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6 **Decontamination of an industrial cotton dyeing wastewater by**
7 **chemical and biological processes**
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38 **Abstract**

39
40 The organic matter mineralization, decolorization, biodegradability improvement and toxicity reduction of
41 an industrial cotton dyeing wastewater was investigated. Different treatment approaches, including single
42 and integrated processes, were studied, namely: coagulation/flocculation per se and its combination with
43 Fenton's oxidation (Approach 1), Fenton's process alone (Approach 2) and its integration with either
44 coagulation/flocculation (Approach 3) or biological oxidation in a sequential batch reactor (Approach 4).
45 All approaches provided a wastewater that meets the Portuguese legislated discharge limits, however
46 Approaches 1 and 3 require smaller operating costs (1.0 €/m³) with global removal efficiencies for these
47 two strategies of 70.8% for COD (Chemical Oxygen Demand), 66.1% for DOC (Dissolved Organic
48 Carbon) and 47.6% for BOD₅ (Biological Oxygen Demand) in Approach 1 and 69.2% for COD, 60.4% for
49 BOD and 72.4% for DOC in Approach 3, along with almost complete color removal in both strategies and
50 toxicity reduction (0.0% inhibition of *Vibrio fischeri* in the effluent from Approach 1). A slight increase of
51 the effluent biodegradability was also observed (BOD₅:COD increased from 0.26 to 0.33-0.46, and SOUR
52 (specific oxygen uptake rate) increased from 8.85 to 9.3-11.3 mgO₂/(g_{vss} h)), depending on the treatment
53 approach. The use of a cheap process (coagulation/flocculation) as pre-treatment allowed reducing the
54 amount of reagents needed in the Fenton process, making the latter treatment slightly cheaper, and thereby
55 reducing the overall costs.

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

71 Introduction

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73 Textile industries consume large amounts of water in the dyeing process and generate highly polluted
74 effluents containing dyes, salts and other organic compounds.¹ When these pollutants come into contact
75 with the environment, many negative effects often occur such as a reduction of the re-oxygenation capacity
76 and a decrease in the sunlight penetration, thereby upsetting the biological activity of the aquatic life.² In
77 order to minimize these impacts it is necessary to implement efficient and effective treatments of the
78 wastewater before discharge.

79 Many studies reported in literature, focused on the treatment of textile wastewaters, show results from the
80 application of physical-chemical processes (such as coagulation/flocculation, adsorption and membrane
81 separation),³⁻⁸ chemical oxidation,⁹⁻¹² or biological processes.¹³⁻¹⁵ Among all these techniques,
82 coagulation/flocculation, advanced chemical oxidation with Fenton's reagent and biological degradation
83 have been widely studied. The first technique has been used to remove dyes, colloidal organic compounds
84 and suspended solids¹⁶ through the addition of coagulants (usually iron or aluminum salts) and flocculants
85 (polymers) that promote the destabilization of the colloids and their aggregation. The removal of the
86 particles formed is achieved through filtration or sedimentation.^{17,18} The Fenton's process allows the
87 oxidation of dyes and organic compounds, while reducing the toxicity and increasing the biodegradability.
88 This process is based on the generation of hydroxyl radicals (with very high oxidation potential)¹⁹ by the
89 decomposition of hydrogen peroxide catalyzed by ferrous ion in acid medium (eq. 1), the catalyst being
90 regenerated by reaction between Fe^{3+} and H_2O_2 (eq. 2). Finally, the hydroxyl radicals oxidize organic
91 compounds and dyes (eq. 3), the complex mechanism being shortly summarized by the following
92 reactions:²⁰

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100 Of course, the intermediates can be also oxidized and ultimately mineralized. The biological treatment in
101 sequential batch reactor (SBR) is a variant of the conventional activated sludge system²¹ operating in 5
102 stages per cycle (influent feeding, reaction, sedimentation, discharge of the clarified effluent, sludge purge
103 and idle).²² The SBR presents some advantages comparatively to the conventional biological treatment,

104 namely flexibility and simplicity, low cost and increased resistance to fluctuations in influent feeding.²³
105 Additionally, equalization, reaction and clarification occur in the same reactor.²⁴
106 This work aimed at evaluating several approaches for treating a real cotton dyeing wastewater (see Figure
107 1) taking into account the characteristics of the effluent as well as the results of a previous study focused
108 on the treatability of a simulated cotton dyeing effluent.²⁵ In Approach 1 coagulation/flocculation was
109 combined with Fenton's reaction (as coagulation/flocculation per se is not effective to comply with
110 legislated discharge standards, as detailed below). In Approach 2 only Fenton's oxidation was applied and
111 in Approaches 3 and 4 the wastewater was pre-treated by Fenton's oxidation and then treated by
112 coagulation/flocculation and a biological process (SBR), respectively. In all situations it was intended to
113 obtain the lowest operating cost and an effluent that meets the discharge limits imposed by the Portuguese
114 legislation for textile effluents. Therefore, to reduce costs, part of the catalyst used in the Fenton's reaction
115 of Approach 1 was the residual dissolved iron resulting from coagulation/flocculation (this methodology
116 has been already applied to industrial wastewaters other than textile dyeing ones).²⁶⁻²⁸ In the same way, in
117 Approach 3 the coagulant used was the residual iron resulting from the Fenton's reaction; however, in this
118 case the final effluent clearly complied with legislated standards, and so the Fenton's stage was also
119 performed with doses of chemicals reduced to 3/4 and 1/2 of the optimum value found in Approach 2 (this
120 methodology has not yet been described in the literature). In Approach 4 the doses of reagents used in the
121 Fenton's oxidation were also reduced, as described above, and the resulting effluent was subjected to a
122 biological process. It has been reported in literature ²⁹ the need of using oxidative processes as a pre-
123 treatment step of industrial textile wastewaters with the aim of generating a biodegradable effluent without
124 extensive testing the behavior of the biological process. Recent works already integrated both processes,
125 particularly combining Fenton's oxidation and biological degradation in SBR.³⁰⁻³⁴ The ultimate choice of
126 the technology to adopt should take also into account economic indicators, and so a cost analysis was
127 performed for each treatment strategy, as detailed in the next section. In this work, all possible treatment
128 strategies were applied for the first time to an industrial wastewater, taking into account current discharge
129 limits and the results of a previous study focused on the treatability of a simulated effluent, comparison
130 being made based on processes performance and associated operating costs (chemicals and energy
131 consumption).

132

133 **2. Operating Costs**

134 To select the better integration of stages for wastewater treatment, but ensuring that the generated effluent
135 meets the discharge standards, the operating costs associated to the consumption of chemicals and energy
136 were assessed. However, to calculate the energy costs only the energy consumed in agitation (power
137 required = 0.61 W) and air insufflated (power = 4.5 W) in the SBR stage was considered because the costs

138 regarding stirring in coagulation/flocculation (0.002 €/m^3) and Fenton oxidation ($\approx 4 \times 10^{-5} \text{ €/m}^3$) are
 139 negligible. The costs concerning the acidification in the Fenton process and further neutralization were also
 140 taken into account (0.06 €/m^3 and 0.11 €/m^3 , respectively). The cost of the energy required to heat the
 141 effluent during the Fenton process was discarded having in mind the high temperature of dyeing
 142 wastewaters ($50\text{-}70 \text{ °C}$ or even higher). Finally, the costs of treatment and disposal of the chemical sludge
 143 generated in coagulation/flocculation and Fenton processes are highly variable and so were not considered.

144 In the economic analysis the costs of main chemicals were those given by Quimitécnica S.A. and Rivaz
 145 Química S.A.: H_2O_2 (49.5% w/v, density at $25 \text{ °C} = 1.2 \text{ g/cm}^3$) – 365 €/ton; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (93 wt.% of purity)
 146 – 233.7 €/ton; Magnafloc 155 – 3850 €/ton; H_2SO_4 (96% w/v, density = 1.84 kg/dm^3) – 140 €/ton; NaOH
 147 (30% w/w, density = 1.33 kg/dm^3) - 185 €/ton. For energy it was considered the average value of 0.10
 148 €/kWh.

149 The operating cost for the coagulation/flocculation step is the sum of costs of Fe^{2+} (eq. 4) and Magnafloc
 150 155 (eq. 5), while for Fenton's reaction is the sum of costs of Fe^{2+} used (eq. 4), H_2O_2 consumed (eq.6), as
 151 well as the acid and base required for acidification and subsequent neutralization, respectively; finally, for
 152 SBR is the cost of energy (eq. 7) only.

$$\text{Cost}_{\text{Fe}^{2+}} = \frac{\text{Price}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}} \left(\frac{\text{€}}{\text{ton}} \right) * [\text{Fe}^{2+}] * 10^{-6} \left(\frac{\text{ton}}{\text{m}^3} \right) * \frac{\text{MM}_{\text{FeSO}_4 \cdot 7\text{H}_2\text{O}}}{\text{MM}_{\text{Fe}^{2+}}}}{\frac{\% \text{ of purity}}{100}} \quad (4)$$

$$\text{Cost}_{\text{Magnafloc155}} = \text{Price}_{\text{Magnafloc155}} \left(\frac{\text{€}}{\text{ton}} \right) * [\text{Magnafloc155}] * 10^{-6} \left(\frac{\text{ton}}{\text{m}^3} \right) \quad (5)$$

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$$\text{Cost}_{\text{H}_2\text{O}_2} = \frac{\text{Price}_{\text{H}_2\text{O}_2} \left(\frac{\text{€}}{\text{ton}} \right) * [\text{H}_2\text{O}_2] * 10^{-3} \left(\frac{\text{ton}}{\text{m}^3} \right) * \rho_{\text{H}_2\text{O}_2} \left(\frac{\text{kg}}{\text{L}} \right)}{\frac{\% \text{H}_2\text{O}_2}{100} (\text{kg/L})} \quad (6)$$

$$\text{Cost}_{\text{energy}} = \frac{(\text{Power}_{\text{airinsufflated}} + \text{Power required}_{\text{agitation}}) * 10^{-3} (\text{kW}) * \text{Price}_{\text{energy}} (\text{kWh}) * \text{time}_{\text{aeration}} (\text{h})}{\text{Volume}_{\text{treatedeffluent}} (\text{m}^3)} \quad (7)$$

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155 In the previous equations, $[i]$ represents the concentration of species i (in g/L for H_2O_2 and mg/L for Fe^{2+}),
 156 MM_i stands for its molar mass (in g/mol) and the power required for agitation is expressed in W .

157 The total operating costs for the integrated processes are calculated by the sum of costs associated with
 158 each process involved.

159

160 **3. Materials and Methods**

161 *3.1. Textile Dyeing Wastewater*

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

165 The main wastewater characteristics are presented in Table 1; the raw effluent presents black color,
166 reasonable concentration of organic compounds (as inferred from the DOC and COD values), low
167 biodegradability (BOD₅:COD ratio <0.4), and high toxicity to *Vibrio fischeri*. As the wastewater does not
168 comply with any of the legislated discharge standards for pH, COD, BOD₅ and color (Ordinance no. 423
169 of June 25, 1997 – cf. Table 1), an appropriate treatment is required before discharge.

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171 *3.2. Experimental Procedure*

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173 *3.2.1 Coagulation/Flocculation*

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175 The coagulation/flocculation experiments were conducted in a *Jar-test* (ISCO, Italy). In all experiments, a
176 sample volume of 500 mL was employed. The pH of wastewater was adjusted and the solution transferred
177 into a beaker. The coagulant (ferrous sulfate) was added under rapid stirring (150 rpm), and the pH
178 readjusted, if necessary (it is worth noting that afterwards it remained constant, i.e. throughout the
179 experiments). After 3 min of rapid mixture the stirring rate was reduced to 20 rpm, the flocculant added
180 (Magnafloc 155) and the agitation proceeded during 15 minutes. After 30 min of sedimentation the
181 supernatant was collected and acidified with HNO₃ (68%, from Merck, Germany) to pH < 4 to keep the
182 iron dissolved (so that it could be used as catalyst in Fenton's reaction).

183 All coagulation/flocculation experiments were conducted at room temperature (22-24 °C). All these
184 conditions were set based on preliminary results achieved with a similar synthetic effluent.³⁵

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186 *3.2.2 Fenton's Reaction*

187

188 In Fenton's oxidation runs 500 mL of wastewater pre-treated by coagulation/flocculation (Approach 1) or
189 raw wastewater (Approaches 2, 3 and 4 – cf. Fig. 1) was put into a batch jacketed reactor, connected to a
190 water thermostatic bath (Grant Y6, England) to maintain the temperature inside the reactor at 50 °C. After
191 temperature stabilization, the pH was adjusted to 3.5 with 2M H₂SO₄ (from Merck, Germany). These values
192 of temperature and pH were found as the optimal ones for the treatment of cotton dyeing synthetic effluent

193 by Fenton's oxidation after coagulation/flocculation.²⁵ The catalyst (FeSO₄, 7H₂O, from Merck - Germany)
194 was then added and the reaction started with addition of H₂O₂ 30% (w/v) (Merck, from Germany). During
195 the reaction the solution was constantly stirred by using a magnetic bar and a stir plate (Falc, Italy).
196 Before measuring the DOC of samples taken over time, the homogeneous reaction in the sampling vial was
197 stopped by addition of excess sodium sulfite, which immediately reacts with the remaining hydrogen
198 peroxide. For the other analytical determinations where sulfite interferes, the residual H₂O₂ was eliminated,
199 with simultaneous iron precipitation, by raising the pH to 12.3 through the addition of 10 M NaOH (from
200 Merck) and heating the samples at 80 °C for 10 minutes.³⁶⁻³⁷ Then the effluent was neutralized (to pH ~7.0)
201 with concentrated H₂SO₄, although the samples used for *V. fischeri* inhibition assessment were neutralized
202 with HCl, as proposed by the analytical methodology.³⁸ This methodology was also applied to stop the
203 reaction when using the combination of the advanced oxidation with biological treatment (Approach 4).
204 In Approach 3 the effluent after the oxidation stage was acidified to pH ≈ 1 to keep the iron dissolved for
205 the coagulation/flocculation study, while simultaneously slowing down or inhibiting the Fenton's reaction;
206 analyses of the effluent were performed immediately.

207

208 3.2.3 Biological Oxidation in SBR

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210 The Sequencing Batch Reactor (SBR) is a jacketed cylindrical-conical tank (20 cm internal diameter, 45
211 cm total height, 30° slope conical bottom, 5.0 L effective working volume – cf. Figure S1 in Supporting
212 Information). Water from a thermostatic bath (Isco GTR 90, Italy) circulates through the jacket to keep the
213 temperature constant (25 °C) inside the reactor.

214 The SBR operated in successive cycles of 12 hours (1 hour for feeding, 6 h of reaction under aeration, 4 h
215 of sedimentation, 0.8 h for discharge and 0.2 h idle), up to 10 cycles. In the first cycle the reactor was fed
216 with 2.5 L of pre-treated wastewater with pH previously adjusted to ~7.0 using 2M H₂SO₄ and 10M NaOH.
217 Then 2.5 L of activated sludge (~ 5 g VSS/L) from the aeration tank of Rabada WWTP (Santo Tirso -
218 Portugal) was added to the reactor. In the subsequent cycles the reactor was fed with 2.5 L of effluent to
219 compensate the amount of treated effluent discharged. During the reaction stage, a mechanical stirrer was
220 employed (stirring rate = 400 rpm) and the dissolved oxygen content was maintained at ~3.0 mgO₂/L by a
221 diffused air aeration system.

222 The values of dissolved oxygen and the duration of each cycle and each cycle stage were established in
223 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
224 0.9 h for treated wastewater discharge and 0.05 to 0.5 h for the idle stage.^{13, 24, 30, 39-42}

225 The acquisition of data and the automatic control of the unit, i.e., operation of the peristaltic pumps
226 (Watson-Marlow 502S, England), Burckert valve (Germany) and mechanical stirrer (VWR VOS power

227 control, Germany), was achieved by Labview 5.0 software (from National Instruments), through a home-
228 made designed interface.

229

230 3.3. Analytical Methods

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

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

244 The inhibition of *Vibrio fischeri* test was performed according to standard DIN/EN/ISO 11348-3.³⁸ The
245 bacteria were placed in contact with samples at 15 °C and the bioluminescence measured after a contact
246 time of 5, 15 or 30 minutes in a Microtox model 500 analyzer (England).

247 Other analytical determinations were carried out according to Standard Methods:⁴⁴ dissolved organic carbon
248 (DOC) was measured in a TC/TOC analyzer (Shimadzu 5000A, from Japan) - Method 5310 D; the
249 biochemical oxygen demand (BOD₅) was determined according to Method 5210 B; the chemical oxygen
250 demand (COD) was assessed by the open reflux method (Method 5220 B); and total phosphorus by Method
251 4500P - E. Total nitrogen was determined by colorimetry according to Method D992-71 of the ASTM
252 Standards⁴⁵ after previous digestion (Method 4500 - N C); the total suspended solids (TSS) and volatile
253 suspended solids (VSS) were evaluated by gravimetry - Method 2540 B and Method 2540 E, respectively.

254 The alkalinity was evaluated by titration with H₂SO₄ at pH 4.5 (Method 2320 D) while the pH was measured
255 using a selective electrode (Hanna Instruments HI 1230, Italy) and a pH meter (Hanna Instruments HI 8424,
256 Italy). The conductivity at 20 °C was determined using a conductivity probe (WTW TetraCon 325,
257 Germany) and a conductivity meter (WTW LF538, Germany) - Method 2510 B. Finally, chlorides, nitrates,
258 sulfates and dissolved phosphorus were measured by ion chromatography (Dionex DX 120, from USA)
259 using a Dionex Ionpac AS9-HC 4 mm (10-32) column (from USA). Total dissolved iron was determined
260 by AAS (GBC 932 AB Plus).

261 All analytical determination were performed in duplicate, and the coefficients of variation were less than
262 2% for DOC, 6% for BOD₅, 4% for COD and k', and 5% for the other parameters.

263

264 4. Results and Discussion

265

266 4.1. Coagulation/Flocculation plus Fenton's Reaction (Approach 1)

267

268 This study started with the application of coagulation/flocculation to the raw industrial wastewater, using
269 ferrous sulfate and Maganafloc 155 as coagulant and flocculant, respectively. The operating conditions
270 used were the optimal ones determined in a prior study on the treatment of a synthetic cotton wastewater:³⁵
271 $V_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}= 3$ min, $[\text{Fe}^{2+}]= 200$ mg/L, $\text{pH}= 9.4$, $V_{\text{flocculation}}=20$ rpm, $t_{\text{flocculation}}= 15$ min,
272 $[\text{Maganafloc 155}] = 0.5$ mg/L. The characteristics of the wastewater after treatment are presented in Table
273 1. One can conclude that coagulation/flocculation is very efficient as regards color removal (95.1% - percent
274 removal efficiencies are within brackets in the table), leads to a considerable removal of organic matter
275 (36.9% and 39.4% respectively for COD and DOC) and phosphorus (47.2%), but it is quite inefficient
276 concerning the removal of BOD₅ (17.2%) and nitrogen (1.9%). Moreover, the values of COD and BOD₅ in
277 the final effluent are above the discharge standards imposed by the Portuguese legislation, which makes
278 necessary an additional treatment.

279 So, for increasing the efficiency of organic matter removal, the effluent from the coagulation/flocculation
280 stage was subjected to Fenton's oxidation, applying the operating conditions already optimized when
281 treating a synthetic effluent by the same integrated process:²⁵ $T= 50$ °C, $\text{pH}= 3.5$, $t= 60$ min, $[\text{H}_2\text{O}_2]= 500$
282 mg/L and $[\text{Fe}^{2+}]_{\text{added}}= 98.3$ mg/L (total iron concentration = 100 mg/L, taking into account that 1.7 mg Fe/L
283 remained from the coagulation/flocculation step). Results included in Table 1 point out that Fenton's
284 oxidation applied to the pre-treated effluent allowed obtaining COD, BOD₅ and DOC removals of 53.7,
285 36.7 and 44.1%, respectively, color reduction of 89.3% and smaller decreases in total phosphorus and total
286 nitrogen concentrations (29.7 and 2.7%, respectively).

287 The global efficiencies for the combined process (coagulation/flocculation plus Fenton's reaction) are
288 significant for color (99.5%), COD (70.8%), DOC (66.1%) and total phosphorous (62.9%), moderate for
289 BOD₅ (47.6%) and low for total nitrogen (4.5%). Except for BOD₅ the efficiencies reached are similar to
290 those obtained when treating a synthetic cotton dyeing effluent by the same integrated process (61.7, 25.8,
291 71.2 and 99.8% for COD, BOD₅, DOC and color, respectively).²⁵ Moreover, the resulting effluent meets
292 the discharge standards (Table 1), and this is reached at a low operating cost (1.0 €/m³), which was
293 calculated taking into account the amounts of chemicals employed in both coagulation/flocculation and
294 Fenton's steps, as described in section 2, as well as the acidification and subsequent neutralization costs in

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

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303 *4.2. Fenton's Oxidation (Approach 2)*

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305 The study proceeded by applying the Fenton's oxidation directly to the raw effluent having in mind the
306 possibility of meeting the discharge standards by this chemical process alone.

307 The effect of the hydrogen peroxide dose was first assessed, starting with the optimal dose found in the
308 treatment of synthetic cotton dyeing effluent by the same process (10 g/L)²⁵ and then gradually decreasing
309 the dose down to 0.938 g/L, to reduce the costs associated with chemicals consumption. Reducing the
310 oxidant consumption, while complying legislated limits, is of paramount importance because it represents
311 the main contribution to the operating costs. The other variables were fixed according to the previous work
312 using simulated wastewater:²⁵ pH = 3.5, T = 50 °C, t = 60 min and [Fe²⁺] = 300 mg/L.

313 BOD₅, COD, DOC, and color removals (see Figure 2 a) increased from 29.4, 46.5, 46.3 and 94.6 % to 38.9,
314 62.4, 63.2, and 97.8%, respectively, when raising the hydrogen peroxide dose from 0.938 to 1.25 g/L, but
315 further increases of the hydrogen peroxide dose did not result in any efficiency improvement. The optimal
316 dose found is much below that obtained in the previous study conducted with a synthetic dyeing cotton
317 wastewater (10 g/L);²⁵ this is due to the fact that the chloride concentration in the real effluent (~ 1.2 g/L))
318 is much lower than in the synthetic one (~ 8.0 g/L), thus decreasing considerably the effect of hydroxyl
319 radical scavenging by this anion.²

320 The existence of an optimum H₂O₂ concentration was also observed by other authors^{9, 10, 44-47} and is
321 explained by the fact that a parallel reaction between H₂O₂, in excess, with the hydroxyl radicals occurs,
322 generating HO₂• species with a lower oxidation potential (HO• + H₂O₂ → H₂O + HO₂•). The optimum
323 value achieved (1.25 g/L) is close to those obtained by other authors, namely, Meriç et al.⁵⁰ reached an
324 optimum H₂O₂ dose of 1.0 g/L for treating a reactive black 5 dye solution, Blanco et al.³¹ found 1.65 g/L as
325 the optimum dose for treating a real textile effluent and Wu and Wang⁴⁹ achieved 1.5 g/L when treating a
326 mixture of printing and dyeing wastewaters by Fenton's reaction.

327 To reduce the operating costs associated with the catalyst use, the Fe²⁺ dose was set at 37.5 mg/L
328 (corresponding to a Fe²⁺:H₂O₂ ratio of 1:33.3 (w/w) – optimum value reached when treating a synthetic

329 cotton wastewater by Fenton's oxidation),²⁵ maintaining the other variables (3.5, 50 °C, 60 min and 1.25
330 g/L for pH, temperature, reaction time and H₂O₂ concentration, respectively). Figure 2 b shows the results
331 obtained for DOC, COD, BOD₅ and color removals; it can be seen that only a small decrease occurred (33.6
332 % for BOD₅, 53.0% for COD, 52.8% for DOC and 94.3% for color) in comparison with that corresponding
333 to the Fe²⁺ concentration previously employed (about one order of magnitude higher – 300 mg/L). It is
334 worthy remarking that this much smaller iron dose still allows obtaining an effluent that meets the legislated
335 discharge limits (see Table 1), although the COD value (232.8 mg/L) is not very far from the legislated
336 limit (250 mg/L). Daily or seasonal variations in the wastewater composition can cause that limit to be
337 exceeded and so additional subsequent treatments could be required to increase the overall efficiency, as
338 described below.

339 The selected dose of ferrous ion (37.5 mg/L) is similar to that reached by other authors to treat dye-
340 containing solutions, as well as synthetic and real wastewaters. Ramirez et al.⁹ obtained an optimum amount
341 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
342 °C) from an orange II dye solution. Bali and Karagözoglu⁵¹ reached 25 mg/L of Fe²⁺ as the dose that
343 maximized the color removal (96.2%) of a synthetic textile effluent containing polyvinyl and remazol
344 turquoise blue G-133. Finally, Papadopoulos et al.¹⁹ needed to add 40 mg/L of Fe²⁺ to treat a real effluent
345 from polyethylene fibers processing.

346 The operating cost associated with chemicals consumption when applying the optimal doses achieved in
347 the treatment of simulated cotton dyeing wastewater (300 mg Fe²⁺/L and 10 g H₂O₂/L), along with the
348 sulfuric acid required for wastewater acidification to the pH required in the process, is 9.3 €/m³. However,
349 this cost is reduced to 1.3 €/m³ when using, in Fenton's oxidation of the real wastewater, the selected doses
350 of 37.5 mg Fe²⁺/L and of 1.25 g H₂O₂/L; such reduced cost is ascribed to the much lower concentration of
351 chlorides in the real wastewater. To achieve a soluble iron concentration below the discharge limit (2 mg/L)
352 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
353 for neutralization is about 0.11 €/m³. So, the operating costs associated with the chemicals consumption,
354 when the effluent is treated using the last operating conditions, is ≈1.4 €/m³.

355

356 *4.3. Integration of Fenton's Oxidation and Coagulation/Flocculation (Approach 3)*

357

358 Coagulation/flocculation was applied to the effluent previously treated by the Fenton process to further
359 increase the organic matter reduction. However, several strategies were considered aiming reducing costs.
360 In this perspective, different conditions were tested in the Fenton's stage: one run was performed in
361 conditions considered as the optimal ones – 1.25 g/L of H₂O₂ and 37.5 mg/l of Fe²⁺ (run #3); in the other
362 runs the doses of H₂O₂ and Fe²⁺ were reduced to 3/4 and 1/2, respectively (see Figure 1), with the objective

363 of decreasing the operating costs (runs #2 and #1, respectively). In the coagulation/flocculation stage the
364 coagulant used was the dissolved iron resulting from Fenton's oxidation (13.3, 23.1 and 32.7 mg/L of Fe
365 in run#1, run#2 and run#3, respectively), for minimizing costs. The other variables correspond to the
366 optimal conditions obtained when treating the simulated cotton dyeing effluent by Fenton's reagent plus
367 coagulation/flocculation:²⁵ $V_{\text{coagulation}}=150$ rpm, $t_{\text{coagulation}}= 3$ min, pH= 5, $V_{\text{flocculation}}=20$ rpm, $t_{\text{flocculation}}= 15$
368 min, [Magnafloc 155] = 2.5 mg/L.

369 Table 2 presents the results obtained after Fenton's oxidation and after coagulation/flocculation, as well as
370 the global removal efficiencies for each strategy (runs #1 to #3). The COD, DOC and color removals
371 reached in Fenton's reaction are in all strategies higher than in the coagulation/flocculation stage, but BOD₅
372 shows an opposite behavior. As expected, much better treatment efficiencies are reached in run #3, where
373 doses of chemicals in the Fenton's stage are higher (69.2, 60.4, 72.4, and 96.6% for COD, BOD₅, DOC and
374 color, respectively).

375 Final COD values below the discharge standards were only reached in runs#2 and #3, where greater H₂O₂
376 (and Fe²⁺) doses were used. However, despite the slightly lower organic matter removal efficiency, the
377 chemical dosages used in run #2 were selected because they originate smaller operating costs (1.0 €/m³),
378 comparatively to run #3 (1.4 €/m³), which is associated with the lower H₂O₂ and Fe²⁺ concentration
379 employed, without compromising compliance with the legislated discharge standards.

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

383

384 4.4. Combination of Fenton's Reaction and SBR (Approach 4)

385

386 As the biodegradability of the raw wastewater (in terms of BOD₅:COD ratio and k') slightly increased after
387 Fenton's oxidation (from 0.26 and 8.85 mg O₂/(g_{vss} h) to 0.36 and 9.5 mg O₂/(g_{vss} h), respectively), and
388 there was also a reduction in *Vibro fischeri* inhibition, as shown in Tables 1 and 2, the alternative integrated
389 process consisting of Fenton's reaction followed by SBR was studied.

390 Three experiments were performed using different doses of chemicals in Fenton's oxidation stage. One
391 experiment (run #3) was performed under the optimal conditions determined in Approach 2 (37.5 mg/L
392 Fe²⁺ and 1.25 g/L H₂O₂); in the other runs the doses of H₂O₂ and Fe²⁺ were reduced to 3/4 and 1/2,
393 respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively) (see Figure
394 1).

395 Figure 3 shows the COD, DOC, BOD₅, color, total nitrogen and total phosphorus removals during 10 cycles
396 of SBR operation for the 3 runs; one can conclude that the removals for all parameters analyzed remained
397 practically constant after 6 cycles in all runs/strategies tested, which means that a pseudo-steady state was
398 reached. The efficiencies increased with the doses of chemicals used in the Fenton's reaction (run #3 > run
399 #2 > run #1), simultaneously with a significant decay of toxicity and a slight increase of biodegradability
400 (see also Table 3). Particularly the inhibition of *Vibrio fischeri* decreased from 44.5-49.2% in run # 1 to 0.0
401 (non-inhibition) in run # 3. The average removals achieved in the last 4 cycles are presented in Table 3.
402 BOD₅ removal was greater in SBR probably due to the breakdown of the more recalcitrant compounds by
403 chemical oxidation. As regards decolorization, about 94% of the absorbance of raw wastewater was
404 removed by the Fenton's reaction and only 38-40% of the residual absorbance was removed in the SBR.
405 As shown in Figure 4, the operating costs associated with the consumption of chemicals and energy increase
406 with the amount of chemicals used in the chemical treatment, i.e, run #3 (2.6 €/m³) > run #2 (2.3 €/m³) >
407 run #1 (2.0 €/m³). However, only runs #2 and #3 allowed obtaining effluents that meet the discharge
408 standards, namely in terms of COD (see Table 3). As the costs are slightly smaller, conditions used in run
409 #2 are proposed for practical applications. The overall efficiencies achieved by the combination of Fenton's
410 oxidation and biological degradation in SBR under such conditions are 63.0, 49.5, 64.6, 12.7, 11.9 and
411 96.5% for COD, BOD₅, DOC, total nitrogen, total phosphorus and color, respectively. It is noteworthy that
412 such integrated process is more expensive than Fenton's oxidation per se (cf. Fig. 4), which is due to energy
413 consumption in the SBR (1.2 €/m³), although doses of chemicals were minimized in the chemical oxidation
414 stage.

415

416 5. Conclusions

417

418 A combination of coagulation/flocculation and Fenton's oxidation (Approach 1), Fenton's oxidation alone
419 (Approach 2), and integrated processes of Fenton's oxidation with coagulation/flocculation (Approach 3)
420 or biological degradation in SBR (Approach 4) were applied to a real cotton dyeing wastewater aiming at
421 organic matter mineralization, color removal and toxicity reduction while obtaining an effluent that meets
422 the legislated discharge limits at the lower operating cost.

423 All the treatment processes tested allowed obtaining an effluent that complies with the discharge limits, but
424 the cheapest alternatives are the application of coagulation/flocculation followed by Fenton's oxidation or,
425 inversely, the combination of Fenton's oxidation with subsequent coagulation/flocculation process. The
426 operating cost associated to the consumption of chemicals is 1.0 €/m³ for both approaches. This is in part
427 explained by initially using a cheaper treatment that permits a reduction of the amounts of chemicals

428 employed in the second process, then decreasing the total costs (Approach 1), and by taking advantage of
429 dissolved iron resulting from Fenton's reaction as coagulant in the coagulation/flocculation step (Approach
430 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
431 for color, COD, DOC and BOD₅, respectively, in the first and second integrated treatment processes
432 (Approaches 1 and 3).

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

439

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441

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448

449 **Supporting Information Available**

450

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

453

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

Parameter	Raw wastewater	Approach 1			Approach 2		Discharge limits****
		Coagulation & flocculation	Fenton	Global removal (%)	Fenton	Removal (%)	
pH	10.0	1.2	7.10	---	7.9	---	5.5-9.0
T (°C)	35.6	n.d.	n.d.	---	n.d.	---	
TSS (mg/L)	38.0	n.d.	n.d.	---	n.d.	---	
Cond. a 20 °C (mS/cm)	11.5	n.d.	n.d.	---	n.d.	---	
Total nitrogen (mg N/L)	1064.4	1043.6 (1.9)	1015.6 (2.7)	4.5	1021.8	4.0	
Nitrates (mg NO ₃ ²⁻ /L)	0.008	n.d.	n.d.	---	n.d.	---	
Total phosphorous (mg P/L)	4.2	2.2 (47.2)	1.5 (29.7)	62.9	4.15	1.2	
Dissolved phosphorous (mg P/L)	0.06	n.d.	n.d.	---	n.d.	---	
Chemical oxygen demand (mg O ₂ /L)	495.0	312.5 (36.9)	144.6 (53.7)	70.8	232.8	53.0	250
Biochemical oxygen demand (mg O ₂ /L)	127.5	105.6 (17.2)	66.9 (36.7)	47.6	84.6	33.6	100
Dissolved organic carbon (mg C/L)	174.7	105.8 (39.4)	59.1 (44.1)	66.1	82.5	57.8	
Chlorides (mg Cl ⁺ /L)	1241.5	n.d.	n.d.	---	n.d.	---	
Sulfates (mg SO ₄ ²⁻ /L)	0.23	n.d.	n.d.	---	n.d.	---	
Alkalinity (mg CaCO ₃ /L)	456.8	n.d.	n.d.	---	n.d.	---	
Specific oxygen uptake rate (k' (mg O ₂ /(g _{vss} h))	8.85	9.9	11.3	---	9.5	---	
BOD ₅ :COD ratio	0.26	0.34	0.46	---	0.36	---	
Absorbance at 600 nm (abs. units)	1.0251	0.0382 (95.1*)	0.0028 (89.3**)	99.5	0.0386	94.3***	
Visible color after dilution 1:40	visible	not visible	not visible	---	not visible	---	not visible
<i>Vibro fischeri</i> Inhibition 5 min (%)	81.1	47.8	0.0	---	0.0	---	
<i>Vibro fischeri</i> Inhibition 15 min (%)	70.4	50.6	0.0	---	0.0	---	
<i>Vibro fischeri</i> Inhibition 30 min (%)	70.5	51.7	0.0	---	0.0	---	

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)

**** Ordinance no 423 of June 25, 1997.

625
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630 Table 2 - Characteristics of the cotton dyeing wastewater after Fenton's oxidation and coagulation/flocculation (Approach 3) and global removal for
 631 the combined process (runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage; percent removal efficiencies are
 632 given within brackets for each isolated process).

Parameter	Run #1 – 0.625 g H ₂ O ₂ /L			Run #2 – 0.938 g H ₂ O ₂ /L			Run #3 – 1.25 g H ₂ O ₂ /L			Discharge limit***
	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	Fenton's oxidation	Coagulation & flocculation	Global removal (%)	
pH	1.20	7.0	-	1.25	7.02	-	1.10	7.03	-	5.5-9.0
Chemical oxygen demand (mg O ₂ /L)	347.5 (29.8)	270.0 (22.3)	45.5	292.5 (40.9)	185.0 (36.8)	62.6	260.0 (47.5)	152.5 (41.3)	69.2	250
Biochemical oxygen demand (mg O ₂ /L)	116.3 (8.8)	91.8 (21.1)	28.0	106.4 (16.5)	66.9 (37.1)	47.5	85.3 (33.1)	50.5 (40.8)	60.4	100
Dissolved organic carbon (mg C/L)	124.9 (28.5)	94.9 (24.0)	45.7	98.4 (43.7)	62.2 (36.8)	64.4	82.4 (52.8)	48.3 (41.4)	72.4	-
BOD ₅ :COD ratio	0.33	0.34	-	0.36	0.36	-	0.33	0.33	-	-
Absorbance at λ_{max} (abs. units)	0.0407 (94.0*)	0.0234 (43.2**)	96.6	0.0392 (94.2*)	0.0230 (41.6**)	96.6	0.0387 (94.3*)	0.0233 (40.4**)	96.6	-
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

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

634 ** 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)

635 *** Portuguese legislation for discharge of textile wastewaters (Ordinance no 423 of June 25, 1997).

636 Table 3 – Characteristics of the cotton dyeing wastewater after Fenton’s reaction and SBR (Approach 4) and average (last four cycles for SBR)
 637 and global removals (respective removal efficiencies are given within brackets for each processes).

Parameter	Run #1 – 0.625 g H ₂ O ₂ /L			Run #2 – 0.938 g H ₂ O ₂ /L			Run #3 – 1.25 g H ₂ O ₂ /L			Discharge limit***
	Fenton	SBR	Global Removal (%)	Fenton	SBR	Global Removal (%)	Fenton	SBR	Global Removal (%)	
pH	7.12	7.17	---	7.05	7.15	---	7.09	7.17	---	5.5-9.0
Total nitrogen (mg N/L)	1021.8 (4.0)	1005.4 (1.6)	5.5	1021.8 (4.0)	929.1 (9.1)	12.7	1021.8 (4.0)	905.5 (11.4)	14.9	
Total phosphorus (mg P/L)	4.2 (1.2)	3.8 (8.4)	9.5	4.2 (1.7)	3.7 (10.4)	11.9	4.2 (1.2)	3.6 (13.3)	14.3	
COD (mg O ₂ /L)	346.5 (30.0)	281.8 (18.7)	43.1	294.1 (40.6)	183.3 (37.7)	63.0	232.8 (53.0)	79.2 (66.0)	84.0	250
BOD ₅ (mg O ₂ /L)	114.2 (10.4)	93.4 (18.2)	26.7	103.4 (18.9)	64.4 (37.7)	49.5	84.7 (32.6)	28.6 (66.2)	77.6	100
DOC (mg C/L)	124.7 (28.5)	103.3 (17.2)	40.8	98.0 (43.8)	61.7 (37.0)	64.6	82.5 (52.7)	28.1 (65.9)	83.9	
SOUR – Specific oxygen uptake rate (k') (mg O ₂ /(gvss .h))	8.9	n.d.	---	9.1	n.d.	---	9.5	n.d.	---	
BOD ₅ :COD ratio	0.33	0.33	---	0.35	0.35	---	0.36	0.36	---	
Absorbance at λ _{max} (a.u.)	0.0410 (94.0*)	0.0257 (38.1**)	96.3	0.0393 (94.2*)	0.0240 (39.5**)	96.5	0.0386 (94.3*)	0.0234 (40.0**)	96.6	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
<i>Vibrio fischeri</i> Inhibition 5 min (%)	44.5	n.d.	---	11.0	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 15 min (%)	46.7	n.d.	---	23.1	n.d.	---	0.0	n.d.	---	
<i>Vibrio fischeri</i> Inhibition 30 min (%)	49.2	n.d.	---	26.7	n.d.	---	0.0	n.d.	---	

638 n.d. – not determined

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

640 ** 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)

641 *** . Ordinance no 423 of June 25, 1997.

642

Figures captions

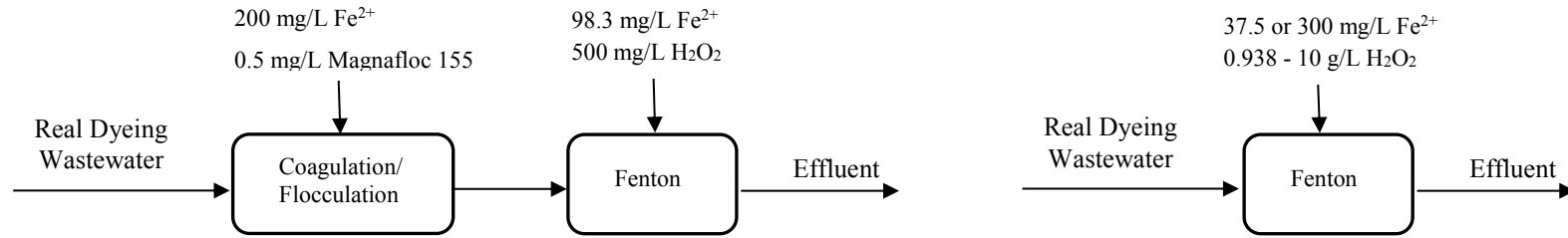
Figure 1 - Schematic diagram of all process configurations adopted.

Figure 2 - Effect of H_2O_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 °C and t = 60 min; in a) Fe^{2+} initial concentration was 300 mg/L while in b) H_2O_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.

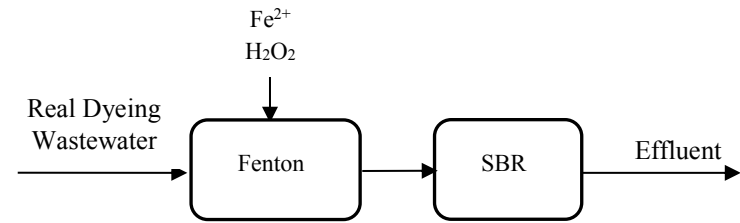
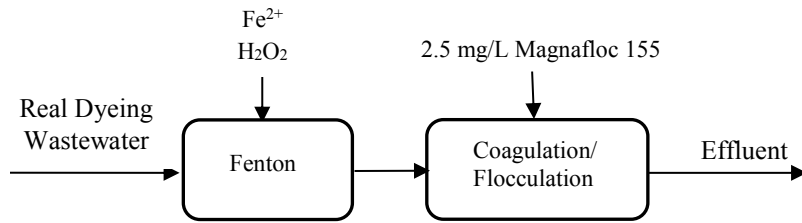
Figure 4 – Operating costs of Fenton alone and Fenton plus SBR for treatment of a real cotton dyeing wastewater.

Figure 1



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 Fe²⁺ and 0.625 mg/L H₂O₂ in Fenton's oxidation
- Run #2: 28.2 mg/L Fe²⁺ and 0.938 mg/L H₂O₂ in Fenton's oxidation
- Run #3: 37.5 mg/L Fe²⁺ and 1.25 mg/L H₂O₂ in Fenton's oxidation

Figure 2

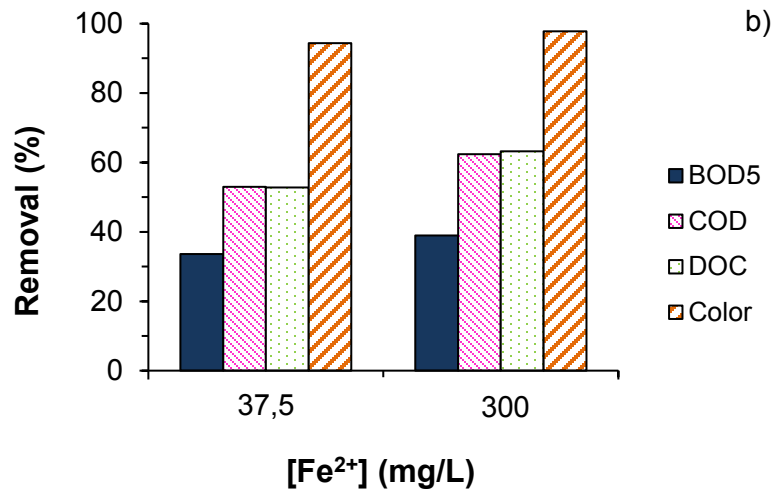
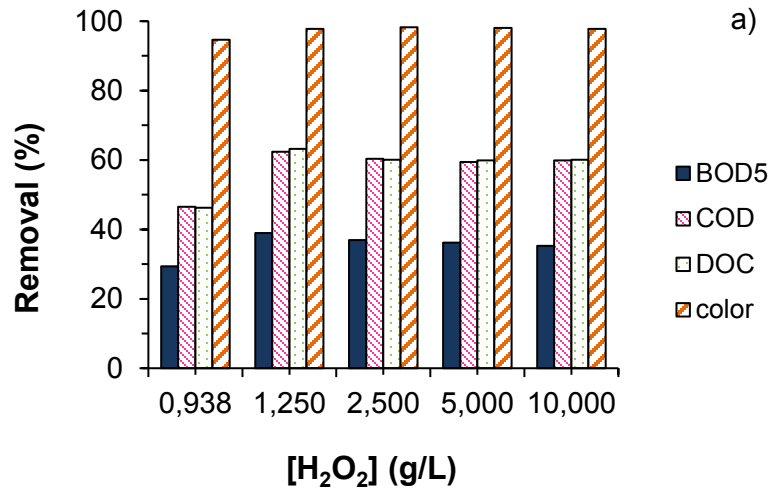


Figure 3

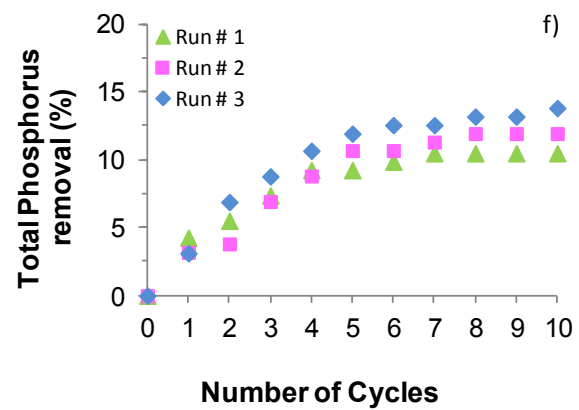
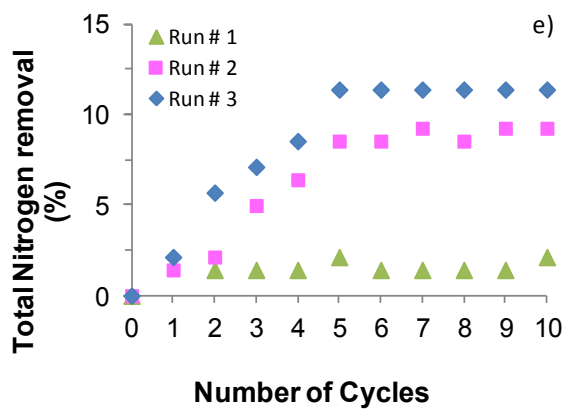
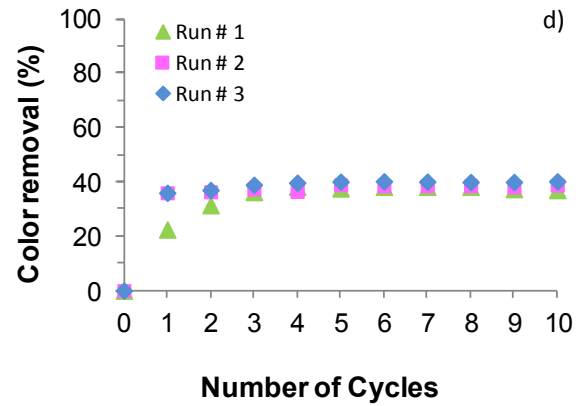
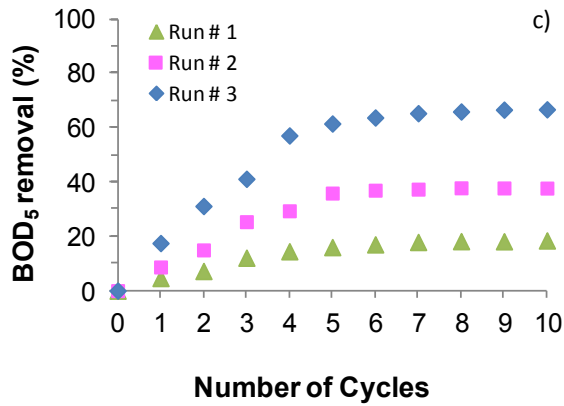
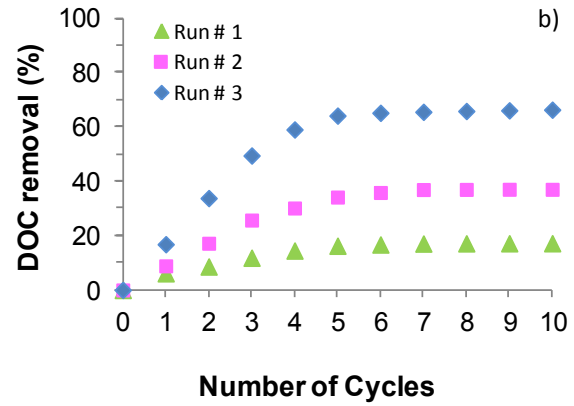
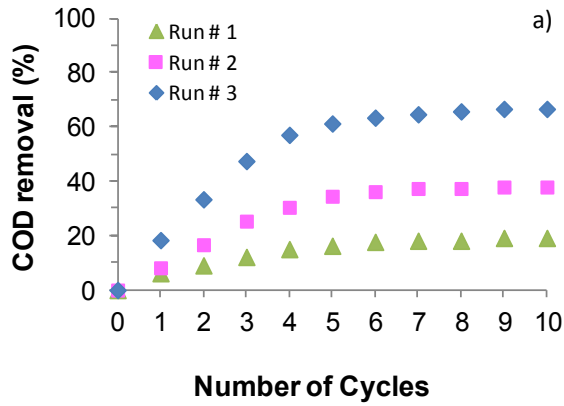


Figure 4

