Journal of Environmental Chemical Engineering 2 (2014) 1027–1039

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Synthetic textile dyeing wastewater treatment by integration of advanced oxidation and biological processes – Performance analysis with costs reduction

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ARTICLE INFO

Article history:
Received 4 February 2014
Accepted 25 March 2014

Keywords:
Textile dyeing wastewaters
Fenton's oxidation
SBR
Economic analysis

ABSTRACT

Color and organic matter removals from acrylic, cotton and polyester dyeing wastewaters were evaluated by biological oxidation in a sequential batch reactor (SBR) and by integration of Fenton's reaction with SBR. Raw and chemically oxidized pre-treated wastewaters were fed into the biological reactor during 10 cycles (i.e., up to pseudo-steady state conditions). Because the biological degradation did not allow obtaining effluents complying with the discharge limits, neither did the chemical oxidation per se, coupling the SBR after chemical oxidation was required. In the integrated chemical-biological process a new strategy was applied in the optimization of Fenton's oxidation, consisting in the application of the optimum doses of Fe(II) and H_2O_2 (for biodegradability enhancement and maximization of color and DOC removals), but with the simultaneous objective of minimizing the operating costs. The integration of Fenton's oxidation with a downstream SBR provides much better removal of organic matter (88–98% for COD, 83–95% for BOD_5 and 91–98% for DOC, values depending on the particular textile effluent being used) and color (>99%) than the biological or chemical treatment alone could do. Besides, such an integrated treatment allows treated wastewaters to meet the discharge limits with a reduction of the operating costs, in the range 24–39% comparatively to Fenton's oxidation alone.

Introduction

Negative environmental impacts are often associated with the textile dyeing industry, mainly due to the discharge of wastewaters, which impair the aquatic environment quality by changing its color and creating conditions for eutrophication, low reoxygenation and a decrease in the solar light penetration [1]. Considering the growing awareness and concern about the negative effects on the environment generated by the discharge of industrial wastewaters, increasingly restrictive legislation regarding the concentrations of pollutants in the effluents has been approved. Therefore, it is necessary to develop and implement treatment technologies more efficient and also economically viable or at least attractive. In the present study, the treatability of acrylic, cotton and polyester dyeing wastewaters by a biological aerobic process (SBR – sequential batch reactor) and a combined process (Fenton's oxidation followed by SBR) was evaluated. While in principle the biological process is economically far more attractive, when used alone it might not be efficient enough, reason integration with other processes has been envisaged by several authors [2].

The Fenton's reaction is based on the decomposition of hydrogen peroxide catalyzed by ferrous iron (Eq. (1)), in acid medium, generating highly reactive species such as $HO^{\bullet}$ radicals, without requiring high pressure and temperature; such features make the process easily applicable and attractive [3]. The hydroxyl radical oxidizes the dyes and other organics (cf. Eq. (3)) present in the wastewaters in accordance with the following simplified reaction scheme [4]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-}, \quad k_1 = 76\ \mathrm{L/(mol\ s)} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+}, \quad k_2 = 0.01 - 0.02\ \mathrm{L/(mol\,s)} \tag{2}$$

$$HO^{\cdot} + RH \rightarrow H_2O + \text{intermediates} \tag{3}$$

Then, the intermediates may suffer further oxidation by the $HO^{\bullet}$ species, hopefully till carbon dioxide, which would represent complete mineralization. In this simplified mechanism, Eq. (2) refers to catalyst regeneration in the redox process.

The textile effluent to treat is very often first subjected to Fenton's oxidation to degrade part of the organic matter, while removing completely the color and increasing the biodegradability and/or reducing the toxicity, which allows a subsequent treatment by a biological process [2]. In the sequential batch reactor aerobic bacteria are used, as in

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2213-3437/$ - see front matter © 2014 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.jece.2014.03.019

Table 1
Chemicals present in each effluent, their doses used and rejections by the fibers, and estimated concentrations in the polyester, acrylic or cotton synthetic effluents.

Reagent	Function	Chemical characteristic	Dyeing stage use	Dyeing stage concentration	Rejection[a]	Concentration in the final effluent
Polyester effluent						
Adranol NL	Anti-oil	–	Fiber preparation	1 g/L	100%	0.33 g/L
Antibacol R	Anti-crease	–	Fiber preparation	1 g/L	100%	0.33 g/L
Trissodic phosphate	Electrolyte	Salt	Fiber preparation	1 g/L	90%	0.30 g/L
Sera Gal PLP	Equalizing/ dispersant	Alkyl polyglycol ether solution	Dyeing	0.5 g/L	100%	0.17 g/L
Antibacol R	Anti-crease	–	Dyeing	1 g/L	100%	0.33 g/L
Ammonium sulfate	Electrolyte	Salt	Dyeing	2 g/L	90%	0.60 g/L
Acetic acid	Acid generation	Acid	Dyeing	0.5 g/L	100%	0.17 g/L
Dianix blue KFBL	Dyeing	Anthraquinone dye	Dyeing	0.71% (w dye/w fiber)	5%	0.012 g/L
Dianix Orange K3G	Dyeing	Azo dye	Dyeing	1.2% (w dye/w fiber)	5%	0.02 g/L
Sodium hydroxide 32% (w/v)	Alkaline system	Base	Washing	3 g/L	100%	1.0 g/L
Sodium hydrosulfite	Reducer system	Reducer	Washing	3 g/L	90%	0.90 g/L
Acrylic effluent						
Sera con N-VS	Acid generator	Carboxylic acid ester solution	Dyeing	0.4 mL/L	100%	0.13 mL/L
Sera sperse M-IW	Dispersant	Alkyl polyglycol ether solution	Dyeing	0.5 g/L	100%	0.17 g/L
Sera tard A-AS	Retarder	N-alkyl-N, N-dimethylbenzylammonium	Dyeing	1 g/L	100%	0.33 g/L
Sodium sulfate	Electrolyte	Salt	Dyeing	3 g/L	90%	0.9 g/L
Sera lube M-CF	Anti-crease/ lubricant	Polymeric amides solution	Dyeing	2 g/L	100%	0.67 g/L
Astrazon blue FGGL 300% 03	Dyeing	Azo dye	Dyeing	1.5% (w dye/w fiber)	5%	0.008 g/L
Cotton effluent						
Mouillant BG/JT	Anti-oil	Composition based in aliphatic ethoxylates	Fiber preparation	0.7 mL/L	90%	0.09 mL/L
Anticassure BG/BD	Anti-crease	Acryamide aqueous solution	Fiber preparation	0.5 mL/L	90%	0.06 mL/L
Sodium hydroxyl 50% (w/v)	Alkaline system	Base	Fiber preparation	4 mL/L	100%	0.57 mL/L
Hydrogen peroxide 200 vol.	Oxidizing the dye	Oxidant reagent	Fiber preparation	1.5 mL/L	85%	0.18 mL/L
Acetic acid	Acid generator	Acid	Fiber preparation	0.8 mL/L	100%	0.11 mL/L
Zerox	Hydrogen peroxide neutralizer	Catalase	Fiber preparation	0.6 mL/L	90%	0.08 mL/L
Enzyme BG/FB	Bleaching	Fungal cellulase	Fiber preparation	0.4 mL/L	90%	0.05 mL/L
Sequion M150	Water corrector	Composed by phosphanates/ carboxylates	Dyeing	1 mL/L	100%	0.14 mL/L
Sodium chloride	Electrolyte	Electrolyte	Dyeing	9 g/L	90%	1.16 g/L
Sodium carbonate	Alkaline system	Base	Dyeing	20 g/L	90%	2.6 g/L
Procion yellow H-EXL gran	Dyeing	Azo dye	Dyeing	0.45% (w dye/w fiber)	10%	0.006 g/L
Procion Deep Red H-EXL gran	Dyeing	Azo dye	Dyeing	2.8% (w dye/w fiber)	10%	0.04 g/L
Sandozin NRW LIQ alt C	Detergent	Polyethylene glycol isotridecyl ether	Washing	0.9 mL/L	90%	0.12 mL/L

[a]Percentage of dyes and auxiliary products not fixed by the fibers.

the conventional activated sludge systems, to degrade the biodegradable fraction of the organic matter into new compounds, cells, salts and gases. The SBR operates in discontinuous mode with five sequential stages in each treatment cycle (influent feeding, reaction, sedimentation, discharge of the clarified effluent and sludge purge and idle). This process presents some advantages, namely simplicity and flexibility, low cost, and increased resistance to fluctuations in the influent, compared to other conventional biological treatments [5]. Additionally, equalization, reaction and clarification occur in the same reactor [6].

SBRs have been successfully employed for the removal of nutrients present in domestic wastewaters [7] and pollutants from industrial effluents, namely dairy [8], paper mill [9], piggery [10], textile wastewaters [11–17] and landfill leachate [18,19]. The combination of chemical oxidation like Fenton's reagent and SBR has also been reported in the literature as regards the removal of dyes in aqueous solution [20,21] and the improvement of textile effluents treatment [22–24]. Additionally one can find studies comparing electrocoagulation, coagulation and Fenton's oxidation [25] or studies focused on the combination of chemical oxidation with biological degradation in aerobic, anoxic and anaerobic conditions [26].

In this work, a treatability study of synthetic acrylic, cotton and polyester dyeing wastewaters (representing typical dyeing industrial effluents) was done, either using an SBR or an integrated process combining the Fenton's reaction with an SBR process. The main purpose of this research was to evaluate the possibility of reducing the chemicals consumption in the Fenton's reaction to make the pre-treated effluents able to be fed to a subsequent biological treatment, while obtaining final effluents that accomplish the maximum allowable limits imposed by legislation for discharge into the aquatic environment, at