

Textile Dyeing Wastewater Treatment by Coupling Fenton's Reagent and Aerobic Sequencing Batch Reactor Processes

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Abstract

The oxidation of organic compounds and color removal of a synthetic dyeing effluent when treated with a combination of Fenton's Reagent and biological oxidation in a sequencing batch reactor was evaluated in this work. A central composite design approach was used to find the best conditions of temperature, hydrogen peroxide and ferrous ion concentrations that maximize color and dissolved organic carbon removal and increase the biodegradability of the effluent submitted Fenton's oxidation. Additional studies on the biological oxidation of the raw and previously treated by Fenton oxidation effluent had been performed up to steady-state. Higher efficiencies were obtained when coupling a pre-oxidation stage with Fenton's Reagent to the biological process, but conditions employed in the first process must be carefully selected. In particular, the chemical oxidation was focused in conditions that maximize the increase in the biodegradability, allowing achieving overall removals of 90.2, 97.3 and 96.1 % for DOC, BOD₅ and color, respectively.

Keywords: Fenton oxidation, Sequencing batch reactor, Experimental design, Textile effluent treatment.

Introduction

The main pollutants in textile wastewater originate from the dyeing and finishing steps [1]. The wastewater generated is characterized by presenting low metal and suspended solid contents, high temperature, alkaline pH in most situations, high chemical oxygen demand and strong color [2]. Therefore, it is necessary to find effective methods for treating such wastewater, both in terms of water recycling and need for nature preservation.

One of the most promising alternatives for textile wastewater treatment is based on the application of advanced oxidation processes - AOP, as a way to reduce the levels of contamination by the destruction of organic pollutants and their conversion to carbon dioxide and water [3]. The AOP used in this work is the Fenton's Reagent. The oxidation is based on ferrous ion and hydrogen peroxide, and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H₂O₂, particularly through the following reaction [4]:



Recently, studies on the combination of advanced chemical oxidation and biological treatment have been developed. The effluent is first submitted to chemical oxidation to partially degrade the organics, generating an uncolored effluent (in the case of dye-containing wastewater), more biodegradable and less toxic that is easily assimilated by the biomass in the biological process. This way, the economical cost and the environmental impact, frequently associated to the chemical processes, are substantially minimized [5]. The biological treatment may be carried out, for instance, in a sequencing batch reactor (SBR), which presents a great simplicity and flexibility of operation, as well as low cost when compared with other possible configurations [6].

In this work, the efficiency of an integrated chemical-biological process (i.e., Fenton's Reagent followed by SBR oxidation) was evaluated, in terms of color and organic matter removal, using a cotton dyeing synthetic effluent.

Material and Methods

Synthetic wastewater

A cotton dyeing synthetic wastewater was used for this study, which was prepared in accordance with the information provided by the dye-house Erfoc - Acabamentos Têxteis S.A. (Famalicão, Portugal). Basically, the concentrations of all the auxiliary products and dyes was determined taking into account the amounts used in the dyeing and rinsing baths and the percentages retained by the cotton fibers. The main characteristics of the wastewater are summarized in Table 1.

Table 1 – Main characteristics of the dyeing cotton synthetic effluent.

Parameter	Value
pH	10.9
Absorbance at 520 nm	0.596
Biochemical oxygen demand (BOD ₅) (mg O ₂ /L)	239 - 247
Dissolved organic carbon (DOC) (mg C/L)	140 - 161
Specific oxygen uptake rate (k') (μg O ₂ /mg C . min)	0.25
Total suspended solid (TSS) (mg/L)	50 - 102
Total phosphorus (mg P/L)	0.9 - 1.2
Total nitrogen (mg N/L)	3.5 - 6.0

Fenton oxidation

The Fenton oxidation was carried out in a closed jacketed batch reactor (1 L capacity) with constant mixing by using a magnetic stirrer in which the temperature was kept constant (thermostatic bath Huber, model Polystat CC1). After stabilizing the temperature of the wastewater, the pH was adjusted to 3.5 with H₂SO₄ 95-97% (Fluka) or NaOH 6N (Merck, analytical grade). Reaction was carried out at pH 3.5 because several other studies pointed for maximal removal at this pH value [e.g., 7]. Then, the iron catalyst (FeSO₄·7H₂O - Panreac) was added and the process initiated with the insertion of hydrogen peroxide (H₂O₂ 30%, Riedel-of Haën) into the reaction mixture. Periodically, samples were taken from the reactor for analysis and the remaining H₂O₂ eliminated by adding a small, but in excess, amount of sodium sulfite p.a. (Riedel-of Haën), in order to stop the reaction.

SBR operation

The SBR was operated at constant temperature (25 ± 0.5 °C) by recirculation of water from a thermostatic bath (Isco GTR 90) and with 11.5 hours per cycle (1.1 h feeding, 6 h reaction, 3.5 h sedimentation and 0.9 h discharge). Operation proceeded during 15 cycles, i.e. up to steady-state conditions, although after 7 cycles a pseudo-steady state has already been reached. In the first cycle, the synthetic wastewater with pH previously adjusted with H₃PO₄ 85% (Pronalab) to 7.0 ± 1.0 was gradually added to 2.5 L of acclimatized sludge (VSS = 5 g/L) proceeding from the aeration tank of Rabada WWTP (Santo Tirso - Portugal) to make up a final volume of 5.0 L. In the subsequent cycles the reactor was fed with 2.5 L of wastewater to compensate the discharge of the treated effluent. During the reaction stage, the mixed liquor was kept under agitation (rotating speed = 150 rpm) and the dissolved oxygen content was maintained at 3.0 ± 0.1 mgO₂/L by controlled aeration using air diffusers. Internal pH was controlled in the range 7.3-7.4 by adding H₂SO₄ 1M and NaOH 1M. At the end of each cycle the discarded effluent was analysed for several parameters. In the wastewater previously treated by Fenton's oxidation, the elimination of the residual hydrogen peroxide by the addition of sodium sulfite was firstly performed and then the pH was adjusted to 7 with NaOH 6N. After sedimentation, the supernatant was fed to the SBR and the reactor operation proceeded in the above-mentioned conditions.

Analytical Methods

The biodegradability of raw and treated effluent was evaluated from the specific oxygen uptake rate (k') at room temperature. Samples were inoculated with biomass from the aeration tank of Rabada WWTP, and then the dissolved oxygen concentration measured using a biological oxygen monitor (YSI Model 5300 B) for 30 min. The k' values were calculated as the ratio between the oxygen concentration decay rate and the amount of organic carbon initially present in the sample. Color removal was evaluated at $\lambda_{\max} = 520$ nm (UV-Vis Pye Unicam spectrophotometer, Model Heyios α). Other routine analyses were conducted according to Standard Methods [8]. DOC was measured in a TC/TOC analyzer (Shimadzu 5000A analyser).

Results and Discussion

Fenton's oxidation

A central composite design in combination with Response Surface Methodology was carried out for the ranges of temperature and concentrations of H_2O_2 and Fe^{2+} shown in Table 2. The values of the variables were based on results from a previous work [7] and other preliminary runs (data not shown). Besides, they take also into account situations of practical interest (e.g., temperatures of textile effluents).

Table 2 - Levels of the parameters selected for the experimental design.

Parameter	Level				
	-1.682	-1	0	+1	+1.682
T (°C)	6.4	20	40	60	73.6
[H_2O_2] (mM)	107	147	206	265	305
[Fe^{2+}] (mM)	0.55	2.68	5.80	8.92	11.05

The Yates algorithmic [9] was then applied to define the conditions and number of experiments to be done (see Table 3). In Table 3 are also shown the responses considered in each run: DOC and color removal and biodegradability (specific oxygen uptake rate, k'). All these values were obtained after 30 min, because differences between 30 and 120 min of reaction are not significant (data not shown). Subsequently, the coefficients associated with the significant effects and interactions of each variable in a quadratic model were determined (by the least squares fitting method, software JMP 5.0.1 being used), just retaining the coefficients statistically significant for a level of significance $\alpha = 0.05$, as indicated by the Student's t -test [10].

The semi-empirical quadratic equations obtained (Eqs. 2-4) allow concluding what are the variables and interactions that affect a given response. For instance, for the DOC removal the temperature (x_1) and the square of Fe^{2+} concentration (x_3^2) are those with statistical meaning (cf. Eq. 2), while the biodegradability, expressed as k' , depends on the values of x_1 , x_2 and x_3 .

$$\text{DOC removal (\%)} = 45.47 + 9.96 \left(\frac{T - 40}{20} \right) - 3.55 \left(\frac{[\text{Fe}^{2+}] - 5.80}{3.12} \right)^2 \quad (2)$$

$$\text{Colour removal (\%)} = 97.73 + 23.18 \left(\frac{T - 40}{20} \right) + 6.84 \left(\frac{[\text{Fe}^{2+}] - 5.80}{3.12} \right) - 13.22 \left(\frac{T - 40}{20} \right)^2 - 7.52 \left(\frac{[\text{Fe}^{2+}] - 5.80}{3.12} \right)^2 \quad (3)$$

$$k' (\mu\text{g O}_2 / \text{mg c min}) = 3.04 + 0.92 \left(\frac{T - 40}{20} \right) + 1.02 \left(\frac{[\text{H}_2\text{O}_2] - 206}{59} \right) + 1.23 \left(\frac{[\text{Fe}^{2+}] - 5.80}{3.12} \right) \quad (4)$$

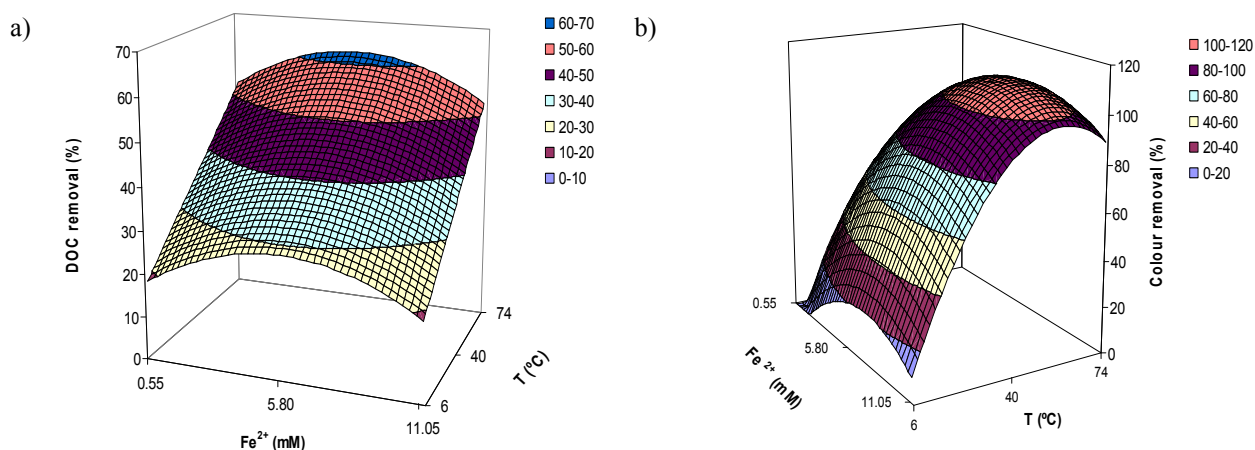
Table 3 – Yates algorithm and responses obtained.

Run	T (x ₁)	[H ₂ O ₂] (x ₂)	[Fe ²⁺] (x ₃)	DOC removal (%)	Color removal (%)	k' (µg O ₂ /mg C. min)
1	-1	-1	-1	31.0	16.3	0.2
2	+1	-1	-1	50.1	96.8	2.2
3	-1	+1	-1	31.2	49.2	1.4
4	+1	+1	-1	60.3	91.2	1.7
5	-1	-1	+1	29.6	53.6	0.7
6	+1	-1	+1	54.6	96.2	4.6
7	-1	+1	+1	32.5	52.7	3.0
8	+1	+1	+1	54.8	93.2	6.0
9	0	0	0	45.1	97.1	3.0
10	0	0	0	41.9	97.0	2.8
11	0	0	0	48.7	97.2	3.1
E1	-1.682	0	0	37.7	31.1	1.6
E2	+1.682	0	0	61.9	97.0	3.7
E3	0	-1.682	0	52.8	93.7	0.6
E4	0	+1.682	0	53.9	76.8	6.1
E5	0	0	-1.682	37.5	65.0	0.8
E6	0	0	+1.682	37.9	95.3	5.5

These equations allow obtaining 3D representations, i.e. response surfaces that more clearly evidence the effects of the variables in the responses. For example, the effects of the relevant variables on DOC removal are shown in Fig. 1a. Maximum performance occurs for [Fe²⁺] = 5.80 mM. At higher concentrations the Fe species in excess might react with hydroxyl radicals through other parallel reactions, namely the following one, detrimentally affecting the overall performance [11]:



In what concerns the effect of temperature, Fig. 1a shows that it presents a positive effect on the mineralization of organic matter.

Figure 1 - Variation of a) DOC removal and b) color removal with [Fe²⁺] and T as predicted by Eqs. 2 and 3.

For color removal, optimum conditions occur at $T = 57.3\text{ }^{\circ}\text{C}$ and $[\text{Fe}^{2+}] = 7.22\text{ mM}$ (Fig. 1b). The existence of an optimum temperature value might be due to the thermal decomposition of hydrogen peroxide at high temperatures [12]:



However, one could expect to notice this effect also in the DOC removal, which is not the case. A possible explanation is the difficulty of the polynomial fit in a wide range of response data (color removals in the range 16.3-97.2%), yielding inclusively predictions slightly above 100%. The biodegradability increases with the increase of the three variables in the study range (see Eq. 4). Optimal conditions are therefore $T = 73.6^{\circ}\text{C}$, $[\text{Fe}^{2+}] = 11.05\text{ mM}$ and $[\text{H}_2\text{O}_2] = 305\text{ mM}$.

Biological treatment in a sequencing batch reactor (SBR)

Afterwards, the study was focused on the biological oxidation, using a SBR, of raw (1st run) and previously submitted to Fenton oxidation effluents. The SBR was thus fed with the partially oxidized effluent from the Fenton's process. Conditions selected for the chemical oxidation were those that maximize the color removal (with $[\text{H}_2\text{O}_2] = 107\text{ mM}$) - 2nd run - or maximize the increase in the biodegradability - 3rd run. The reactor was operated up to steady-state (15 cycles). Even so, the results obtained indicated that in the 1st run (SBR alone) only 63.9% of color removal was reached, which can still be in part attributed to the dyes adsorption into the biomass flocs. The organic matter removal is also low (36.0% of BOD_5 and 28.9% of DOC), which can be explained by the presence of non-biodegradable compounds. In the 2nd and 3rd runs the Fenton pre-oxidation alone was responsible for a higher color decrease (more than 95% in both cases - cf. Table 4)), as well as for a higher organic load removal. In terms of overall performance, the combined process revealed to be much more effective, particularly under conditions that favor the biodegradability increase in the chemical oxidation (cf. Table 4, 3rd run). As expected, higher efficiencies are obtained when coupling the Fenton's Reagent to the biological process, but conditions employed in the first process must be carefully selected so that maximum degradation of organic matter can be achieved.

Table 4 – Values of DOC, BOD_5 and color removals in each stage of the integrated process.

Parameter	Efficiencies in the 2 nd experiment			Efficiencies in the 3 rd experiment		
	Fenton stage (%)	SBR stage (%)	Overall removal efficiency (%)	Fenton stage (%)	SBR stage (%)	Overall removal efficiency (%)
DOC	56.8	31.2	70.3	58.6	76.3	90.2
BOD_5	63.7	49.4	81.6	72.9	85.5	96.1
Color	99.0	*	99.0	95.9	35.0	97.3

* Absorbance increases induced by the inoculum addition (thus global efficiency is computed based on Fenton's efficiency).

Conclusions

A combination of Fenton's reagent with biological degradation in a SBR has been applied to a synthetic textile effluent with the purpose of oxidizing the organic matter and removing color. The combination of the two treatment processes provides better performances than any of the treatment methods alone. However, if the pre-treatment is applied to the effluent in conditions that maximize the biodegradability increase, the final results are further improved.

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