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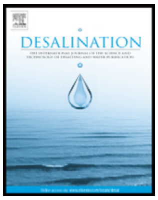

Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse

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ABSTRACT

Both Fenton oxidation and the combination of aerobic Sequencing Batch Reactor (SBR) + Fenton oxidation were investigated in a bench-scale study to degrade and reuse a real textile wastewater with a TOC = 465 mg L^{-1} C, COD = 2100 mg L^{-1} O_2 and *Escherichia coli* = 80,000 CFU mL^{-1}, according to RD 1620/2007 (Spanish Normative for wastewater reclamation and reuse). The independent variables considered for the optimization of the oxidative process were temperature, H_2O_2 and Fe (II) concentrations. Under the best stand-alone Fenton operating conditions: T = 25 °C, pH = 3; [H_2O_2] = 1650 mg L^{-1} and [Fe (II)] = 216 mg L^{-1}, we achieved 64% TOC reduction and > 99% *E. coli* removal. However, the best results were obtained when applying Fenton process with [H_2O_2] = 1518 mg L^{-1} and [Fe (II)] = 66.5 mg L^{-1}, as a biological polishing step. The aerobic biological treatment was conducted using a SBR with 1 day HRT. In this case 92% TOC and > 99% *E. coli* removal were accomplished.

The obtained results showed the feasibility of both processes to achieve suitable water qualities for internal reuse, according to RD 1620/2007.

1. Introduction

Textile mills are major consumers of water and one of the largest sectors causing intense water pollution. The impact of textile effluents on aquatic medium has been traditionally of great concern, because they contain a large variety of raw materials and reagents: synthetic dyes, pigments, biocides, oils, heavy metals, salts, nutrients and organic compounds. Consequently, these effluents are characterized by high values of chemical oxygen demand (COD), temperature, colour, changeable pH, suspended solids and organic chlorine compounds [1,2].

The physical, chemical and mostly biological technologies have been widely used to treat textile effluents [3,4]. Afterwards, they are normally discharged into the sewer system. However, most of the organic matter in the effluent is not biodegradable and/or toxic, so that a biological treatment is inefficient [5]. Moreover, physical and chemical treatment techniques are effective for colour removal but consisting only in a phase transfer of pollutants that requires additional treatment or disposal. Consequently, the increased public concern and the tighter international regulations have challenged the textile industry to explore new lines to reduce environmental problems associated with such wastewaters.

In this frame, the Advanced Oxidation Processes (AOPs) are alternative processes involving the generation of highly oxidizing radicals, specially the hydroxyl radical (•OH, $E^0 = 2.8$ V versus NHE), capable of oxidizing high recalcitrant contaminants to CO_2 and H_2O. Among the different existing AOPs, the Fenton process arises as very promising and alternative wastewater technique that can be applied to the remediation of textile wastewaters, either alone or in combination with an aerobic biological treatment (pre or post biological treatment). The process is highly effective in the degradation of toxic and/or non-biodegradable compounds (e.g. aliphatic compounds, nitroaromatics, azo-dyes, phenols, chlorobencene, etc.) [6–9] and has a special interest because it make possible the achievement of high reactions yields with a low cost treatment.

The generation of hydroxyl radicals takes place when hydrogen peroxide and an iron salt are combined in aqueous solution (reaction 1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH \qquad k = 76.5 \ \ L \ mol^{-1} \ s^{-1} \tag{1}$$

Fe (III) ion can be recovered in a closing loop mechanism (reactions 2–4):

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH_2{}^{+} + H^{+} \quad K_{eq} = 3.10 \cdot 10^{-3} \tag{2}$$

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$$FeOOH^{2+} \rightarrow HO^{\bullet}_2 + Fe^{2+} \quad k = 2.70 \cdot 10^{-3} \ s^{-1} \tag{3}$$

$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + O_2 + H^{+} \quad k < 2.00 \cdot 10^{3} \ L \ mol^{-1} \ s^{-1} \tag{4}$$

On the other hand, the worldwide water stress, especially in arid areas, has caused the apparition of more stringent regulations and an increasing development of new water management policies. These new policies are in accordance with the guidelines set by the Water Framework Directive (Directive 2000/60/EC), which suggest the reuse as a way to obtain new sources of water. Consequently, an important challenge of textile industry will be the water reuse in order to overcome irrational fresh water consumption.

Nowadays, the quality of water for reuse is regulated by guidelines and specific regulations [10–12]. However, the required levels of the different guidelines and regulations vary greatly. According to Spanish RD 1620/2007 (Spanish Normative for wastewater reclamation) [12], different chemical and microbiological parameters need to be controlled in order to assess water quality for reuse. Among these parameters, we can find suspended solids, turbidity, *Legionella* spp and *Escherichia coli*. Moreover, each industry can need the control of some additional specific parameters. For instance, an important parameter in textile industry is the iron content.

Different papers in literature deal with the combination of physicochemical treatment and membrane technologies [13,14] to textile effluents for its reuse. Also, the nanofiltration and reverse osmosis of biologically treated textile wastewater have been successfully used to treat textile effluents for reuse [15–17].

However, at the present, we can find in literature few papers that deal with the use of AOPs in order to reuse treated water [18–23] and to remove microbiological contaminants. The papers [24,25] deal with the use of photocatalysis in order to abate *E. coli*, while the paper [26] deals with the use of immobilized photo-Fenton reagent on structured silica surfaces to inactivate *E. coli*. However, there are any AOP-based study dealing with the removal of both physicochemical and microbiological parameters for real wastewater treatment and reuse.

In the present work, the remediation of a real textile wastewater from Catalonia (North East of Spain) was carried out by means of two processes: Fenton alone and Fenton as a post-treatment of an aerobic Sequential Batch Reactor (SBR). The effect of the key variables in the Fenton process ([Fe^{2+}], [H_2O_2] and T) has been studied, as well as a comparison between both processes in terms of remediation effectiveness, considering the alternative of water reuse in the same textile process.

The obtained results showed the feasibility of both processes to achieve suitable water qualities according to RD 1620/2007 for internal reuse. Both physicochemical and microbiological parameters are considered as process effectiveness indicators. Moreover, from obtained results, the applicability SBR + Fenton strategy could be also considered in WWTP facilities to achieve suitable final qualities for water reuse.

2. Experimental

2.1. Textile wastewater

The textile wastewater was a real textile effluent from a textile mill situated in Catalonia (North East of Spain). The current treatment of the effluent at the firm consists of two homogenization and aeration ponds that minimize peak loads on the landfill, reduce organic matter, and reduce temperature from 60 °C to 25–35 °C.

Samples were taken directly from the second homogenization pond and stored at 4 °C temperature.

2.2. Chemicals for pH adjustment

Concentrated reagent-grade H_2SO_4 and NaOH solutions (Panreac) were used for pH adjustment. All solutions were prepared with deionised water prepared using a Millipore Milli-Q system.

2.3. Fenton reagent

The hydroxyl radical, $\cdot OH$, was generated *in situ* by adding the following reagents in aqueous media: hydrogen peroxide, H_2O_2, Panreac, 33% w/v and ferrous sulphate, $FeSO_4 \cdot 7H_2O$, Merck, 99.5%.

2.4. Chemical reactor

Fenton oxidation was carried out using a cylindrical Pyrex thermostatic cell of 2 L capacity, equipped with a magnetic stirrer to provide good mixing with the defined Fenton reagent inside the reactor. The operating liquid volume was 1.5 L. It was equipped with a jacket to be cooled or heated according to experimental conditions. The reactor was inside a black box which keeps dark conditions for the Fenton reaction.

2.5. SBR set-up and operation conditions

The aerobic biological treatment was carried out by means of a 2 L bench-scale Sequencing Batch Reactor (SBR), equipped with magnetic stirring and air diffusers previously cleaned in a gas trap. The operating liquid volume was 1.5 L and Hydraulic Retention Time (HRT) = 1 day. Temperature was maintained under room conditions (25 °C), while keeping the concentration of dissolved oxygen (DO, mg L^{-1} O_2) not lower than 3 mg L^{-1}. Fresh activated sludge biomass was used as inoculum.

The strategy in the SBR was as follows: The bioreactor was fed with the required sample volume during the filling stage. At the end of the aeration–reaction period, the agitation and the airflow were switched off to allow settling the activated sludge for 1 h. Next, the corresponding volume of treated solution was decanted from the supernatant during the draw step, according to the defined HRT. Finally, the reactor was fed with the same volume of fresh solution and the aeration–agitation turned again. This process was repeated cycle by cycle as many times as necessary to allow biomass acclimation and to obtain repetitive results.

The pH of solution was adjusted between 6.5 and 7.5. Suitable proportions of essential biological nutrients ($MgSO_4$, $CaCl_2$, NH_4Cl and NaH_2PO_4 buffer at pH 7) were also added to the solution [27].

2.6. Chemical assays

COD (mg L^{-1} O_2) was measured using the closed-reflux colorimetric method [27] with a HACH DR/2000 spectrophotometer.

H_2O_2 consumption was measured according to the vanadate spectrophotometric method [28]. Residual H_2O_2 was removed with the precise amount of sulphite [29]. Any remaining sulphite was removed by bubbling O_2.

The UV/vis–absorption spectra were recorded by using a Shimatzu UV-2450 double beam spectrophotometer in the 200–700 nm range and 10-mm light path cells.

Absorbance at 254 nm was taken as aromatic content in the sample [21].

Colour index was determined according to [30]. Prior to analysis, samples were filtered through 0.45 μm pore size filter (Scheleicher & Schuell, FP 30/0.45 CA-S).

Fe ion was determined according to spectrophotometric phenantroline method [31].

TOC was determined with a Shimadzu TOC-VCSH analyser with a solution of potassium phthalate as standard of calibration.