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Synthetic Textile Dyeing Wastewater Treatment by Integration of Advanced Oxidation and Biological Processes – Performance Analysis with Costs Reduction

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Abstract

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

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

1. Introduction

Negative environmental impacts are often associated with the textile dyeing industry, mainly due to the discharge of wastewaters, which impair the aquatic environment quality by changing its color and creating conditions for eutrophication, low reoxigenation and a decrease in the solar light penetration [1]. Considering the growing awareness and concern about the negative effects on the environment generated by the discharge of industrial wastewaters, increasingly restrictive legislation regarding the concentrations of pollutants in the effluents has been approved. Therefore, it is necessary to develop and implement treatment technologies more efficient and also economically viable or at least attractive.

In the present study, the treatability of acrylic, cotton and polyester dyeing wastewaters by a biological aerobic process (SBR - sequential batch reactor) and a combined process (Fenton's oxidation followed by SBR) was evaluated. While in principle the biological process is economically far more attractive, when used alone it might not be efficient enough; so, integration with other processes has been envisaged by several authors [2].

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

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \qquad k_1 = 76\ L/(mol.s) \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \qquad k_2 = 0.01\text{-}0.02\ L/(mol.s) \qquad (2)$$

$$HO^{\bullet} + RH \rightarrow H_2O + \text{intermediates} \qquad (3)$$

Then, the intermediates may suffer further oxidation by the HO• species, hopefully till carbon dioxide, which would represent complete mineralization. In this simplified mechanism, eq. 2 refers to catalyst regeneration in the redox process.

The textile effluent to treat is very often first subjected to Fenton´s oxidation to degrade part of the organic matter, while removing completely the color and increasing the biodegradability and/or reducing the toxicity, which allows a subsequent treatment by a biological process [2]. In the sequential batch reactor aerobic bacteria are used, as in the conventional activated sludge systems, to degrade the biodegradable fraction of the organic matter into new compounds, cells, salts and gases. The SBR operates in discontinuous mode with five sequential stages in each treatment cycle (influent feeding, reaction, sedimentation, discharge of the clarified effluent and sludge purge and idle). This process present some advantages compared to other conventional biological treatments, namely simplicity and flexibility, low cost, and increased resistance to fluctuations in the influent [5]. Additionally, equalization, reaction and clarification occur in the same reactor [6].

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

In this work, a treatability study of synthetic acrylic, cotton and polyester dyeing wastewaters (representing typical dyeing industrial effluents) was done, either using an SBR or an integrated process combining the Fenton's reaction with an SBR process. The main purpose of this research was to evaluate the possibility of reducing the chemicals consumption in the Fenton's reaction to make the pre-treated effluents able to be fed to a subsequent biological treatment, while obtaining final effluents that accomplish the maximum allowable limits imposed by legislation for discharge into the aquatic environment, at a lower operating cost. So, an economic analysis was also performed, since it is very important to maximize wastewater treatment efficiency while reducing running costs. Up to the author's knowledge, none scientific report in this area has addressed a similar approach, i.e., maximizing treatment efficiency while simultaneously minimizing operating costs.

2. Materials and Methods

2.1 Synthetic Wastewaters Preparation

In this work a real wastewater was not used because its characteristics change dramatically from day to day, which is inherent to the operation mode of textile dye-houses. So, synthetic effluents with composition similar to real wastewaters were prepared in accordance with the information presented in Table 1. Basically, it was taken into account the amount of dyes (Procion Deep Red H-EXL gran, Procion Yellow H-EXL gran, Astrazon Blue FGGL 300%, Dianix Orange K3G and Dianix Blue KFBL) and auxiliaries used in the dyeing baths, and the percentage of these products unfixed by the fibers (rejection percentage). Such information was supplied by the dye-house Erfoc – Acabamentos Têxteis S.A. (Famalicão, Portugal) – and by DyStar Anilinas Têxteis, Unip Ltd (Portugal), allowing thus estimating the concentration of each species in the polyester, acrylic or cotton synthetic effluents.

2.2. Experimental Procedure

Fenton´s oxidation was carried out as follows: a given volume of synthetic dyeing wastewater was put into a batch jacketed reactor. After temperature stabilization (at 50 ºC), the pH was adjusted to 3.5 with 0.5 M H_2SO_4 (from Merck). The catalyst ($FeSO_4.7H_2O$, from Merck) was then added and the reaction started with the addition of H_2O_2 30% (w/v) (Merck). During the reaction the solution was constantly stirred by using a mechanic stirrer (VWR VOS power control, from Germany). After 60 minutes of reaction, the residual hydrogen peroxide was eliminated 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 [27, 28]. Under alkaline conditions, the iron precipitated and was then removed by sedimentation. The supernatant was neutralized (to pH ~7.0) with concentrated H_2SO_4 (from Merck) and then analyzed and/or fed to the SBR (Sequential Batch Reactor).

The pH, temperature and reaction time were fixed at the values that maximize color and DOC removals and improve the biodegradability of the raw wastewaters, which were reached in previous studies where Fenton's oxidation alone was applied to the same effluents [29-31].

The SBR is a jacketed cylinder (20 cm internal diameter, 45 cm total height and 30º slope conical bottom; effective working volume = 5.0 L) connected to a thermostatic bath (Isco GTR 90, from Italy). Figure 1 illustrates the installation set-up. The biological reactor was operated at constant temperature (25 °C) during 12 hours per cycle (1 h for feeding, 6 h of reaction, 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 wastewater with pH previously adjusted to ~7.0 using 1M H_2SO_4 and 10 M NaOH, after adding phosphorus (as phosphate buffer) or nitrogen (as urea) whenever necessary to ensure the minimum quantity required for biological treatment (BOD_5:N:P ratio of 100:5:1). Then 2.5 L of activated sludge (~ 5 g VSS/L) from the aeration tank of the Rabada WWTP (Santo Tirso - Portugal) were added to the reactor, resulting in a final volume of 5.0 L. In 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±1.3 mg O_2/L by aeration using air diffusers. The values of temperature, dissolved oxygen and duration of each cycle and each cycle stage were established in accordance with literature [6,14,23,32-36].

The pH (electrode HI 1332 and pH-meter HI 8720E from Hanna Instruments, Italy), temperature (thermocouple type K) and ORP - Oxidation-Reduction Potential (electrode HI 3230 and mV-meter HI 8711E from Hanna Instruments, Italy) were continuously monitored (cf. Fig. 1). At the end of each cycle, total suspended solids (TSS), biological oxygen demand (BOD_5), chemical oxygen demand

(COD), dissolved organic carbon (DOC), absorbance at a predefined wavelength (which depends on the effluent to be treated), total nitrogen and total phosphorus were determined in the effluent discharged, as detailed in the following section. The content of volatile suspended solids (VSS) was measured, in some cycles, in samples collected inside the reactor.

The data acquisition and the automatic control of the unit, i.e., operation of the peristaltic pumps (Watson-Marlow 502S, England), Burckert valve (from Germany) and mechanical stirrer (VWR VOS power control, Germany), were achieved by using the software Labview 5.0 (National Instruments), through a home-designed interface.

2.3. Analytical Methods

The color of the samples was quantified by measuring the absorbance at the wavelength corresponding to the maximum absorbance of each effluent (610 nm and 520 nm for acrylic and cotton dyeing wastewater, respectively; polyester effluents are colorless), using a molecular absorption spectrophotometer (Pye Unicam, model Helios α, Germany). As the absorbance of the synthetic wastewater varies with pH, this was previously adjusted to the value of the treated effluent.

The biodegradability was evaluated by measuring the specific oxygen uptake rate (SOUR) at 20 ºC. 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, from USA). SOUR ($mgO_2/g_{VSS}.h$) was calculated as the ratio between the oxygen concentration decay rate (which was linear during the above-mentioned period) and the volatile suspended solids (VSS) concentration after the addition of the inoculum (700 mg VSS/L) [36-37].

The inhibition of *Vibrio fischeri* test was performed according to the standard DIN/EN/ISO 11348-3 [38]. The bacteria were put 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 [37]: dissolved organic carbon (DOC) was measured in a TC/TOC analyzer (Shimadzu 5000A, from Japan) - Method 5310 D; the biochemical oxygen demand (BOD_5) was determined according to Method 5210 B; the chemical oxygen demand (COD) was assessed by the open reflux method (Method 5220 B) for acrylic and polyester effluents, as higher dilutions are required due to the high chloride concentration, and by the closed reflux method (Method 5220 D) for the cotton wastewater; and total phosphorus by Method 4500P - E. Total nitrogen was determined by colorimetry according to Method D992-71 from ASTM Standards [39] after previous digestion (Method 4500 - N C). Total suspended solids (TSS) and volatile suspended solids (VSS) were quantified by gravimetry - Method 2540 B and Method 2540 E, respectively. Finally the alkalinity was evaluated by titration with H_2SO_4 at pH 4.5 (Method 2320 D) while the pH was measured using a selective electrode (Hanna Instruments HI 1230) 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.

All analytical determinations were performed in duplicate and the coefficients of variation were less than to 2% for DOC, 8% for BOD_5, 4% for COD and SOUR, 3% for inhibition of *V. fisheri* and 5% for the other parameters.

3. Results and Discussion

The more relevant characteristics of the synthetic acrylic, cotton and polyester dyeing wastewaters used in this study are reported in Table 2. Cotton and acrylic wastewaters are colored even at 1:40 dilution but polyester effluent is practically colorless. The organic load (expressed as COD or DOC) is moderate for all wastewaters but the biodegradability is low as indicated by the BOD_5:COD ratio and the values of SOUR; actually, the acrylic wastewater can be classified as non biodegradable and the other wastewaters can be considered as only slightly biodegradable. Acrylic and polyester effluents strongly inhibit *V. fisheri* activity, which proves their toxicity. Taking into account the low biodegradability and the high toxicity (except for the cotton wastewater), a biological treatment of these wastewaters does not probably allow meeting the discharge limits, as established by the Portuguese legislation (cf. Table 2). Even so, the feasibility of using a biological process (SBR) alone or downstream from a chemical oxidation process (Fenton's reaction) to achieve the discharge limits was investigated in this study. The results obtained when applying this strategy for treating the three different kinds of textile dyeing wastewaters are shown in the next sections.

3.1. Biological Treatment

The biological degradation was only applied to raw polyester and cotton effluents because the acrylic one presents very low biodegradability (BOD_5/COD ratio <0.0012 and SOUR <0.2 mg O_2/g_{VSS}.h (Table 2), also confirmed by the Zhan Wells test (data not shown), which indicated that the degradation obtained after 28 days does not exceed 15%.

Figure 2 shows the COD, BOD_5, DOC, total nitrogen and color removals obtained in 10 successive cycles of SBR treatment of polyester and cotton effluents; no further cycles were applied because nearly steady-state conditions were reached in all cases, i.e., stable performances in consecutive cycles. The polyester effluent exhibits a considerable increase of COD, BOD_5, DOC and total nitrogen removal during the first 5 cycles that continue to increase, albeit more slowly, up to the 7th cycle, and then remain almost constant with average values of 24, 39, 40 and 16% for COD, BOD_5, DOC and nitrogen, respectively. For the cotton effluent the removals also increase during the first 5 cycles and then the removal rate decreases or maintains constant leading to average final values of 20% for COD, BOD_5, and COD and 21% for nitrogen. The low efficiencies achieved can be explained by the presence in the effluents of a significant proportion of refractory or only slightly biodegradable compounds, as could be inferred from the low BOD_5/COD ratios and SOUR values, particularly for the cotton one (cf. Table 2). As regards color removal, in the cotton wastewater the values of absorbance at 520 nm decreased in the first 4 cycles and kept constant in the subsequently cycles, achieving an average value of 51% of decolorization. The removal may be the result of some biological degradation of the textile dyes present in the effluent but the adsorption onto the biomass flocs probably also contributes for color elimination [40]. The color removal obtained for cotton wastewater is similar to that reported by Vaigan et al. [41]. These authors achieved color removals of 31-57% when treating 20 to 40 mg/L of reactive Blue B-16, respectively, in an SBR.

With regard to other monitored parameters, whose values are not presented in Fig. 2, it was noted that during all SBR cycles the concentrations in the treated effluents were in the range 2.4 - 2.9 mg P/L, 22 – 29 mg TSS/L and 2530-2970 mg VSS/L for the polyester effluent and 5.7 - 5.9 mg P/L, 27 - 32 mg TSS/L and 2350-2680 mg VSS/L for the cotton one.

The pseudo-steady state was reached after ca. 7 cycles for both cotton and polyester effluents. Table 2 presents the average values of different parameters after reaching the pseudo-steady state. It can be concluded that the effluents resulting from biological treatment do not meet the discharge limits, since the valuesof COD (392.4 and 280.4 mg/L for polyester and cotton, respectively) are above 250 mg/L and the color of the cotton effluent is visible after 1:40 dilution. So, a pre-treatment or subsequent treatment is required. We choose to apply the chemical oxidation by Fenton's reagent as pre-treatment to enhance the biodegradability and remove color and, then, subject the wastewater to biological treatment. The results obtained from the combined process are presented in the following section.

3.2. Integration of Fenton's Reagent followed by Biological Treatment

As the oxidation process allows increasing the biodegradability of the acrylic and cotton effluents while reducing the toxicity of the acrylic and polyester effluents, as shown below (cf. Tables 3-5), the combination of Fenton reaction with the biological oxidation in SBR was studied. Aiming reducing the doses of chemicals, and inherently the operating costs (described in the following section), three experiments were performed, i.e., the preliminary Fenton reaction stage was performed with different doses of reagents. The 1st run was performed at the best conditions for maximizing color and DOC removals and improving biodegradability already determined in previous studies [29-31], for effluents that have exactly the same composition as those used in this work: $[H_2O_2]$=20 g/L and $[Fe^{2+}]$=350 mg/L for acrylic, $[H_2O_2]$=10 g/L and $[Fe^{2+}]$=300 mg/L for cotton and $[H_2O_2]$=2.5 g/L and $[Fe^{2+}]$=350 mg/L for polyester wastewaters, all at pH 3.5 and 50 ºC. In runs #2 and #3 the doses of hydrogen peroxide and ferrous iron were reduced to 3/4 and 1/2 for acrylic and 1/2 and 1/4 for polyester and cotton effluents, respectively, with the aim of decreasing the treatment cost (associated with the consumption of chemicals in the Fenton's process) while obtaining a final effluent that should meet the discharge limits imposed by the national legislation for the textile industry.

Results obtained during the Fenton's oxidation stage have been reported previously (in the works mentioned above) and only overall performances reached are described herein – run #1 in Tables 3, 4 and 5 for the acrylic, cotton and polyester effluents, respectively. It is noteworthy that the selected H_2O_2 concentrations are high, particularly for the acrylic and cotton wastewaters (20 and 10 g/L, respectively). The effluents under study are medium-strength ones (in terms of organic matter) but rather complex as concerns the inorganic content. So, unwanted parallel reactions (e.g. $HO^{\bullet}$ scavenging by chlorides, sulfates and carbonates, etc.) take place and therefore an excess of oxidant is required [29-31].

Regarding the results obtained in the SBR, Figure 3 shows the removal performances obtained, in terms of COD, BOD_5, DOC, total nitrogen and color for the acrylic wastewater. It can be observed that removals increased during the first 4 cycles, although the improvement is more notorious in the 1st and 2nd runs; therefore, we can say that the pseudo-steady state was reached at end of 4-5 cycles. After reaching the pseudo-steady sate, the average removals achieved in the SBR for the parameters analyzed are higher in run #1 (95, 95, 95, 45 and 68% for COD, BOD_5, DOC, total nitrogen and color, respectively), followed by run #2 (65, 85, 72, 42 and 69% for COD, BOD_5, DOC, total nitrogen and color, respectively) and then by run #3 (22, 69, 17, 23 and 72% for COD, BOD_5, DOC, total nitrogen and color, respectively). The reason is that from run #1 to run #3 less chemicals were used in the Fenton's stage, so that the effluent fed to the SBR is less biodegradable (cf. Table 3). In runs #1 and #2 it was possible to reach, after the integrated treatment, an effluent that is ready for discharge into water bodies – see Table 3. On the other hand, although in run #3 less chemicals were employed in the Fenton's stage as compared to run #2, it was not possible to fulfill the limits imposed by the national legislation for the discharge of textile effluents, namely in terms of COD (cf. Table 3).

The removals obtained during 10 cycles of SBR for the cotton effluent previously treated by Fenton's oxidation are shown in Figure 4. During the first 6 cycles an increase was observed for all runs, and then the removals remain nearly constant, which means that the pseudo-steady state was reached. In runs #1 and #2 the average values of COD, BOD_5 and visible color (after dilution of 1:40) at the outlet of the SBR, during the last 4 cycles of operation, are smaller than the maximum allowable discharge values (see Table 4). This is however not the case of run #3, in which very low doses of chemicals were used in the Fenton's oxidation (25% of those employed in run #1); thus, final effluent shows COD values not complying with the legislated standard.

As far as concerns the polyester dyeing wastewater biological treatment, 6-7 cycles are needed for reaching the pseudo-steady state (cf. Figure 5), after the Fenton's oxidation. The average removal values achieved after 7 cycles are higher in the 1st run (80, 82, 80 and 19% for COD, BOD_5, DOC and total nitrogen, respectively), followed by the 2nd one (64, 63, 66 and 19% for COD, BOD_5, DOC and total nitrogen, respectively) and then by 3rd one (31, 48, 46 and 16% for COD, BOD_5, DOC and total nitrogen, respectively); this is the order of decreased doses of chemicals in the previous chemical oxidation process. Again, the wastewater resulting from the SBR operating in the conditions used in runs #1 and #2 can be discharged into water bodies, because the values of the legislated parameters are smaller than the discharge limits for the textile industry (see Table 5).

The high overall COD and color removal efficiencies obtained in run#1, for the three effluents, are very similar to those reported by Tantak and Chaudhari [20] (> 95% for color vs. > 98% in our work, and in the range 78-86% for COD vs. 88-98% in our work); such authors treated, by Fenton´s oxidation and SBR, aqueous solutions of textile dyes (Reactive Black 5, Reactive Blue 13 and Acid Orange 7).

3.3. Costs Evaluation

The overall costs of the treatment process are represented by the sum of the capital, operating and maintenance costs. For a full-scale system these costs depend on the flow rate of the effluent, the nature of the wastewater, as well as on the configuration of the reactor(s). Moreover, the neutralization of pre-treated effluent by the Fenton process generates chemical sludge. The costs associated with the deposition of the sludge were not accounted for because they can vary considerably, depending on the treatment processes adopted (thickening / conditioning / drying) and on the price to landfill the industrial waste. So, in this study, we considered only the costs with chemicals: ferrous sulfate and hydrogen peroxide, as well as the acid and base required for acidification (0.01, 0.11 and 0.63 €/m^3 for acrylic, polyester and cotton effluents, respectively) and subsequent neutralization (0.01 €/m^3 for acrylic, 0.19 €/m^3 for polyester and 1.09 €/m^3 for cotton effluents, respectively), and energy consumed in agitation (power required = 0.61 W) and air insufflation (power required = 4.5 W) in the SBR stage.

The costs of reagents used in the Fenton's stage were obtained from Quimitécnica S.A. (Portugal) and the average values considered were as follows: H_2O_2 (49.5% w/v, density at 25 ºC = 1.2 g/cm^3) – 365 €/ton; $FeSO_4.7H_2O$ (93% of purity) – 233.7 €/ton; H_2SO_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.

Figure 6 shows the total operating cost of the Fenton's oxidation alone, biological treatment and the combination of both techniques, considering the conditions of runs #1, #2 and #3 mentioned above. The inclusion of a pre-treatment (Fenton´s reaction) led to a significant increase in the operating costs (overall cost for the different runs amounting to values in the range 2.2 - 4.2 and 5.2 - 12.1 €/m^3 in the combination Fenton+SBR for polyester and cotton, respectively, compared with 1.2 €/m^3 in SBR alone). However, the biological treatment directly applied to the effluents does not allow meeting the discharge limits. As could be expected, in the integrated process (chemical and biological oxidation), the costs raised when increasing the doses of the reagents used in the Fenton stage (higher in run #1, for all effluents).

Since the objective of this study was to obtain an effluent complying with the discharge limits after treatment (runs #1 and #2 for the acrylic, cotton and polyester effluents) at the lowest treatment cost, the selected operating conditions were those of run# 2 for acrylic (total cost of 14.8 €/m^3), cotton (7.5 €/m^3) and polyester (2.9 €/m^3) wastewaters, using an integrated process of Fenton' oxidation and SBR. The operating costs are associated with the consumption of hydrogen peroxide and iron in the oxidative process, which follows the order: acrylic > cotton > polyester. The hydrogen peroxide consumption is associated with the larger amount of organic matter (acrylic has higher values of COD and DOC), but also with the high content of chlorides (~ 9 g / L in the cotton effluent).

The total costs of the integrated process (run# 2) are smaller than those corresponding to the Fenton's reaction alone (18.1, 10.9 and 2.7 €/m^3 for acrylic, cotton and polyester effluents, respectively), which, even so, did not allowed per se obtaining effluents respecting legislated standards.

4. Conclusions

The treatability of synthetic acrylic, cotton and polyester dyeing wastewaters by SBR and an integrated process consisting of Fenton's reaction and SBR was investigated. It was found that the biological degradation in SBR per se did not allow obtaining effluents complying with the discharge limits, the same applying for the chemical oxidation stage when used alone. Fenton's oxidation improved the biodegradability of all dyeing wastewaters while reducing their toxicity, which allows its integration with a biological treatment. The application of Fenton's process in optimized conditions followed by biological oxidation (SBR) provided effluents that comply with discharge limits, with global organic matter removals of 98, 88 and 91% for COD, 95, 83 and 91% for BOD_5 and 98, 92 and 91% for DOC, for acrylic, cotton and polyester wastewaters, respectively, and almost complete color reduction (>99%). Under such conditions total operating costs are significant: 19.4 €/m^3 for acrylic, 12.2 €/m^3 for cotton and 4.2 €/m^3 for polyester. However, the operating costs might be decreased by reducing the H_2O_2 and Fe^{2+} doses without compromising compliance with discharge limits. The use of the lowest doses of reagents that allowed meeting the discharge limits led to operating costs of 14.8, 7.5 and 2.9 €/m^3 for acrylic, cotton and polyester effluents, respectively. These costs represent a reduction of 24-39% as regards the application of Fenton's oxidation alone.

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

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

* Percentage of dyes and auxiliary products not fixed by the fibers.

Table 2 – Characteristics of the synthetic dyeing raw wastewaters and after SBR treatment and respective removal efficiencies.

Parameter	**Acrylic**	**Polyester**			**Cotton**			**Maximum Allowable Value***
	Raw Wastewater	**Raw Wastewater**	**After SBR**	**Removal (%)**	**Raw Wastewater**	**After SBR**	**Removal (%)**	
pH	6.8	8.3		---	11.4		---	5.5-9.0
Conductivity at 20 ºC (mS/cm)	1503.0	2.9	n.d.	---	23.2	n.d.	---	
Total suspended solids (mg/L)	16.0	21.7	25.1		67.0	28.3		
Total nitrogen (mg N/L)	16.4	15.9	13.3	16	3.9	3.1	21	
Nitrates (mg NO_3^-/L)	15.7	7.5	n.d.	---	4.25	n.d.	---	
Total phosphorus (mg P/L)	0.2	3.0	2.4	20	5.9	5.7	3	
Dissolved phosphorus (mg P/L)	< 0.06	2.7	n.d.	---	0.1	n.d.	---	
COD – Chemical oxygen demand (mg O_2/L)	828.1	517.9	392.4	24	350.0	280.4	20	250
BOD_5 – Biochemical oxygen demand (mg O_2/L)	< 1.0	130.7	79.1	39	77.5	62.3	20	100
DOC – Dissolved organic carbon (mg C/L)	334.1	143.1	86.3	40	117.5	94.1	20	
Sulfates (mg/L)	598.0	885.8	n.d.	---	41.0	n.d.	---	
Chlorides (mg Cl^-/L)	44.1	17.3	n.d.	---	7981.8	n.d.	---	
Alkalinity (mg $CaCO_3$/L)	51.8	774.4	n.d.	---	4425.0	n.d.	---	
SOUR – Specific oxygen uptake rate (mg O_2/(g_{VSS} .h))	< 0.2	27.0	n.d.	---	5.6	n.d.	---	
BOD_5:COD ratio	< 0.0012	0.26	0.20	---	0.22	0.22	---	
Maximum absorbance wavelength, λ_{max} (nm)	610	---	n.d.	---	520	n.d.		
Absorbance at λ_{max} (a.u.)	1.592	---	n.d.	---	0.437	0.179	51**	
Visible color after dilution 1:40	visible	not visible	not visible	---	visible	visible	---	not visible
Vibrio fischeri Inhibition 5 min (%)	94.0	74.5	n.d.	---	0.0	n.d.	---	
Vibrio fischeri Inhibition 15 min (%)	96.0	82.5	n.d.	---	0.0	n.d.	---	
Vibrio fischeri Inhibition 30 min (%)	97.0	84.5	n.d.	---	0.0	n.d.	---	

n.d. – not determined

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

** calculated from the absorbance of raw wastewater at pH 7.0 (0.3617 abs. units)

Table 3 – Characteristics of the synthetic acrylic dyeing wastewaters after Fenton reaction and SBR and respective removal efficiencies (within brackets) and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

Parameter	**Run #1 – Optimal dose of chemicals**			**Run #2 – 0.75 of optimal dose of chemicals**			**Run #3 – 0.5 of optimal dose of chemicals**			**Maximum Allowable Value***
	Fenton (removal (%))	**SBR (removal (%))**	**Global Removal (%)**	**Fenton (removal (%))**	**SBR (removal (%))**	**Global Removal (%)**	**Fenton (removal (%))**	**SBR (removal (%))**	**Global Removal (%)**	
pH	7.10	7.15	---	7.06	7.09	---	7.01	6.98	---	5.5-9.0
Total nitrogen (mg N/L)	16.0 (2)	8.8 (45)	46	16.1 (2)	9.3 (42)	43	16.3 (2)	12.4 (23)	24	
Total phosphorus (mg P/L)	0.2 (0)	0.61 (47**)	48	0.2 (0)	0.20 (75**)	75	0.2 (0)	0.16 (68**)	68	
COD (mg O_2/L)	289.0 (65)	14.6 (95)	98	294.5 (64)	104.3 (65)	87	349.7 (58)	273.7 (22)	67	250
BOD_5 (mg O_2/L)	116.5	6.4 (95)	95	78.8	12.0 (85)	85	46.8	14.5 (69)	69	100
DOC (mg C/L)	112.0 (66)	5.4 (95)	98	124.7 (63)	34.5 (72)	90	132.3 (60)	109.3 (17)	67	
SOUR – Specific oxygen uptake rate (mg O_2/(g_{VSS} .h))	17.9	n.d.	---	10.2	n.d.	---	2.7	n.d.	---	
BOD_5:COD ratio	0.40	0.46	---	0.27	0.12	---	0.13	0.05	---	
Absorbance at λ_{max} (a.u.)	0.0079 (99***)	0.0025 (68****)	≥99	0.0080 (99***)	0.0025 (69****)	≥99	0.0089 (99***)	0.0025 (72****)	≥99	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
Vibrio fischeri Inhibition 5 min (%)	29	n.d.	---	38	n.d.	---	77	n.d.	---	
Vibrio fischeri Inhibition 15 min (%)	27	n.d.	---	41	n.d.	---	81	n.d.	---	
Vibrio fischeri Inhibition 30 min (%)	29	n.d.	---	41	n.d.	---	82	n.d.	---	

n.d. – not determined

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

** calculated from total phosphorus in effluent after Fenton reaction after adding phosphate buffer (1.17, 0.79, 0.5 mg P/L in run #1, #2, #3, respectively)

*** calculated from the absorbance at 610 nm of raw wastewater at pH 3.5 (1.624 abs. units)

**** calculated from the absorbance at 610 nm of wastewater after Fenton at pH 7.0 (0.0079, 0.0080 and 0.0089 abs. units in run #1, #2 and #3, respectively)

Table 4 – Characteristics of the synthetic cotton dyeing wastewater after Fenton reaction and SBR and respective removal efficiencies (within brackets) and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

Parameter	**Run #1– Optimal dose of chemicals**			**Run #2 – 0.5 of optimal dose of chemicals**			**Run #3 – 0.25 of optimal dose of chemicals**			**Maximum Allowable Value***
	Fenton (removal (%))	**SBR (removal (%))**	**Global Removal (%)**	**Fenton (removal (%))**	**SBR (removal (%))**	**Global Removal (%)**	**Fenton (removal (%))**	**SBR (removal (%))**	**Global Removal (%)**	
pH	6.99	7.05	---	7.04	7.10	---	7.09	7.03	---	5.5-9.0
Total nitrogen (mg N/L)	3.9 (0)	1.2 (82)	82	3.9 (0)	2.1 (63)	63	3.8 (3)	3.7 (16)	18	
Total phosphorus (mg P/L)	5.9 (0)	4.8 (19)	19	5.9 (0)	5.2 (12)	12	5.8 (2)	5.6 (3)	5	
COD (mg O_2/L)	262.1 (25)	43.2 (84)	88	281.9 (20)	113.2 (60)	68	318.6 (9)	261.8 (18)	25	250
BOD_5 (mg O_2/L)	135.7 (0)	22.8 (83)	83	112.9 (0)	45.1 (60)	60	88.0 (0)	72.3 (18)	18	100
DOC (mg C/L)	60.2 (49)	9.95 (84)	92	94.1 (20)	37.6 (60)	68	100.3 (15)	82.0 (18)	30	
SOUR – Specific oxygen uptake rate (mg O_2/(g_{VSS} .h))	15.51	n.d.	---	8.11	n.d.	---	2.54	n.d.	---	
BOD_5:COD ratio	0.52	0.53	---	0.40	0.40	---	0.33	0.28	---	
Absorbance at λ_{max} (a.u.)	0.0331 (90***)	0.0037 (87****)	99	0.0310 (91***)	0.0053 (82****)	98	0.0349 (89***)	0.0126 (67****)	96	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
Vibrio fischeri Inhibition 5 min (%)	0.0	n.d.	---	0.0	n.d.	---	0.0	n.d.	---	
Vibrio fischeri Inhibition 15 min (%)	0.0	n.d.	---	0.0	n.d.	---	0.0	n.d.	---	
Vibrio fischeri Inhibition 30 min (%)	0.0	n.d.	---	0.0	n.d.	---	0.0	n.d.	---	

n.d. – not determined

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

** calculated from total phosphorus in effluent after Fenton reaction after adding urea (6.8, 5.6, 4.4 mg N/L in run #1, #2, #3, respectively)

*** calculated from the absorbance at 520 nm of raw wastewater at pH 3.5 (0.3615 abs. units)

**** calculated from the absorbance at 520 nm of wastewater after Fenton at pH 7.0 (0.0276, 0.0293 and 0.0368 abs. units in run #1, #2 and #3, respectively)

Table 5 – Characteristics of the synthetic polyester dyeing wastewaters after Fenton reaction and SBR and respective removal efficiencies (within brackets), and global removals. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage.

Parameter	**Run #1 – Optimal dose of chemicals**			**Run #2 – 0.5 of optimal dose of chemicals**			**Run #3– 0.25 of optimal dose of chemicals**			**Maximum Allowable Value***
	Fenton (removal (%))	**SBR (removal (%))**	**Global Removal (%)**	**Fenton (removal (%))**	**SBR (removal (%))**	**Global Removal (%)**	**Fenton (removal (%))**	**SBR (removal (%))**	**Global Removal (%)**	
pH	7.05	7.10	---	7.11	7.08	---	7.15	7.10	---	5.5-9.0
Total nitrogen (mg N/L)	15.1 (5)	12.3 (19)	23	15.3 (4)	12.4 (19)	22	15.9 (0)	13.3 (16)	16	
Total phosphorus (mg P/L)	2.8 (7)	2.2 (20)	25	2.9 (3)	2.2 (23)	25	3.0 (0)	2.4 (20)	20	
COD (mg O_2/L)	221.1 (57)	44.4 (80)	91	291.7 (44)	104.3 (64)	80	389.7 (25)	267.7 (31)	48	250
BOD_5 (mg O_2/L)	62.8 (52)	11.4 (82)	91	80.2 (39)	29.4 (63)	78	103.8 (21)	54.3 (48)	58	100
DOC (mg C/L)	63.4 (56)	12.6 (80)	91	80.6 (44)	27.7 (66)	81	106.9 (25)	58.1 (46)	59	
SOUR – Specific oxygen uptake rate (mg O_2/(g_{VSS} .h))	30.0	n.d.	---	29.0	n.d.	---	28	n.d.	---	
BOD_5:COD ratio	0.28	0.26	---	0.28	0.28	---	0.27	0.20	---	
Visible color after dilution 1:40	not visible	not visible	---	not visible	not visible	---	not visible	not visible	---	not visible
Vibrio fischeri Inhibition 5 min (%)	0.0	n.d.	---	10.4	n.d.	---	43.3	n.d.	---	
Vibrio fischeri Inhibition 15 min (%)	0.0	n.d.	---	15.0	n.d.	---	55.8	n.d.	---	
Vibrio fischeri Inhibition 30 min (%)	0.0	n.d.	---	17.6	n.d.	---	59.4	n.d.	---	

n.d. – not determined

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

Figures captions

Figure 1 - Diagram of the SBR set-up.

Figure 2 - Variation of COD (a), BOD_5 (b), DOC (c), total nitrogen (d) and color removals during 10 cycles of SBR operation for polyester and cotton wastewaters (concentrations in the raw effluents are given in Table 2).

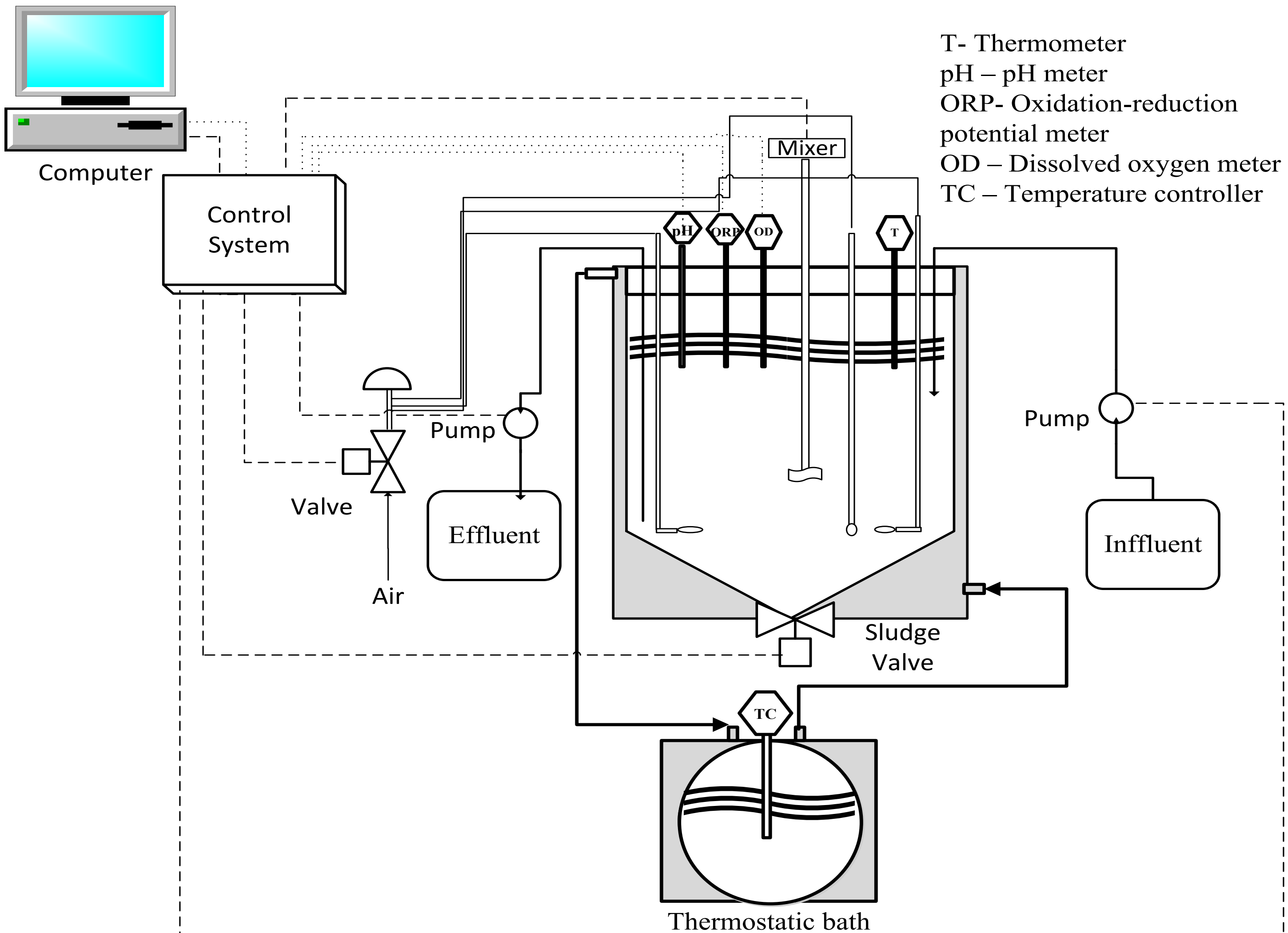
Figure 3 - Variation of COD, BOD_5, DOC, total nitrogen and color removals during 10 cycles of SBR operation for acrylic effluent, previously treated by Fenton's oxidation. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage (concentrations in the starting effluent are given in Table 3).

Figure 4 - Variation of COD, BOD_5, DOC, total nitrogen and color removals during 10 cycles of SBR operation for synthetic cotton dyeing effluent, previously treated by Fenton's reaction. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage (concentrations in the starting effluent are given in Table 4).

Figure 5 - Evolution of COD, BOD_5, DOC and total nitrogen removals during 10 cycles of SBR operation for polyester dyeing wastewater, previously treated by Fenton's reaction. Runs#1 to #3 represent experiments with decreasing doses of chemicals in the Fenton's stage (concentrations in the starting effluent are given in Table 5).

Figure 6 - Total operating costs for biological, Fenton alone and integrated treatment of acrylic, cotton and polyester dyeing wastewaters.

Figure 1



Computer
Control System
Mixer
T- Thermometer
pH – pH meter
ORP- Oxidation-reduction potential meter
OD – Dissolved oxygen meter
TC – Temperature controller
pH
ORP
OD
T
Pump
Valve
Air
Effluent
Pump
Inffluent
Sludge Valve
TC
Thermostatic bath

Figure 2

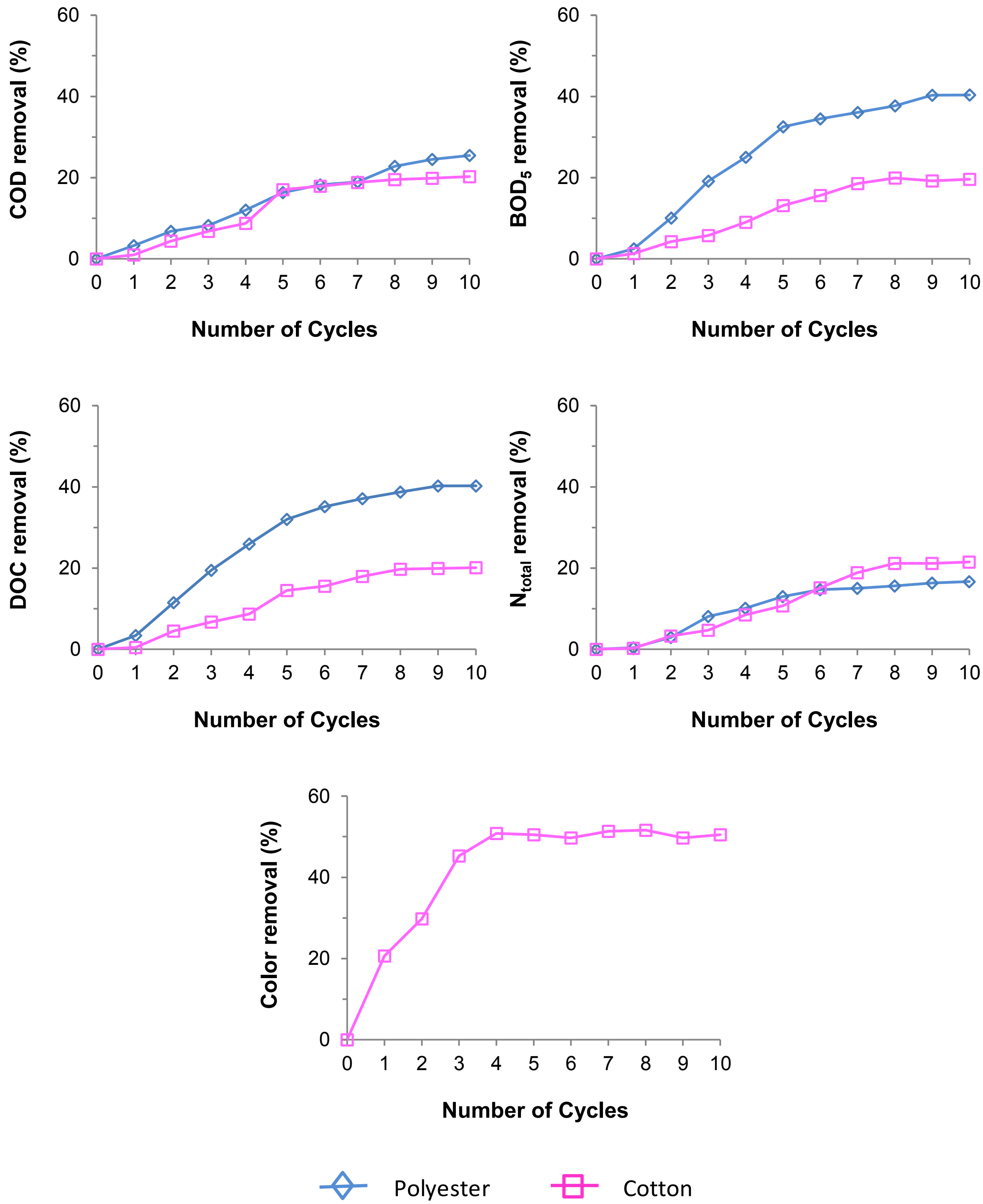

COD removal (%)
BOD5 removal (%)
DOC removal (%)
Ntotal removal (%)
Color removal (%)
Number of Cycles
0
20
40
60
0 1 2 3 4 5 6 7 8 9 10
Polyester
Cotton

Figure 3

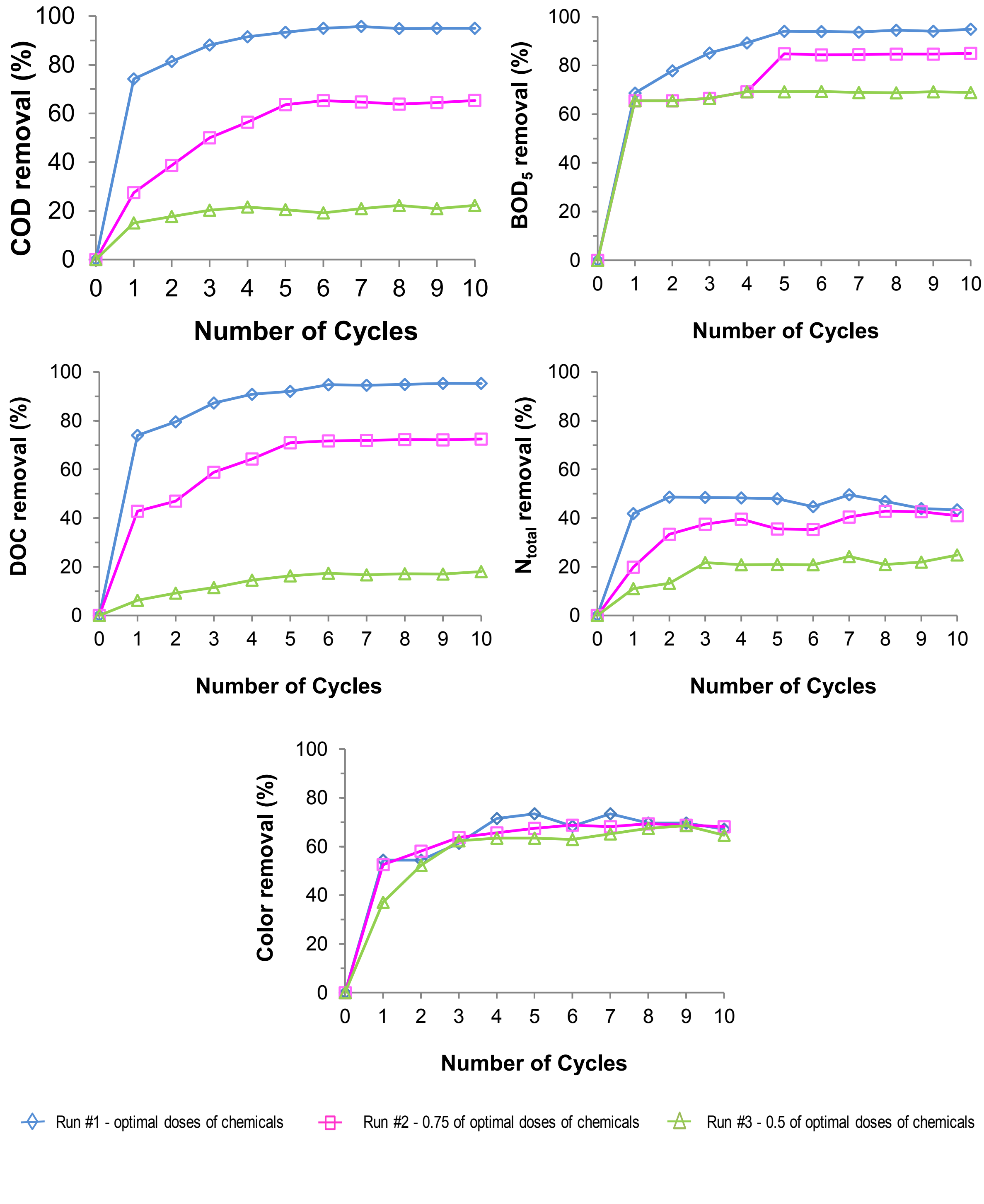

100
80
60
40
20
0
0 1 2 3 4 5 6 7 8 9 10
COD removal (%)
Number of Cycles
BOD5 removal (%)
Number of Cycles
DOC removal (%)
Number of Cycles
Ntotal removal (%)
Number of Cycles
Color removal (%)
Number of Cycles
Run #1 - optimal doses of chemicals
Run #2 - 0.75 of optimal doses of chemicals
Run #3 - 0.5 of optimal doses of chemicals

Figure 4

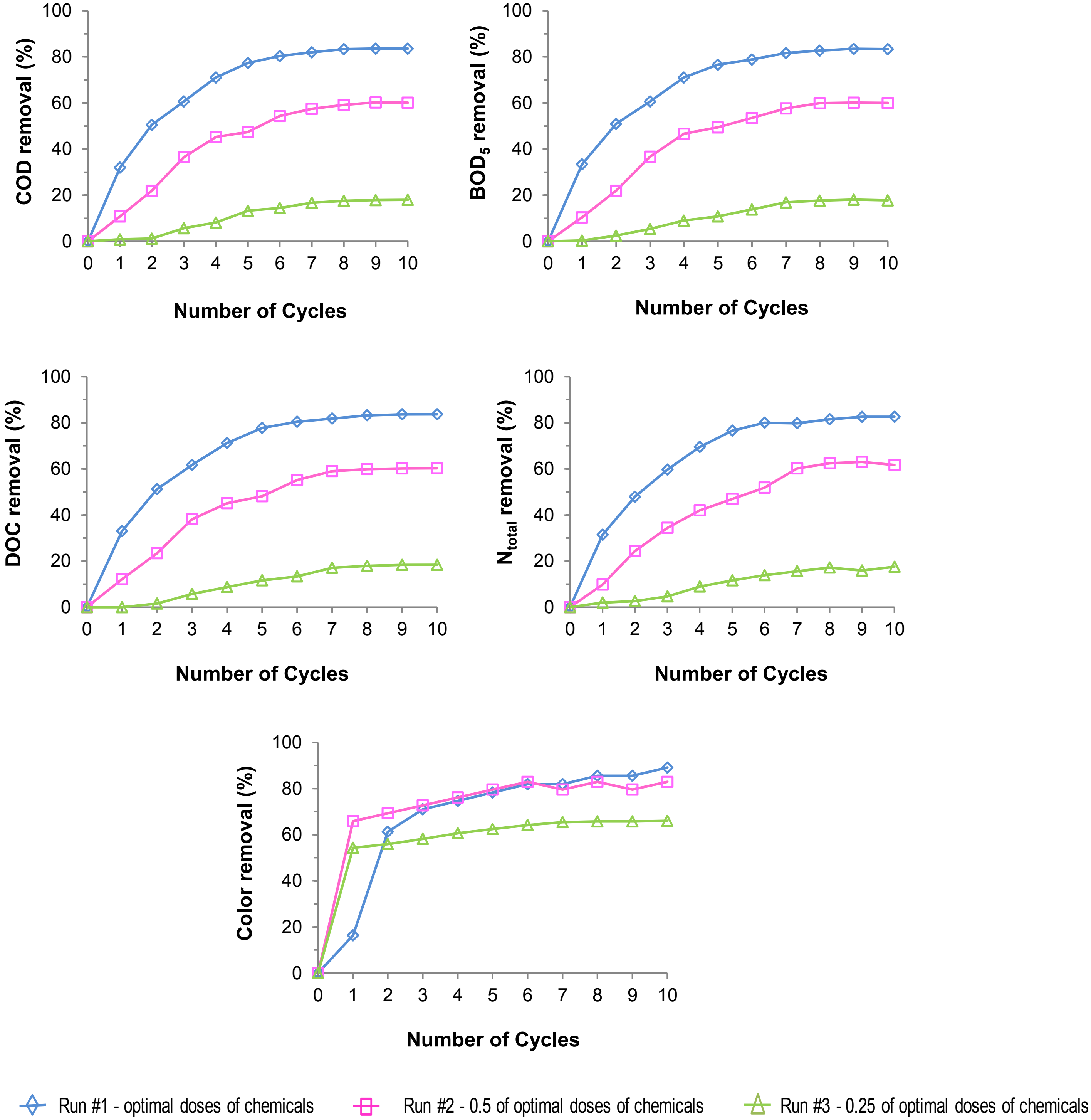

COD removal (%)
Number of Cycles
BOD5 removal (%)
Number of Cycles
DOC removal (%)
Number of Cycles
Ntotal removal (%)
Number of Cycles
Color removal (%)
Number of Cycles
Run #1 - optimal doses of chemicals
Run #2 - 0.5 of optimal doses of chemicals
Run #3 - 0.25 of optimal doses of chemicals

Figure 5

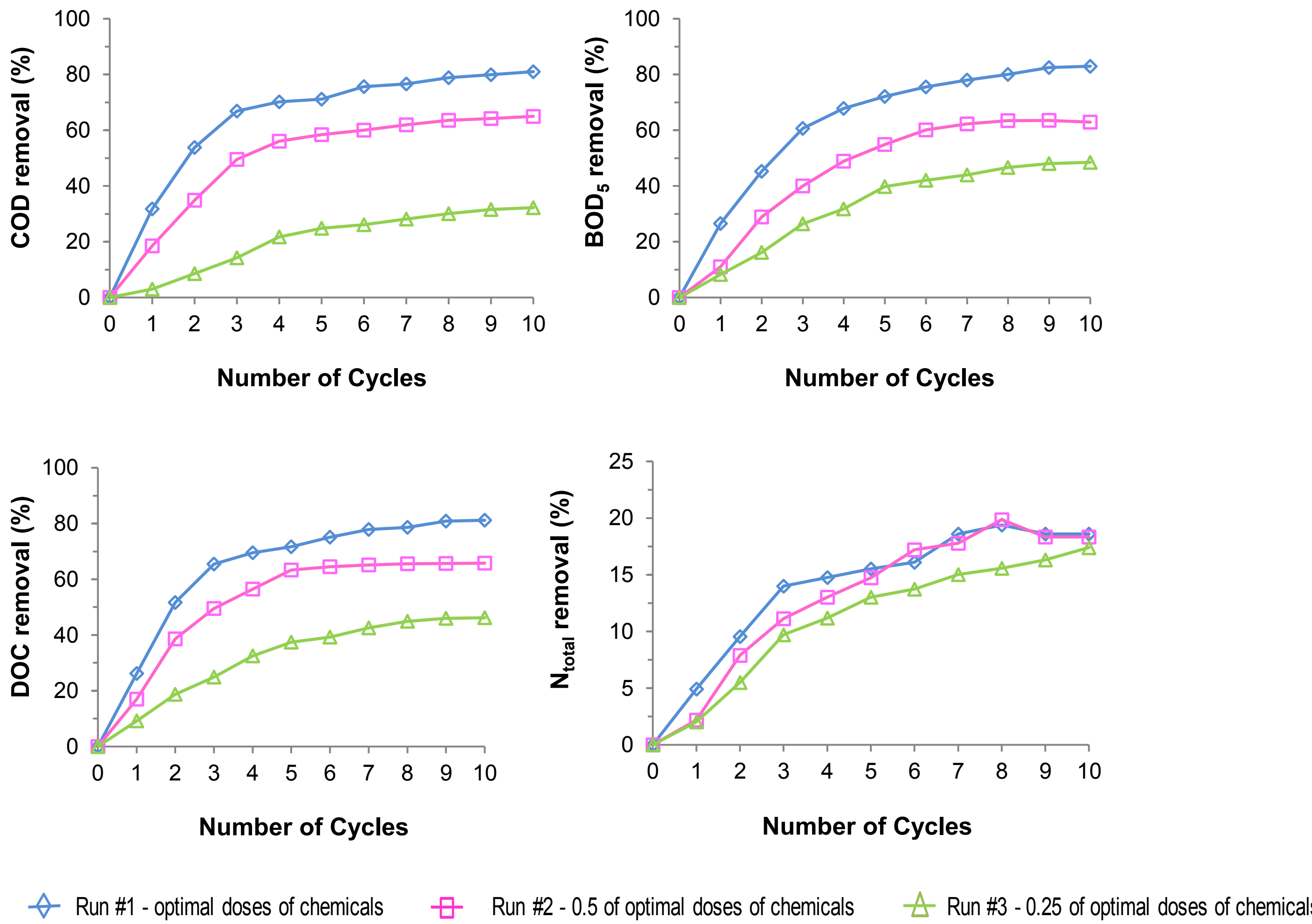
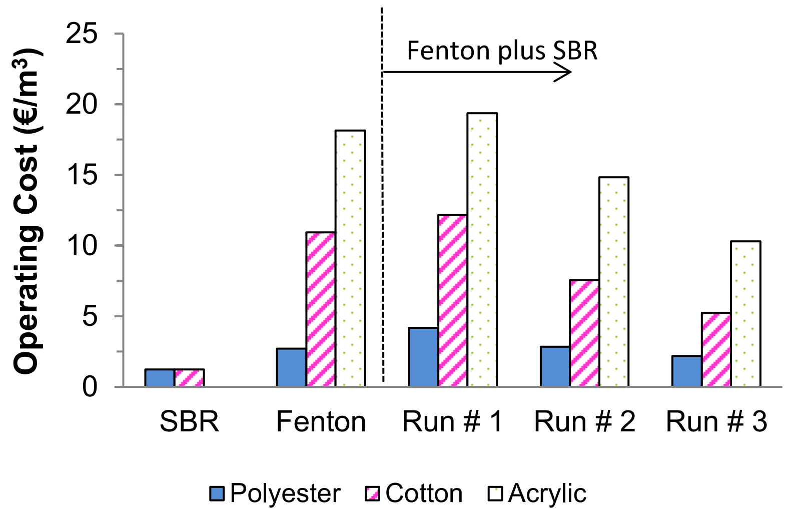

COD removal (%)
Number of Cycles
BOD5 removal (%)
Number of Cycles
DOC removal (%)
Number of Cycles
Ntotal removal (%)
Number of Cycles
Run #1 - optimal doses of chemicals
Run #2 - 0.5 of optimal doses of chemicals
Run #3 - 0.25 of optimal doses of chemicals

Figure 6


Operating Cost (€/m³)
25
20
15
10
5
0
Fenton plus SBR
SBR
Fenton
Run # 1
Run # 2
Run # 3
Polyester
Cotton
Acrylic