H_2O_2 in solution. Activated sludge with mixed liquor volatile suspended solids (MLVSS)/mixed liquor suspended solids (MLSS) = 0.83, collected at a municipal wastewater treatment plant in Freixo (Porto, Portugal), was used as inoculum in the biological reactor.

2.2. Analytical measurements

The anions and cations in solution were quantified by ion chromatography (Dionex, ICS-2100 and DX-120). Dissolved organic carbon (DOC) and total dissolved nitrogen were measured in a TC-TOC-TN analyzer (Shimadzu, model TOC-V_{CSN}). Soluble nitrogen was determined by chemiluminescence. An UNICAM Helios spectrophotometer was used to measure the absorbance at 228, 254, 284 and 310 nm for aromatic compounds and maximum absorbance (641 nm) from the UV–vis spectrum of the textile wastewater. H_2O_2 concentration was determined by the metavanadate method [47]. Dissolved iron concentration was determined by a colorimetric method [48]. Chemical oxygen demand (COD) was measured using a Merck Spectroquant kit (ref: 1.14541.0001). Measurements of pH, temperature, dissolved oxygen and conductivity were performed using a multiparameter analyzer (Hanna, model HI 9829). The total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to Standard Methods [46]. All samples were previously centrifuged at 4000 rpm for 5 min, except for the determination of TSS, VSS and COD.

2.3. EC experiments

A lab-scale EC reactor, consisting of a 1.5 L cylindrical glass container, a set of iron electrodes with eight plates and a magnetic stirrer, was used and operated in monopolar mode. A 900 mL effective volume and electrode surface area of 0.035 m^2 were regarded. A similar EC reactor was previously employed [15] to treat textile wastewaters, with a suitable operation at a current density of 142.9 A m^{-2}, initial pH solution of 7.0 and electrolysis time of 5 min for the lowest toxic load. Such optimal EC operating conditions were used in the present work. Before each run, the pH value