Decontamination of an industrial cotton dyeing wastewater by chemical and biological processes

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Abstract

The organic matter mineralization, decolorization, biodegradability improvement and toxicity reduction of an industrial cotton dyeing wastewater was investigated. Different treatment approaches, including single and integrated processes, were studied, namely: coagulation/flocculation per se and its combination with Fenton’s oxidation (Approach 1), Fenton’s process alone (Approach 2) and its integration with either coagulation/flocculation (Approach 3) or biological oxidation in a sequential batch reactor (Approach 4).

All approaches provided a wastewater that meets the Portuguese legislated discharge limits, however Approaches 1 and 3 require smaller operating costs (1.0 €/m³) with global removal efficiencies for these two strategies of 70.8% for COD (Chemical Oxygen Demand), 66.1% for DOC (Dissolved Organic Carbon) and 47.6% for BOD₅ (Biological Oxygen Demand) in Approach 1 and 69.2% for COD, 60.4% for BOD and 72.4% for DOC in Approach 3, along with almost complete color removal in both strategies and toxicity reduction (0.0% inhibition of *Vibrio fischeri* in the effluent from Approach 1). A slight increase of the effluent biodegradability was also observed (BOD₅:COD increased from 0.26 to 0.33-0.46, and SOUR (specific oxygen uptake rate) increased from 8.85 to 9.3-11.3 mgO₂/(gVSS h)), depending on the treatment approach. The use of a cheap process (coagulation/flocculation) as pre-treatment allowed reducing the amount of reagents needed in the Fenton process, making the latter treatment slightly cheaper, and thereby reducing the overall costs.

Keywords: Industrial textile dyeing wastewater; Coagulation/Flocculation; Fenton’s reagent; SBR; Economic analysis.
Introduction

Textile industries consume large amounts of water in the dyeing process and generate highly polluted effluents containing dyes, salts and other organic compounds. When these pollutants come into contact with the environment, many negative effects often occur such as a reduction of the re-oxygenation capacity and a decrease in the sunlight penetration, thereby upsetting the biological activity of the aquatic life. In order to minimize these impacts it is necessary to implement efficient and effective treatments of the wastewater before discharge.

Many studies reported in literature, focused on the treatment of textile wastewaters, show results from the application of physical-chemical processes (such as coagulation/flocculation, adsorption and membrane separation), chemical oxidation, or biological processes. Among all these techniques, coagulation/flocculation, advanced chemical oxidation with Fenton’s reagent and biological degradation have been widely studied. The first technique has been used to remove dyes, colloidal organic compounds and suspended solids through the addition of coagulants (usually iron or aluminum salts) and flocculants (polymers) that promote the destabilization of the colloids and their aggregation. The removal of the particles formed is achieved through filtration or sedimentation. The Fenton’s process allows the oxidation of dyes and organic compounds, while reducing the toxicity and increasing the biodegradability. This process is based on the generation of hydroxyl radicals (with very high oxidation potential) by the decomposition of hydrogen peroxide catalyzed by ferrous ion in acid medium (eq. 1), the catalyst being regenerated by reaction between Fe^{3+} and H_{2}O_{2} (eq. 2). Finally, the hydroxyl radicals oxidize organic compounds and dyes (eq. 3), the complex mechanism being shortly summarized by the following reactions:

\[ \text{Fe}^{2+} + \text{H}_{2}\text{O}_{2} \rightarrow \text{Fe}^{3+} + \text{HO}^{\cdot} + \text{OH}^{-} \]  
\[ \text{Fe}^{3+} + \text{H}_{2}\text{O}_{2} \rightarrow \text{Fe}^{2+} + \text{HO}_{2}^{\cdot} + \text{H}^{+} \]  
\[ \text{HO}^{\cdot} + \text{RH} \rightarrow \text{H}_{2}\text{O} + \text{intermediates} \]  

Of course, the intermediates can be also oxidized and ultimately mineralized. The biological treatment in sequential batch reactor (SBR) is a variant of the conventional activated sludge system operating in 5 stages per cycle (influent feeding, reaction, sedimentation, discharge of the clarified effluent, sludge purge and idle). The SBR presents some advantages comparatively to the conventional biological treatment,
namely flexibility and simplicity, low cost and increased resistance to fluctuations in influent feeding.\textsuperscript{23} Additionally, equalization, reaction and clarification occur in the same reactor.\textsuperscript{24} This work aimed at evaluating several approaches for treating a real cotton dyeing wastewater (see Figure 1) taking into account the characteristics of the effluent as well as the results of a previous study focused on the treatability of a simulated cotton dyeing effluent.\textsuperscript{25} In Approach 1 coagulation/flocculation was combined with Fenton’s reaction (as coagulation/flocculation per se is not effective to comply with legislated discharge standards, as detailed below). In Approach 2 only Fenton’s oxidation was applied and in Approaches 3 and 4 the wastewater was pre-treated by Fenton’s oxidation and then treated by coagulation/flocculation and a biological process (SBR), respectively. In all situations it was intended to obtain the lowest operating cost and an effluent that meets the discharge limits imposed by the Portuguese legislation for textile effluents. Therefore, to reduce costs, part of the catalyst used in the Fenton’s reaction of Approach 1 was the residual dissolved iron resulting from coagulation/flocculation (this methodology has been already applied to industrial wastewaters other than textile dyeing ones).\textsuperscript{26-28} In the same way, in Approach 3 the coagulant used was the residual iron resulting from the Fenton’s reaction; however, in this case the final effluent clearly complied with legislated standards, and so the Fenton’s stage was also performed with doses of chemicals reduced to 3/4 and 1/2 of the optimum value found in Approach 2 (this methodology has not yet been described in the literature). In Approach 4 the doses of reagents used in the Fenton’s oxidation were also reduced, as described above, and the resulting effluent was subjected to a biological process. It has been reported in literature \textsuperscript{29} the need of using oxidative processes as a pre-treatment step of industrial textile wastewaters with the aim of generating a biodegradable effluent without extensive testing the behavior of the biological process. Recent works already integrated both processes, particularly combining Fenton’s oxidation and biological degradation in SBR.\textsuperscript{30-34} The ultimate choice of the technology to adopt should take also into account economic indicators, and so a cost analysis was performed for each treatment strategy, as detailed in the next section. In this work, all possible treatment strategies were applied for the first time to an industrial wastewater, taking into account current discharge limits and the results of a previous study focused on the treatability of a simulated effluent, comparison being made based on processes performance and associated operating costs (chemicals and energy consumption).

2. Operating Costs

To select the better integration of stages for wastewater treatment, but ensuring that the generated effluent meets the discharge standards, the operating costs associated to the consumption of chemicals and energy were assessed. However, to calculate the energy costs only the energy consumed in agitation (power required = 0.61 W) and air insufflated (power = 4.5 W) in the SBR stage was considered because the costs
regarding stirring in coagulation/flocculation (0.002 €/m$^3$) and Fenton oxidation ($\approx 4 \times 10^{-5}$ €/m$^3$) are negligible. The costs concerning the acidification in the Fenton process and further neutralization were also taken into account (0.06 €/m$^3$ and 0.11 €/m$^3$, respectively). The cost of the energy required to heat the effluent during the Fenton process was discarded having in mind the high temperature of dyeing wastewaters (50-70 °C or even higher). Finally, the costs of treatment and disposal of the chemical sludge generated in coagulation/flocculation and Fenton processes are highly variable and so were not considered.

In the economic analysis the costs of main chemicals were those given by Quimitécnica S.A. and Rivaz Química S.A.: H$_2$O$_2$ (49.5% w/v, density at 25 °C = 1.2 g/cm$^3$) – 365 €/ton; FeSO$_4$•7H$_2$O (93 wt.% of purity) – 233.7 €/ton; Magnafloc 155 – 3850 €/ton; H$_2$SO$_4$ (96% w/v, density = 1.84 kg/dm$^3$) – 140 €/ton; NaOH (30% w/w, density = 1.33 kg/dm$^3$) - 185 €/ton. For energy it was considered the average value of 0.10 €/kWh.

The operating cost for the coagulation/flocculation step is the sum of costs of Fe$^{2+}$ (eq. 4) and Magnafloc 155 (eq. 5), while for Fenton’s reaction is the sum of costs of Fe$^{2+}$ used (eq. 4), H$_2$O$_2$ consumed (eq.6), as well as the acid and base required for acidification and subsequent neutralization, respectively; finally, for SBR is the cost of energy (eq. 7) only.

$$\text{Cost}_{\text{Fe}^{2+}} = \frac{\text{Price}_{\text{FeSO}_4\cdot 7\text{H}_2\text{O}} \left( \frac{\text{€}}{\text{ton}} \right) \cdot \left[ \text{Fe}^{2+} \right] \cdot 10^{-6} \left( \frac{\text{ton}}{\text{m}^3} \right) \cdot \frac{\text{MM}_{\text{FeSO}_4\cdot 7\text{H}_2\text{O}}}{\text{MM}_{\text{Fe}^{2+}}} \cdot \% \text{of purity}}{100}$$

(4)

$$\text{Cost}_{\text{Magnafloc155}} = \text{Price}_{\text{Magnafloc155}} \left( \frac{\text{€}}{\text{ton}} \right) \cdot \left[ \text{Magnafloc155} \right] \cdot 10^{-6} \left( \frac{\text{ton}}{\text{m}^3} \right)$$

(5)

$$\text{Cost}_{\text{H}_2\text{O}_2} = \frac{\text{Price}_{\text{H}_2\text{O}_2} \left( \frac{\text{€}}{\text{ton}} \right) \cdot \left[ \text{H}_2\text{O}_2 \right] \cdot 10^{-3} \left( \frac{\text{ton}}{\text{m}^3} \right) \cdot \text{\rho}_{\text{H}_2\text{O}_2} \left( \frac{\text{kg}}{\text{L}} \right) \cdot \% \text{H}_2\text{O}_2 \cdot (\text{kg/L})}{100}$$

(6)

$$\text{Cost}_{\text{energy}} = \frac{\left( \text{Power}_{\text{airinsufflated}} + \text{Power required agitation} \right) \cdot 10^{-3} (\text{kW}) \cdot \text{Price}_{\text{energy}} (\text{kWh}) \cdot \text{time}_{\text{aeration}} (\text{h})}{\text{Volume}_{\text{treated effluent}} (\text{m}^3)}$$

(7)

In the previous equations, $[i]$ represents the concentration of species $i$ (in g/L for H$_2$O$_2$ and mg/L for Fe$^{2+}$), MM$_i$ stands for its molar mass (in g/mol) and the power required for agitation is expressed in W.

The total operating costs for the integrated processes are calculated by the sum of costs associated with each process involved.
3. Materials and Methods

3.1. Textile Dyeing Wastewater

The industrial wastewater used in this study was the cotton dyeing effluent coming from the equalization tank of the dye-house Têxtil Luís Simões (Manhente – Barcelos, Portugal). The dyes used in the dyeing bath are reactive ones but no information was provided about the specific dyes present in the tank.

The main wastewater characteristics are presented in Table 1; the raw effluent presents black color, reasonable concentration of organic compounds (as inferred from the DOC and COD values), low biodegradability (BOD$_5$/COD ratio <0.4), and high toxicity to *Vibrio fischeri*. As the wastewater does not comply with any of the legislated discharge standards for pH, COD, BOD$_5$ and color (Ordinance no. 423 of June 25, 1997 – cf. Table 1), an appropriate treatment is required before discharge.

3.2. Experimental Procedure

3.2.1 Coagulation/Flocculation

The coagulation/flocculation experiments were conducted in a *Jar-test* (ISCO, Italy). In all experiments, a sample volume of 500 mL was employed. The pH of wastewater was adjusted and the solution transferred into a beaker. The coagulant (ferrous sulfate) was added under rapid stirring (150 rpm), and the pH readjusted, if necessary (it is worth noting that afterwards it remained constant, i.e. throughout the experiments). After 3 min of rapid mixture the stirring rate was reduced to 20 rpm, the flocculant added (Magnafloc 155) and the agitation proceeded during 15 minutes. After 30 min of sedimentation the supernatant was collected and acidified with HNO$_3$ (68%, from Merck, Germany) to pH < 4 to keep the iron dissolved (so that it could be used as catalyst in Fenton’s reaction).

All coagulation/flocculation experiments were conducted at room temperature (22-24 ºC). All these conditions were set based on preliminary results achieved with a similar synthetic effluent.\(^{35}\)

3.2.2 Fenton’s Reaction

In Fenton’s oxidation runs 500 mL of wastewater pre-treated by coagulation/flocculation (Approach 1) or raw wastewater (Approaches 2, 3 and 4 – cf. Fig. 1) was put into a batch jacketed reactor, connected to a water thermostatic bath (Grant Y6, England) to maintain the temperature inside the reactor at 50 ºC. After temperature stabilization, the pH was adjusted to 3.5 with 2M H$_2$SO$_4$ (from Merck, Germany). These values of temperature and pH were found as the optimal ones for the treatment of cotton dyeing synthetic effluent...
by Fenton’s oxidation after coagulation/flocculation. The catalyst (FeSO₄, 7H₂O, from Merck - Germany) was then added and the reaction started with addition of H₂O₂ 30% (w/v) (Merck, from Germany). During the reaction the solution was constantly stirred by using a magnetic bar and a stir plate (Falc, Italy). Before measuring the DOC of samples taken over time, the homogeneous reaction in the sampling vial was stopped by addition of excess sodium sulfite, which immediately reacts with the remaining hydrogen peroxide. For the other analytical determinations where sulfite interferes, the residual H₂O₂ was eliminated, with simultaneous iron precipitation, by raising the pH to 12.3 through the addition of 10 M NaOH (from Merck) and heating the samples at 80 °C for 10 minutes. Then the effluent was neutralized (to pH ~7.0) with concentrated H₂SO₄, although the samples used for V. fischeri inhibition assessment were neutralized with HCl, as proposed by the analytical methodology. This methodology was also applied to stop the reaction when using the combination of the advanced oxidation with biological treatment (Approach 4).

In Approach 3 the effluent after the oxidation stage was acidified to pH ≈ 1 to keep the iron dissolved for the coagulation/flocculation study, while simultaneously slowing down or inhibiting the Fenton’s reaction; analyses of the effluent were performed immediately.

3.2.3 Biological Oxidation in SBR

The Sequencing Batch Reactor (SBR) is a jacketed cylindrical-conical tank (20 cm internal diameter, 45 cm total height, 30° slope conical bottom, 5.0 L effective working volume – cf. Figure S1 in Supporting Information). Water from a thermostatic bath (Isco GTR 90, Italy) circulates through the jacket to keep the temperature constant (25 °C) inside the reactor. The SBR operated in successive cycles of 12 hours (1 hour for feeding, 6 h of reaction under aeration, 4 h of sedimentation, 0.8 h for discharge and 0.2 h idle), up to 10 cycles. In the first cycle the reactor was fed with 2.5 L of pre-treated wastewater with pH previously adjusted to ~7.0 using 2M H₂SO₄ and 10M NaOH. Then 2.5 L of activated sludge (~ 5 g VSS/L) from the aeration tank of Rabada WWTP (Santo Tirso - Portugal) was added to the reactor. In the subsequent cycles the reactor was fed with 2.5 L of effluent to compensate the amount of treated effluent discharged. During the reaction stage, a mechanical stirrer was employed (stirring rate = 400 rpm) and the dissolved oxygen content was maintained at ~3.0 mgO₂/L by a diffused air aeration system. The values of dissolved oxygen and the duration of each cycle and each cycle stage were established in accordance with literature: 0.05 to 1.1 h for filling, reaction between 6 to 19 h, 1 to 3.5 h for settling, 0.5 to 0.9 h for treated wastewater discharge and 0.05 to 0.5 h for the idle stage. The acquisition of data and the automatic control of the unit, i.e., operation of the peristaltic pumps (Watson-Marlow 502S, England), Burckert valve (Germany) and mechanical stirrer (VWR VOS power
3.3. Analytical Methods

Color was quantified by measuring the absorbance at the wavelength of maximum absorbance (λ_max = 600 nm), using a molecular absorption spectrophotometer (Pye Unicam, model Helios α, Germany). As the absorbance varies with pH, in the treated effluent or samples taken over time, pH values were adjusted to the initial ones before any absorbance measurements.

The specific oxygen uptake rate (k’) was evaluated at 20 ºC and calculated as the ratio between the oxygen concentration decay rate (which was linear in the below-mentioned period) and the volatile suspended solids (VSS) concentration after the addition of the inoculum (700 mg VSS/L).\textsuperscript{43,44} The samples were inoculated with biomass from the activated sludge tank of a WWTP treating textile effluent, and the dissolved oxygen concentration measured for 30 min (using a YSI Model 5300 B biological oxygen monitor, USA). The activity of the activated sludge used in the k’ assessment was checked by using methanol as substrate and the results showed that the biomass was in good status. The evaluation of the effluent biodegradability was complemented by the value of the BOD₅:COD ratio.

The inhibition of Vibrio fischeri test was performed according to standard DIN/EN/ISO 11348-3.\textsuperscript{38} The bacteria were placed in contact with samples at 15 ºC and the bioluminescence measured after a contact time of 5, 15 or 30 minutes in a Microtox model 500 analyzer (England).

Other analytical determinations were carried out according to Standard Methods:\textsuperscript{44} dissolved organic carbon (DOC) was measured in a TC/TOC analyzer (Shimadzu 5000A, from Japan) - Method 5310 D; the biochemical oxygen demand (BOD₅) was determined according to Method 5210 B; the chemical oxygen demand (COD) was assessed by the open reflux method (Method 5220 B); and total phosphorus by Method 4500P - E. Total nitrogen was determined by colorimetry according to Method D992-71 of the ASTM Standards\textsuperscript{45} after previous digestion (Method 4500 - N C); the total suspended solids (TSS) and volatile suspended solids (VSS) were evaluated by gravimetry - Method 2540 B and Method 2540 E, respectively. The alkalinity was evaluated by titration with H₂SO₄ at pH 4.5 (Method 2320 D) while the pH was measured using a selective electrode (Hanna Instruments HI 1230, Italy) and a pH meter (Hanna Instruments HI 8424, Italy). The conductivity at 20 ºC was determined using a conductivity probe (WTW TetraCon 325, Germany) and a conductivity meter (WTW LF538, Germany) - Method 2510 B. Finally, chlorides, nitrates, sulfates and dissolved phosphorus were measured by ion chromatography (Dionex DX 120, from USA) using a Dionex Ionpac AS9-HC 4 mm (10-32) column (from USA). Total dissolved iron was determined by AAS (GBC 932 AB Plus).
All analytical determination were performed in duplicate, and the coefficients of variation were less than 2% for DOC, 6% for BOD₅, 4% for COD and k’, and 5% for the other parameters.

4. Results and Discussion

4.1. Coagulation/Flocculation plus Fenton’s Reaction (Approach 1)

This study started with the application of coagulation/flocculation to the raw industrial wastewater, using ferrous sulfate and Maganafloc 155 as coagulant and flocculant, respectively. The operating conditions used were the optimal ones determined in a prior study on the treatment of a synthetic cotton wastewater: V_{coagulation}=150 \text{ rpm}, t_{coagulation}=3 \text{ min}, [\text{Fe}^{2+}]=200 \text{ mg/L, pH}=9.4, V_{flocculation}=20 \text{ rpm}, t_{flocculation}=15 \text{ min}, [\text{Maganafloc 155}]=0.5 \text{ mg/L}. The characteristics of the wastewater after treatment are presented in Table 1. One can conclude that coagulation/flocculation is very efficient as regards color removal (95.1% - percent removal efficiencies are within brackets in the table), leads to a considerable removal of organic matter (36.9% and 39.4% respectively for COD and DOC) and phosphorus (47.2%), but it is quite inefficient concerning the removal of BOD₅ (17.2%) and nitrogen (1.9%). Moreover, the values of COD and BOD₅ in the final effluent are above the discharge standards imposed by the Portuguese legislation, which makes necessary an additional treatment.

So, for increasing the efficiency of organic matter removal, the effluent from the coagulation/flocculation stage was subjected to Fenton’s oxidation, applying the operating conditions already optimized when treating a synthetic effluent by the same integrated process: T=50 \text{ ºC, pH}=3.5, t=60 \text{ min, } [\text{H}_2\text{O}_2]=500 \text{ mg/L and } [\text{Fe}^{2+}]_{added}=98.3 \text{ mg/L (total iron concentration = 100 mg/L, taking into account that 1.7 mg Fe/L remained from the coagulation/flocculation step). Results included in Table 1 point out that Fenton’s oxidation applied to the pre-treated effluent allowed obtaining COD, BOD₅ and DOC removals of 53.7, 36.7 and 44.1%, respectively, color reduction of 89.3% and smaller decreases in total phosphorus and total nitrogen concentrations (29.7 and 2.7%, respectively).

The global efficiencies for the combined process (coagulation/flocculation plus Fenton’s reaction) are significant for color (99.5%), COD (70.8%), DOC (66.1%) and total phosphorous (62.9%), moderate for BOD₅ (47.6%) and low for total nitrogen (4.5%). Except for BOD₅ the efficiencies reached are similar to those obtained when treating a synthetic cotton dyeing effluent by the same integrated process (61.7, 25.8, 71.2 and 99.8% for COD, BOD₅, DOC and color, respectively). Moreover, the resulting effluent meets the discharge standards (Table 1), and this is reached at a low operating cost (1.0 €/m³), which was calculated taking into account the amounts of chemicals employed in both coagulation/flocculation and Fenton’s steps, as described in section 2, as well as the acidification and subsequent neutralization costs in


the Fenton process. Fenton’s oxidation contributes to the overall cost by about 70%. This puts into evidence the importance of the integrated treatment strategy adopted. A cheaper process (coagulation/flocculation) used as pre-treatment permits reducing the amounts of chemicals required by Fenton’s oxidation, thus lowering the global operating cost. To the best of our knowledge no studies regarding the combination of coagulation/flocculation with the Fenton process to treat industrial textile dyeing effluents are reported in the literature.

4.2. Fenton’s Oxidation (Approach 2)

The study proceeded by applying the Fenton’s oxidation directly to the raw effluent having in mind the possibility of meeting the discharge standards by this chemical process alone. The effect of the hydrogen peroxide dose was first assessed, starting with the optimal dose found in the treatment of synthetic cotton dyeing effluent by the same process (10 g/L) and then gradually decreasing the dose down to 0.938 g/L, to reduce the costs associated with chemicals consumption. Reducing the oxidant consumption, while complying legislated limits, is of paramount importance because it represents the main contribution to the operating costs. The other variables were fixed according to the previous work using simulated wastewater: pH = 3.5, T = 50 ºC, t = 60 min and [Fe²⁺] = 300 mg/L. BOD₅, COD, DOC, and color removals (see Figure 2a) increased from 29.4, 46.5, 46.3 and 94.6 % to 38.9, 62.4, 63.2, and 97.8%, respectively, when raising the hydrogen peroxide dose from 0.938 to 1.25 g/L, but further increases of the hydrogen peroxide dose did not result in any efficiency improvement. The optimal dose found is much below that obtained in the previous study conducted with a synthetic dyeing cotton wastewater (10 g/L): this is due to the fact that the chloride concentration in the real effluent (~ 1.2 g/L)) is much lower than in the synthetic one (~ 8.0 g/L), thus decreasing considerably the effect of hydroxyl radical scavenging by this anion.

The existence of an optimum H₂O₂ concentration was also observed by other authors and is explained by the fact that a parallel reaction between H₂O₂, in excess, with the hydroxyl radicals occurs, generating HO₂⁺ species with a lower oxidation potential (HO⁺ + H₂O₂ → H₂O + HO₂⁺). The optimum value achieved (1.25 g/L) is close to those obtained by other authors, namely, Merič et al. reached an optimum H₂O₂ dose of 1.0 g/L for treating a reactive black 5 dye solution, Blanco et al. found 1.65 g/L as the optimum dose for treating a real textile effluent and Wu and Wang achieved 1.5 g/L when treating a mixture of printing and dyeing wastewaters by Fenton’s reaction.

To reduce the operating costs associated with the catalyst use, the Fe²⁺ dose was set at 37.5 mg/L (corresponding to a Fe²⁺:H₂O₂ ratio of 1:33.3 (w/w) – optimum value reached when treating a synthetic
cotton wastewater by Fenton’s oxidation, maintaining the other variables (3.5, 50 °C, 60 min and 1.25 g/L for pH, temperature, reaction time and H$_2$O$_2$ concentration, respectively). Figure 2 b shows the results obtained for DOC, COD, BOD$_5$ and color removals; it can be seen that only a small decrease occurred (33.6 % for BOD$_5$, 53.0% for COD, 52.8% for DOC and 94.3% for color) in comparison with that corresponding to the Fe$^{2+}$ concentration previously employed (about one order of magnitude higher – 300 mg/L). It is worthy remarking that this much smaller iron dose still allows obtaining an effluent that meets the legislated discharge limits (see Table 1), although the COD value (232.8 mg/L) is not very far from the legislated limit (250 mg/L). Daily or seasonal variations in the wastewater composition can cause that limit to be exceeded and so additional subsequent treatments could be required to increase the overall efficiency, as described below.

The selected dose of ferrous ion (37.5 mg/L) is similar to that reached by other authors to treat dye-containing solutions, as well as synthetic and real wastewaters. Ramirez et al.\textsuperscript{9} obtained an optimum amount of catalyst of 27.2 mg/L for 99.7% color removal (T=29 °C) and 23.5 mg/L for 70.7% TOC reduction (T=50 ºC) from an orange II dye solution. Bali and Karagözoglu\textsuperscript{51} reached 25 mg/L of Fe$^{2+}$ as the dose that maximized the color removal (96.2%) of a synthetic textile effluent containing polyvinyl and remazol turquoise blue G-133. Finally, Papadopoulos et al.\textsuperscript{19} needed to add 40 mg/L of Fe$^{2+}$ to treat a real effluent from polyethylene fibers processing.

The operating cost associated with chemicals consumption when applying the optimal doses achieved in the treatment of simulated cotton dyeing wastewater (300 mg Fe$^{2+}$/L and 10 g H$_2$O$_2$/L), along with the sulfuric acid required for wastewater acidification to the pH required in the process, is 9.3 €/m$^3$. However, this cost is reduced to 1.3 €/m$^3$ when using, in Fenton’s oxidation of the real wastewater, the selected doses of 37.5 mg Fe$^{2+}$/L and of 1.25 g H$_2$O$_2$/L; such reduced cost is ascribed to the much lower concentration of chlorides in the real wastewater. To achieve a soluble iron concentration below the discharge limit (2 mg/L) it is necessary to precipitate the iron as Fe(OH)$_3$ by adjusting the pH to 6.0-9.0. The cost of NaOH required for neutralization is about 0.11 €/m$^3$. So, the operating costs associated with the chemicals consumption, when the effluent is treated using the last operating conditions, is $\approx$1.4 €/m$^3$.

4.3. Integration of Fenton’s Oxidation and Coagulation/Flocculation (Approach 3)

Coagulation/flocculation was applied to the effluent previously treated by the Fenton process to further increase the organic matter reduction. However, several strategies were considered aiming reducing costs. In this perspective, different conditions were tested in the Fenton’s stage: one run was performed in conditions considered as the optimal ones – 1.25 g/L of H$_2$O$_2$ and 37.5 mg/l of Fe$^{2+}$ (run #3); in the other runs the doses of H$_2$O$_2$ and Fe$^{2+}$ were reduced to 3/4 and 1/2, respectively (see Figure 1), with the objective
of decreasing the operating costs (runs #2 and #1, respectively). In the coagulation/flocculation stage the coagulant used was the dissolved iron resulting from Fenton’s oxidation (13.3, 23.1 and 32.7 mg/L of Fe in run#1, run#2 and run#3, respectively), for minimizing costs. The other variables correspond to the optimal conditions obtained when treating the simulated cotton dyeing effluent by Fenton’s reagent plus coagulation/flocculation: $V_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}= 3$ min, pH = 5, $V_{\text{flocculation}}=20$ rpm, $t_{\text{flocculation}}= 15$ min, [Magnafloc 155] = 2.5 mg/L.

Table 2 presents the results obtained after Fenton’s oxidation and after coagulation/flocculation, as well as the global removal efficiencies for each strategy (runs #1 to #3). The COD, DOC and color removals reached in Fenton’s reaction are in all strategies higher than in the coagulation/flocculation stage, but BOD$_5$ shows an opposite behavior. As expected, much better treatment efficiencies are reached in run #3, where doses of chemicals in the Fenton’s stage are higher (69.2, 60.4, 72.4, and 96.6% for COD, BOD$_5$, DOC and color, respectively).

Final COD values below the discharge standards were only reached in runs#2 and #3, where greater H$_2$O$_2$ (and Fe$^{2+}$) doses were used. However, despite the slightly lower organic matter removal efficiency, the chemical dosages used in run #2 were selected because they originate smaller operating costs ($1.0$ €/m$^3$), comparatively to run #3 ($1.4$ €/m$^3$), which is associated with the lower H$_2$O$_2$ and Fe$^{2+}$ concentration employed, without compromising compliance with the legislated discharge standards.

The use of dissolved iron resulting from Fenton process as coagulant in the subsequently stage of coagulation/flocculation represents an economic advantage, since the operating cost is reduced by 27.5% comparatively to Fenton’s oxidation alone.

4.4. Combination of Fenton’s Reaction and SBR (Approach 4)

As the biodegradability of the raw wastewater (in terms of BOD$_5$/COD ratio and k') slightly increased after Fenton’s oxidation (from 0.26 and 8.85 mg O$_2$/g vss h to 0.36 and 9.5 mg O$_2$/g vss h, respectively), and there was also a reduction in Vibro fischeri inhibition, as shown in Tables 1 and 2, the alternative integrated process consisting of Fenton’s reaction followed by SBR was studied.

Three experiments were performed using different doses of chemicals in Fenton’s oxidation stage. One experiment (run #3) was performed under the optimal conditions determined in Approach 2 (37.5 mg/L Fe$^{2+}$ and 1.25 g/L H$_2$O$_2$); in the other runs the doses of H$_2$O$_2$ and Fe$^{2+}$ were reduced to 3/4 and 1/2, respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively) (see Figure 1).
Figure 3 shows the COD, DOC, BOD₅, color, total nitrogen and total phosphorus removals during 10 cycles of SBR operation for the 3 runs; one can conclude that the removals for all parameters analyzed remained practically constant after 6 cycles in all runs/strategies tested, which means that a pseudo-steady state was reached. The efficiencies increased with the doses of chemicals used in the Fenton’s reaction (run #3 > run #2 > run #1), simultaneously with a significant decay of toxicity and a slight increase of biodegradability (see also Table 3). Particularly the inhibition of *Vibrio fischeri* decreased from 44.5-49.2% in run #1 to 0.0 (non-inhibition) in run #3. The average removals achieved in the last 4 cycles are presented in Table 3. BOD₅ removal was greater in SBR probably due to the breakdown of the more recalcitrant compounds by chemical oxidation. As regards decolorization, about 94% of the absorbance of raw wastewater was removed by the Fenton’s reaction and only 38-40% of the residual absorbance was removed in the SBR.

As shown in Figure 4, the operating costs associated with the consumption of chemicals and energy increase with the amount of chemicals used in the chemical treatment, i.e, run #3 (2.6 €/m³) > run #2 (2.3 €/m³) > run #1 (2.0 €/m³). However, only runs #2 and #3 allowed obtaining effluents that meet the discharge standards, namely in terms of COD (see Table 3). As the costs are slightly smaller, conditions used in run #2 are proposed for practical applications. The overall efficiencies achieved by the combination of Fenton’s oxidation and biological degradation in SBR under such conditions are 63.0, 49.5, 64.6, 12.7, 11.9 and 96.5% for COD, BOD₅, DOC, total nitrogen, total phosphorus and color, respectively. It is noteworthy that such integrated process is more expensive than Fenton’s oxidation per se (cf. Fig. 4), which is due to energy consumption in the SBR (1.2 €/m³), although doses of chemicals were minimized in the chemical oxidation stage.

5. Conclusions

A combination of coagulation/flocculation and Fenton’s oxidation (Approach 1), Fenton’s oxidation alone (Approach 2), and integrated processes of Fenton’s oxidation with coagulation/flocculation (Approach 3) or biological degradation in SBR (Approach 4) were applied to a real cotton dyeing wastewater aiming at organic matter mineralization, color removal and toxicity reduction while obtaining an effluent that meets the legislated discharge limits at the lower operating cost. All the treatment processes tested allowed obtaining an effluent that complies with the discharge limits, but the cheapest alternatives are the application of coagulation/flocculation followed by Fenton’s oxidation or, inversely, the combination of Fenton’s oxidation with subsequent coagulation/flocculation process. The operating cost associated to the consumption of chemicals is 1.0 €/m³ for both approaches. This is in part explained by initially using a cheaper treatment that permits a reduction of the amounts of chemicals.
employed in the second process, then decreasing the total costs (Approach 1), and by taking advantage of dissolved iron resulting from Fenton’s reaction as coagulant in the coagulation/flocculation step (Approach 3). Global removal efficiencies of 99.5, 70.8, 66.1, 47.6% and 96.6, 62.6, 64.4 and 47.5 % were obtained for color, COD, DOC and BOD5, respectively, in the first and second integrated treatment processes (Approaches 1 and 3).

This study showed that: i) industrial cotton dyeing effluents often present low biodegradability (BOD5:COD ratio < 0.4), ii) Fenton’s oxidation slightly increases the biodegradability of the effluent; iii) Fenton’s oxidation generates an effluent able to be discharged but with an organic load in terms of COD near the discharge limit, so the integration of this process with coagulation/flocculation is a better treatment approach; iv) The combination of Fenton’s oxidation with biological treatment in SBR is more expensive than the above mentioned Approaches 1 and 3.

Acknowledgments

Carmen Rodrigues is grateful to FCT – Fundação para a Ciência e Tecnologia – for the financial support through the PhD grant (Ref. SFRH/BD/46704/2008).

The authors are thankful to dye-house Têxtil Luís Simões (Manhente - Barcelos, Portugal) for kindly supplying the industrial wastewater, to TRATAVE S.A. (WWTP of Rabada) for providing the aerobic biological sludge for the respirometric tests and SBR inoculation, and to Quimitécnica S.A and Rivaz Química S.A. for providing the prices of chemicals.

Supporting Information Available

A diagram of the SBR set-up is available in this section. This information is available free of charge via the Internet at http://pubs.acs.org/.

Literature Cited


Table 1 - Characteristics of the industrial cotton dyeing wastewater, after coagulation/flocculation and after coagulation/flocculation plus Fenton’s oxidation (Approach 1), after Fenton’s oxidation (Approach 2) and global removals for the combined processes (percent removal efficiencies are given within brackets for each isolated process in Approach 1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw wastewater</th>
<th>Coagulation &amp; flocculation</th>
<th>Fenton</th>
<th>Global removal (%)</th>
<th>Fenton</th>
<th>Removal (%)</th>
<th>Discharge limits****</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.0</td>
<td>1.2</td>
<td>7.10</td>
<td>---</td>
<td>7.9</td>
<td>---</td>
<td>5.5-9.0</td>
</tr>
<tr>
<td>T (°C)</td>
<td>35.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>38.0</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Cond. a 20 °C (mS/cm)</td>
<td>11.5</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Total nitrogen (mg N/L)</td>
<td>1064.4</td>
<td>1043.6 (1.9)</td>
<td>1015.6 (2.7)</td>
<td>4.5</td>
<td>1021.8</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Nitrates (mg NO(_3)-/L)</td>
<td>0.008</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Total phosphorous (mg P/L)</td>
<td>4.2</td>
<td>2.2 (47.2)</td>
<td>1.5 (29.7)</td>
<td>62.9</td>
<td>4.15</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Dissolved phosphorous (mg P/L)</td>
<td>0.06</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Chemical oxygen demand (mg O(_2)/L)</td>
<td>495.0</td>
<td>312.5 (36.9)</td>
<td>144.6 (53.7)</td>
<td>70.8</td>
<td>232.8</td>
<td>53.0</td>
<td>250</td>
</tr>
<tr>
<td>Biochemical oxygen demand (mg O(_2)/L)</td>
<td>127.5</td>
<td>105.6 (17.2)</td>
<td>66.9 (36.7)</td>
<td>47.6</td>
<td>84.6</td>
<td>33.6</td>
<td>100</td>
</tr>
<tr>
<td>Dissolved organic carbon (mg C/L)</td>
<td>174.7</td>
<td>105.8 (39.4)</td>
<td>59.1 (44.1)</td>
<td>66.1</td>
<td>82.5</td>
<td>57.8</td>
<td></td>
</tr>
<tr>
<td>Chlorides (mg Cl/L)</td>
<td>1241.5</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Sulfates (mg SO(_4)-/L)</td>
<td>0.23</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Alkalinity (mg CaCO(_3)/L)</td>
<td>456.8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>---</td>
<td>n.d.</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Specific oxygen uptake rate (k’’)</td>
<td>8.85</td>
<td>9.9</td>
<td>11.3</td>
<td>---</td>
<td>9.5</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>(mg O(_2)/(g VSS h))</td>
<td>0.26</td>
<td>0.34</td>
<td>0.46</td>
<td>---</td>
<td>0.36</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>BOD(_5):COD ratio</td>
<td>1.0251</td>
<td>0.0382 (95.1*)</td>
<td>0.0028 (89.3**)</td>
<td>99.5</td>
<td>0.0386</td>
<td>94.3***</td>
<td></td>
</tr>
<tr>
<td>Absorbance at 600 nm (abs. units)</td>
<td>visible</td>
<td>not visible</td>
<td>not visible</td>
<td>---</td>
<td>not visible</td>
<td>---</td>
<td>not visible</td>
</tr>
<tr>
<td>Visible color after dilution 1:40</td>
<td>81.1</td>
<td>47.8</td>
<td>0.0</td>
<td>---</td>
<td>0.0</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>* calculated from the absorbance of real wastewater at pH 9.4 (0.7865 abs. units)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vibro fischeri Inhibition 15 min (%)</td>
<td>70.4</td>
<td>50.6</td>
<td>0.0</td>
<td>---</td>
<td>0.0</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Vibro fischeri Inhibition 30 min (%)</td>
<td>70.5</td>
<td>51.7</td>
<td>0.0</td>
<td>---</td>
<td>0.0</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

n.d. – not determined

* calculated from the absorbance of real wastewater at pH 9.4 (0.7865 abs. units)
** calculated from the absorbance after coagulation/flocculation at pH 3.5 (0.0261 abs. units)
*** calculated from the absorbance at pH 3.5 (0.6805 abs. units)
Table 2 - Characteristics of the cotton dyeing wastewater after Fenton’s oxidation and coagulation/flocculation (Approach 3) and global removal for the combined process (runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton’s stage; percent removal efficiencies are given within brackets for each isolated process).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run #1 – 0.625 g H₂O₂/L</th>
<th>Run #2 – 0.938 g H₂O₂/L</th>
<th>Run #3 – 1.25 g H₂O₂/L</th>
<th>Discharge limit***</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.20</td>
<td>7.0</td>
<td>-</td>
<td>1.25</td>
</tr>
<tr>
<td>Chemical oxygen demand (mg O₂/L)</td>
<td>347.5</td>
<td>270.0</td>
<td>45.5</td>
<td>292.5</td>
</tr>
<tr>
<td>Biochemical oxygen demand (mg O₂/L)</td>
<td>116.3</td>
<td>91.8</td>
<td>28.0</td>
<td>106.4</td>
</tr>
<tr>
<td>Dissolved organic carbon (mg C/L)</td>
<td>124.9</td>
<td>94.9</td>
<td>45.7</td>
<td>98.4</td>
</tr>
<tr>
<td>BOD₅:COD ratio</td>
<td>0.33</td>
<td>0.34</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>Absorbance at λ_max (abs. units)</td>
<td>0.0407</td>
<td>0.0234</td>
<td>96.6</td>
<td>0.0392</td>
</tr>
<tr>
<td>Visible color after dilution 1:40</td>
<td>not visible</td>
<td>not visible</td>
<td>-</td>
<td>not visible</td>
</tr>
</tbody>
</table>

* calculated from the absorbance of wastewater at pH 3.5 (0.6805 abs. units)

** calculated from the absorbance after Fenton at pH 5.0 (0.0412, 0.0394 and 0.0391 abs. units for run #1, #2 and #3, respectively)
Table 3 – Characteristics of the cotton dyeing wastewater after Fenton’s reaction and SBR (Approach 4) and average (last four cycles for SBR) and global removals (respective removal efficiencies are given within brackets for each processes).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run #1 – 0.625 g H$_2$O$_2$/L</th>
<th>Run #2 – 0.938 g H$_2$O$_2$/L</th>
<th>Run #3 – 1.25 g H$_2$O$_2$/L</th>
<th>Discharge limit***</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.12</td>
<td>7.17</td>
<td>---</td>
<td>7.05</td>
</tr>
<tr>
<td>Total nitrogen (mg N/L)</td>
<td>1021.8 (4.0)</td>
<td>1005.4 (1.6)</td>
<td>5.5</td>
<td>1021.8 (4.0)</td>
</tr>
<tr>
<td>Total phosphorus (mg P/L)</td>
<td>4.2 (1.2)</td>
<td>3.8 (8.4)</td>
<td>9.5</td>
<td>4.2 (1.7)</td>
</tr>
<tr>
<td>COD (mg O$_2$/L)</td>
<td>346.5 (30.0)</td>
<td>281.8 (18.7)</td>
<td>43.1</td>
<td>294.1 (40.6)</td>
</tr>
<tr>
<td>BOD$_5$ (mg O$_2$/L)</td>
<td>114.2 (10.4)</td>
<td>93.4 (18.2)</td>
<td>26.7</td>
<td>103.4 (18.9)</td>
</tr>
<tr>
<td>DOC (mg C/L)</td>
<td>124.7 (28.5)</td>
<td>103.3 (17.2)</td>
<td>40.8</td>
<td>98.0 (43.8)</td>
</tr>
<tr>
<td>SOUR – Specific oxygen uptake rate (k') (mg O$_2$/gVSS.h)</td>
<td>8.9</td>
<td>n.d.</td>
<td>---</td>
<td>9.1</td>
</tr>
<tr>
<td>BOD$_5$:COD ratio</td>
<td>0.33</td>
<td>0.33</td>
<td>---</td>
<td>0.35</td>
</tr>
<tr>
<td>Absorbance at $\lambda_{max}$ (a.u.)</td>
<td>0.0410</td>
<td>0.0257</td>
<td>96.3</td>
<td>0.0393</td>
</tr>
<tr>
<td>Visible color after dilution 1:40</td>
<td>not visible</td>
<td>not visible</td>
<td>---</td>
<td>not visible</td>
</tr>
<tr>
<td>Vibrio fischeri Inhibition 5 min (%)</td>
<td>44.5</td>
<td>n.d.</td>
<td>---</td>
<td>11.0</td>
</tr>
<tr>
<td>Vibrio fischeri Inhibition 15 min (%)</td>
<td>46.7</td>
<td>n.d.</td>
<td>---</td>
<td>23.1</td>
</tr>
<tr>
<td>Vibrio fischeri Inhibition 30 min (%)</td>
<td>49.2</td>
<td>n.d.</td>
<td>---</td>
<td>26.7</td>
</tr>
</tbody>
</table>

n.d. – not determined

* calculated from the absorbance at 520 nm of raw wastewater at pH 3.5 (0.6805 abs. units)

** calculated from the absorbance at 520 nm of wastewater after Fenton at pH 7.0 (0.0415, 0.0397 and 0.0390 abs. units in run #1, #2 and #3, respectively)

Figures captions

Figure 1 - Schematic diagram of all process configurations adopted.

Figure 2 - Effect of H$_2$O$_2$ (a) and Fe$^{2+}$ (b) concentration on COD, BOD$_5$, DOC and color removals during Fenton’s oxidation (Approach 2) (initial pH=3.5, T=50 ºC and t = 60 min; in a) Fe$^{2+}$ initial concentration was 300 mg/L while in b) H$_2$O$_2$ dose was 1.25 g/L).

Figure 3 - Variation of COD (a), DOC (b), BOD$_5$ (c), color (d) total nitrogen (e) and total phosphorus (f) removals during 10 cycles of SBR operation, after treatment by Fenton’s oxidation. Runs #3 to #1 refer to employing the Fenton’s stage with progressively decreasing doses of chemicals.

Figure 4 – Operating costs of Fenton alone and Fenton plus SBR for treatment of a real cotton dyeing wastewater.
Approach 1: Coagulation/flocculation followed by Fenton’s reaction

Approach 2: Fenton’s oxidation alone

Approach 3: Fenton’s oxidation followed by coagulation/flocculation

Approach 4: Integration of Fenton’s oxidation plus SBR

Approaches 3 and 4

Run #1: 18.8 mg/L Fe$^{2+}$ and 0.625 mg/L H$_2$O$_2$ in Fenton’s oxidation
Run #2: 28.2 mg/L Fe$^{2+}$ and 0.938 mg/L H$_2$O$_2$ in Fenton’s oxidation
Run #3: 37.5 mg/L Fe$^{2+}$ and 1.25 mg/L H$_2$O$_2$ in Fenton’s oxidation
Figure 3

a) COD removal (%)

b) DOC removal (%)

c) BOD removal (%)

d) Color removal (%)

e) Total Nitrogen removal (%)

f) Total Phosphorus removal (%)
Figure 4

Operating Cost (€/m³)

Fenton plus SBR

Fenton | Run #1 | Run #2 | Run #3
--- | --- | --- | ---
1.0 | 2.0 | 2.5 | 3.0