# PHOTO-FENTON, COUPLED BIOLOGICAL-PHOTO-FENTON AND REVERSE OSMOSIS PROCESSES FOR TEXTILE WASTEWATER RECLAMATION: FEASIBILITY OF USE IN DYEING PROCESSES

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#### ABSTRACT

Both photo-Fenton oxidation and the combination of aerobic Sequencing Batch Reactor (SBR) + photo-Fenton oxidation were investigated in a bench-scale study to degrade and reuse, a real textile wastewater with TOC = 390 mg·L<sup>-1</sup>, COD = 1560 mg·L<sup>-1</sup> O<sub>2</sub> and *Escherichia coli* =  $80000 \text{ CFU} \cdot \text{mL}^{-1}$ , for dyeing processes according to RD 1620/2007 (Spanish Normative for wastewater reclamation and reuse) and required water qualities for internal reuse. The independent variables considered for the optimization of the oxidative process were temperature,  $H_2O_2$  and Fe (II) concentrations. The best results were obtained when applying photo-Fenton process as a polishing step. In this case, the previous aerobic biological treatment conducted by using a SBR with HRT = 1 day, gave 75 % TOC reduction after 25 cycles. Subsequently, the coupled photo-Fenton process applied under optimal conditions ([Fe (II) = 66.5 mg·L<sup>-1</sup>;  $[H_2O_2] = 1518 \text{ mg} \cdot \text{L}^{-1}$ ; T = 25 °C and pH = 2.7) gave final COD and TOC reductions of 97 and 95 % respectively; Escherichia coli accomplished RD 1620/2007. However, this treated water could not be 100% used and was further conditioned by reverse osmosis accomplishing suitable water qualities for internal reuse. This resultant water was used in dyeing processes and gave similar dyeing results in terms of K/S than those obtained by using fresh water.

**Keywords:** Textile wastewater treatment and reuse; photo-Fenton treatment; Biological + photo-Fenton treatment; reverse osmosis; dyeing processes; *Escherichia coli* removal

#### **1. Introduction**

The textile industry is known to be one of the extremely water and energy intensive consuming industries, causing intense pollution. Indeed, the impact of textile effluents on aquatic medium has been traditionally of great concern because they contain high concentrations of salts, total suspended solids, colour, Chemical Oxygen Demand (COD), nutrients and toxic compounds such as surfactants, heavy metals, and chlorinated organic compounds [1]. In addition, the release of such coloured effluents into the environment is a dramatic source of aesthetic pollution, causing important perturbation in aquatic life.

The physical, chemical and mostly biological technologies have been widely used to treat textile effluents. However, most of textile effluents are not amenable to common chemical or biological treatments [2, 3]. In this sense, the increased public concern and the stringent international environmental standards (Water Framework Directive 2000/60/EC) have prompted the need to develop novel treatment methods for managing wastewater and preserving the ecosystem from persistent pollutants release.

Advanced Oxidation Processes (AOPs) are powerful technologies for the remediation of wastewaters containing recalcitrant organic pollutants [4]. Although AOPs include different reacting systems, their mechanisms are basically characterised by the in situ generation of highly reactive and non selective hydroxyl radicals (HO•,  $E^{\circ} = 2.8 V$  versus NHE), able to oxidise and mineralise almost all organic compounds to CO<sub>2</sub> and inorganic ions. Among available AOPs, the Fenton and photo-Fenton processes are of special interest because they offer high reaction yields with a low treatment cost [5]. In

dark Fenton reaction (equation (1),  $H_2O$  ligands on iron sphere coordination are omitted in the successive), hydroxyl radicals are generated by interaction of  $H_2O_2$  with ferrous salts. Generated Fe (III) can be reduced by reaction with exceeding  $H_2O_2$  to form again ferrous ion in a catalytic mechanism (equations (2) and (3)) [6]:

$$Fe (II) + H_2O_2 \rightarrow Fe (III) + HO + HO$$
(1)

$$Fe (III) + H_2O_2 \rightarrow HO_2 + Fe (II) + H^+$$
(2)

$$Fe (III) + HO_2 \rightarrow Fe (II) + O_2 + H^+$$
(3)

Radiation can play different roles that lead to an improvement of the reaction yields. It drives photo-Fenton reaction by means of ferric aquo complexes photolysis, producing extra HO· and the recovery of Fe (II) needed in Fenton reaction (equation (4), being [Fe (III) HO]<sup>2+</sup> the dominant ferric species in solution at pH = 2-3) [7]. The irradiated process may also involve photolysis of a Fe (III) - H<sub>2</sub>O<sub>2</sub> complex to form high-valent Fe intermediates, which can directly oxidize organic matter. Moreover, it can drive ligand to metal charge transfer in the potentially photolabile complexes formed by Fe (III) and organic compounds (equation (5)), a process that has been well proven for the complexes formed between Fe (III) and the carboxylic acid moiety [8]. In photo-Fenton system, as in the dark process, iron acts as a catalyst and the rate-limiting step is the regeneration of ferrous ion.

$$[Fe (III) HO]^{2+} \xrightarrow{\mathbf{h}\upsilon} Fe (II) + HO$$

$$[Fe (III) L]^{2+} \xrightarrow{\mathbf{h}\upsilon} Fe (II) + L \cdot \qquad (L = \text{organic ligand})$$
(5)

However, owing to water scarcity and tighter international regulations, an increasing development of new water management policies has appeared in the last years. These new policies are in accordance with the guidelines set by the Water Framework Directive, which suggest the reuse as a further step to water treatment to obtain new sources of water. In consequence, an important challenge of textile industry will be the wastewater treatment and reuse to overcome environmental impact associated to the sector [9].

Nowadays, the quality of water for reuse is regulated by guidelines and specific regulations [10-12]. According to Spanish RD 1620/2007 (Spanish Normative for wastewater reclamation) [12], different chemical and microbiological parameters need to be controlled in order to assess suitable water quality for reuse. Among these parameters, we can find Suspended Solids, Turbidity, *Legionella spp* and *Escherichia Coli*. Moreover, the specific final use of each reclaimed water (for instance, reclaimed water for dyeing processes in our specific case) implies the control of some additional specific parameters. The control of iron content is an important parameter in textile industry that should be also considered.

In order to achieve this goal, we can find different technologies to treat textile effluents in the literature. Most of these technologies include the use of membranes, often combined with other treatments [13-16]. This combination of different processes is usually required in order to obtain an effluent with the required final quality for reuse. In this frame, Advanced Oxidation Processes alone or in combination with biological treatments and/or membranes technologies arise as very promising alternatives for real wastewater treatment and reuse. However, so far we can find in the literature few papers

that include the use of AOPs in order to reuse treated water [9, 17-19] and to remove microbiological contaminants [20-22].

In the present work, the remediation of a real textile wastewater from Catalonia (North East of Spain) was carried out by means of the following processes: photo-Fenton alone and photo-Fenton as a post-treatment of an aerobic Sequential Batch Reactor (SBR). Moreover, reverse osmosis (RO) was used in a final stage to achieve suitable water qualities in order to be internally reused in dyeing processes.

The obtained results showed the feasibility of the studied processes to achieve suitable water qualities according to RD 1620/2007, as well as specific firm requirements for internal reuse. Both physicochemical and microbiological parameters were considered as process effectiveness indicators. Treated water after RO was suitable to be used in a 100 % for dyeing processes.

#### 2. Experimental

#### 2.1. Textile wastewater

The textile effluent used in this study was collected from a textile industry located in Catalonia (North East of Spain). The effluent was the output of the existing wastewater treatment at the firm, that consists of two homogenization and aeration ponds that minimize peak loads on the discharge, reduce organic matter, and reduce temperature from 60  $^{\circ}$  C to 35  $^{\circ}$  C.

Samples were directly taken from the second homogenization pond and stored at 4 ° C temperature.

The effluent was characterized in the terms showed in Table 1. As can be seen, it had high Chemical Oxygen Demand (COD), low-medium suspended solids and neutral pH, as expected from a representative textile process. Though, the effluent had no excessive coloration because of the high exhaustion degree of dyes in the considered textile process (residual water contained less than 5 % of the concentration of dyes). On the other hand, absence of *Legionella spp* (CFU·L<sup>-1</sup>) and a significant level of *Escherichia coli* (CFU·100 mL<sup>-1</sup>) was detected due to mixing grey and textile wastewater in the homogenization pond.

Finally, the Biochemical Oxygen demand for 5 days (BOD<sub>5</sub>,  $mg \cdot L^{-1} O_2$ ) to COD ratio gives a 0.35 value, which mean a partially biodegradable sample.

#### 2.2. Chemicals

All chemicals used throughout this study were of the highest commercially available grade. Iron sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O, Merck 99.5 %) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Panreac 33 % (w/v)) were used as received. Concentrated sulphuric acid and sodium hydroxide solutions were used for pH adjustments.

All solutions were prepared with deionised water, prepared using a Millipore Milli-Q system.

#### 2.3. Sample analysis

Total Organic carbon (TOC,  $mg \cdot L^{-1}$  C) was determined with a Shimadzu TOC-VCSH analyser with a solution of potassium phthalate as standard of calibration.

COD (mg $\cdot$ L<sup>-1</sup> O<sub>2</sub>) was measured using the closed-reflux colorimetric method [23] with a HACH DR/2000 spectrophotometer.

 $H_2O_2$  consumption was measured according to the vanadate spectrophotometric method [24]. Residual  $H_2O_2$  was removed with the precise amount of sulphite [25]. Any remaining sulphite was removed by bubbling  $O_2$ .

The UV/vis-absorption spectra were recorded by using a Shimatzu UV-2450 double beam spectrophotometer in the 200-700 nm range and 10-mm light path cells. Absorbance at 254 nm was taken as aromatic content in the sample [26]. Colour index was determined according to [27]. Prior analysis, samples were filtered through 0.45  $\mu$ m pore size filter (Scheleicher & Schuell, FP 30/0.45 CA-S). Fe ion was determined according to spectrophotometric phenantroline method [28]. Turbidity (NTU) was determined with a Lamotte 2008 turbidity meter based on the measure of scattered light at an angle of 90 °, and suspended solids parameter (SS, g·L<sup>-1</sup>) was carried out gravimetrically following Standard Methods recommendations [29].

 $BOD_5$  measurement, was performed by means of a mercury-free WTW 2000 Oxytop thermostated at 20 °C. When  $BOD_5$  determination took place after photo-Fenton treatment stage, due to the toxic character of hydrogen peroxide, its removal with the precise amount of  $SO_3^{2-}$  [25] was found to be necessary.

The *Zahn-Wellens* test was carried out under conditions close to those of a conventional municipal wastewater treatment plant (WWTP). Fresh activated sludge coming from the Manresa WWPT (Catalonia, Spain) was used to prepare the 0.2 g·L<sup>-1</sup> of Total Suspended Solids (TSS) required in the test specifications [30].

The presence of *Escherichia coli* was studied using the membrane filtration procedure according to UNE-EN ISO 9308-1: 2001 and *Legionella spp* was determined according to UNE-EN ISO 1173-1:2007.

Efficiency of dyeing processes was measured in terms of K/S values calculated by Kubelka-Munk equation (K/S =  $(1-R)^2/2R$ ), where R is the decimal fraction of the reflectance at  $\lambda_{max}$ , K is the absorption coefficient and S is the scattering coefficient [31]. K/S values were determined with the CM-2500C spectrophotometer with horizontal alignment for reflectance and transmission measurements, from the company Konica Minolta.

#### 2.4. Photo-Fenton experimental set-up

All photo-Fenton experiments were carried out using a cylindrical Pyrex thermostatic cell of 2 L capacity. The reaction mixture inside the cell, consisting of 1.5 L of effluent and the precise amount of Fenton's reagent, was continuously stirred with a magnetic bar to provide good mixing and the temperature fixed at the required level. It was equipped with a jacket to be cooled or heated according to experimental conditions. Four 25 W Philips black light fluorescent lamps, which basically emits at 350-400 nm, were used as artificial light source. The intensity of the incident UVA light, measured employing a luminometer, was  $27.96 \text{ W} \cdot \text{m}^{-2}$ .

#### 2.5. SBR set-up and operation conditions

The biological treatment system was composed of a 2 L aerobic bench-scale sequencing batch reactor (SBR), equipped with an air diffuser and agitation. The operating liquid volume was 1.5 L and Hydraulic Retention Time (HRT) = 1 day. The fill and draw SBR procedure is described elsewhere [32]. Temperature remained stable and close to room conditions. The concentration of dissolved oxygen (DO, mg·L<sup>-1</sup> O<sub>2</sub>) was kept not lower than 3 mg·L<sup>-1</sup>. Daily analyses of Volatile Suspended Solids (VSS, g·l<sup>-1</sup>), DO and TOC was carried out.

The pH of solution was adjusted between 6.5 and 7.5. Suitable proportions of essential biological nutrients (MgSO<sub>4</sub>, CaCl<sub>2</sub>, NH<sub>4</sub>Cl and NaH<sub>2</sub>PO<sub>4</sub> buffer at pH 7) were also added to the solution [23].

#### 2.6. Reverse osmosis (RO) experimental set-up

The RO treatment system used to perform different bench-scale experiments was a tangential filtration equipment (SEPA CF II of GE Osmonics). The membrane used was a polyamide membrane (AG of GE Osmonics) which had 99.5 % of salts rejection. The system worked at an equilibrium pressure of 24.4 bar and flow rate of 340  $L \cdot h^{-1}$ .

#### 3. Results and discussion

#### 3.1. Photo-Fenton treatment

In a first stage, photo-Fenton AOP was applied as a stand-alone treatment. Taking into account that wastewater to be treated was collected at around 35 °C temperature, and the fact that temperature is an important parameter in the photo-Fenton process [33-35], the influence of this parameter was studied. TOC was followed at four different temperatures (25, 30, 35 and 45 °C) under optimal photo-Fenton conditions: [Fe (II)] = 216 mg·L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 4950 mg·L<sup>-1</sup> and pH =2.7 [22]. Obtained results are shown in Fig. 1. From this Figure, we can say that raising temperature increases the speed of the process in the first 40 min reaction. However, the final degradation level was similar in almost temperatures [35]. Contrarily, the degradation process was significantly slower at 45 °C. This is due to a significant loss of iron by precipitation detected at the beginning of the 45 °C experiment [36]. From the obtained results, 35 °C was consequently taken as optimal temperature. It should be pointed out that this temperature was in accordance with the exit temperature of the raw effluent, and no extra energy would be needed in order to raise temperature.

At this point, the importance of a previous filtration by using a filter paper of 0.45  $\mu$ m pore size was tested. The presence of suspended solids could interfere in UV radiation in the photo-Fenton process. In this case, TOC elimination was followed at 35 °C with and without sample filtration. Obtained results are shown in Figure 2, in which no significant differences exist between the two processes.

Moreover, the pulsed addition of  $H_2O_2$  was considered. Fe (II) concentration was maintained at 216 mg·L<sup>-1</sup> while different pulses of 330 mg·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> were added every 30 min. From Figure 3, and comparing with results in Figures 1 and 2, it can be concluded that best results were obtained when Fenton's reagent was added in a sole time. This could be due to the fact that when  $H_2O_2$  was added by pulses, the oxidation gives place to the fast appearance of short chain organic compounds, which are difficult to oxidize and can capture Fe (II) [37]. Consequently, Fenton's reagent was added in a sole time from that point.

The treated textile wastewater was characterized again under optimum photo-Fenton conditions. The obtained results are shown in Table 1. These results show a good degradation level of organic matter; COD was reduced in a 79 % and TOC in a 75 %, *Escherichia coli* (*Legionella spp* was not present in the original sample) and aromatic compounds (UV<sub>254</sub>), and also give suitable water quality for reuse in accordance with RD 1620/2007. However, the internal reuse of the resultant effluent could not be 100 %

since the total iron parameter overcomes the limits set by the firm for their own dyeing process ( $<0.05 \text{ mg} \cdot \text{L}^{-1}$  Fe), as well as hardness and chloride content (Table 2). Therefore, the treated textile wastewater would need any dilution with fresh water in order to be suitable for reuse.

#### 3.2. Biological-photo-Fenton coupled processes and reverse osmosis

Next point was the consideration of the AOP in combination with a biological treatment. In general, the AOP can be used as a pre or post treatment. Taking into account that samples with a ratio of  $BOD_5/COD \ge 0.4$  are generally accepted as biodegradable, while those with ratios situated among 0.2 and 0.3 units result partially biodegradable; our effluent with 0.35  $BOD_5$  to COD ratio value could be considered as partially biodegradable.

Subsequently, in addition to the  $BOD_5$  to COD estimation, the Zahn-Wellens test was carried out to confirm the inherent aerobic biodegradability of organic substances in the textile wastewater.

This test takes place under conditions close to those of a conventional WWTP using non-acclimated activated sludge as inoculum. This test was performed in a duplicated sample (textile wastewater), a diluted sample (1:3) and a fully biodegradable standard (aniline) for 28 days, T = 25 °C and under aeration. The obtained results are shown in Figure 4. We could see a good level of biodegradability in the sample during the 28 days of the test, achieving TOC reductions between 69 and 77 %. The biodegradability was easier in the diluted sample, achieving the same successful results. In consequence, it could be stated that the biological treatment would be the first stage of the treatment as the major part of organic matter was biologically eliminated.

The biological treatment was simulated using the system SBR described before. TOC evolution was followed during 25 cycles at HRT = 1 day. A first glucose pulse was conducted in order to ensure the correct performance of the biomass (data not shown). As it can be seen in Figure 5; 75 % TOC reduction was achieved. However, some studies [38] have shown that an effluent could be biodegradable or highly biodegradable, but not eliminate some biorecalcitrant compounds that would remain in the treated water. Consequently, the photo-Fenton process was applied as a biological post-treatment in order to eliminate the non biodegradable part of textile wastewater. This resulting solution had a TOC = 114 mg·L<sup>-1</sup> C and a COD = 557 mg·L<sup>-1</sup>O<sub>2</sub>. Prior to the photo-Fenton process, the treated textile wastewater was filtered through 0.45 µm pore size filter in order to eliminate solids present in the sample. The pH was also adjusted at 2.7 units. The concentrations of Fe (II) and H<sub>2</sub>O<sub>2</sub> used were according to the optimum molar ratio obtained in section 3.1, adapted to the new COD value and to assure sufficient  $H_2O_2$  concentration in the medium. In consequence, we used a [Fe (II)] = 66.5 mg·L<sup>-1</sup> and a  $[H_2O_2] = 1518$  mg·L<sup>-1</sup>. The TOC evolution is shown in Figure 6. The Figure shows a gradual reduction of the remaining organic matter from biological treatment, with a final TOC value of  $18 \text{ mg} \cdot \text{L}^{-1}$  C. This means 95 % TOC reduction in the textile wastewater.

The effluent was characterized again after the biological + photo-Fenton treatment in order to assess the possibility for treated textile wastewater reuse. In this sense, we could say that obtained results in Table 1 show a good degradation level of organic matter, *E. coli* and aromatic compounds ( $UV_{254}$ ) according to RD 1620/2007. However, obtained results in Table 1 must also be compared with additional qualities for internal reuse required by the firm (Table 2). According to this, hardness, chloride and iron parameters should be decreased before 100 % of reclaimed water reuse could be

accomplished. Consequently, a filtration procedure by means of RO was applied in a last stage [39, 40]. The obtained results are shown in Table 3 while the appearance of the sample is shown in Figure 7. From these results, we could state that the treated textile wastewater was therefore able to be 100% internally reused for dyeing purposes.

#### 3.3. Dyeing experiments

Once established the best treatment strategies for the textile wastewater, next goal was the use of this reused water in dyeing processes. Two different dyeing processes with polyamide (PA) and polyester (PES) fibres were simulated according to the firm specifications (confidential protocol) by using acid dyes and disperse dyes, respectively. The liquor ratio used was 1/10 (1 g of fibre for 10 mL water).

Three different dyeing strategies with different types of water qualities were studied and compared; type A: tap water without calcium (this is the water usually used by the firm, which can be considered the standard water); type B: reclaimed water obtained after RO in a last stage, applied in all dyeing stages (dyeing, washing, softening...) and type C: reclaimed water obtained after RO treatment, applied only in the dyeing process; the rest of stages carried out with reclaimed water without further RO treatment.

Efficiency of dyeing processes was measured in terms of K/S values. These values are shown in Figures 8 and 9. The highest K/S value, the best dyeing quality is obtained. From these Figures, it can be concluded that K/S difference was less than 2 points (the accepted difference by the firm) when dyeing PES and PA fibres with both B and C reclaimed waters. Consequently, obtained waters were suitable to be internally used in

new PA and PES dyeing processes. The dyeing quality obtained when using B and C reclaimed waters was similar that obtained with conventional tap water (type A).

The obtained results were very promising for the firm as well as for the textile industry in general. Indeed, water reclamation as a further step to conventional water treatment practices offers new sources of water meanwhile great quantities of fresh water could be saved. In our case, the total spent of water in this firm was around 87,663 m<sup>3</sup>/year, with 92.4 % consumption in dyeing processes (81.000 m<sup>3</sup>/year). Obtained results show that this huge water quantity could be reused when combining aerobic treatment, photo-Fenton and reverse osmosis processes.

#### 4. Conclusions

Best water treatment and reuse results were obtained when combining aerobic biological treatment + photo-Fenton + RO processes.

In the single photo-Fenton process, the optimum photo-Fenton conditions were: [Fe (II) = 216 mg·L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 4950 mg·L<sup>-1</sup>; pH =2.7 and T = 35 °C. Under these conditions, results showed a good organic matter degradation level (COD was reduced in a 79 % and TOC in a 75 %), *Escherichia coli* removal (*Legionella spp* was not present in the original sample), aromatic compounds (UV<sub>254</sub>) removal, and gave suitable water quality for reuse in accordance with RD 1620/2007 and internal firm requirements. However, the reuse of effluent could not be 100 % since the total iron parameter overcame the limits set by the firm for its specific dyeing process (<0.05 mg·L<sup>-1</sup> Fe), in addition to chloride and hardness content.

Highest remediation yields were obtained when applying photo-Fenton process as a biological polishing step. In this case, the previous aerobic biological treatment conducted using a SBR with HRT = 1 day gave 75 % TOC reduction after 25 cycles. Subsequently, the coupled photo-Fenton process under optimal Fenton conditions ([Fe (II)] =  $66.5 \text{ mg} \cdot \text{L}^{-1}$  and a [H<sub>2</sub>O<sub>2</sub>] =  $1518 \text{ mg} \cdot \text{L}^{-1}$ ) gave final COD and TOC reductions of 97 % and 95 %, respectively; *Escherichia coli* also accomplished RD 1620/2007. Though, Fe content (0.095 mg $\cdot \text{L}^{-1}$ ) was higher than 0.05 mg $\cdot \text{L}^{-1}$  and chloride and hardness content were higher than recommended by internal limit values. Consequently, the obtained effluent could not completely reused and a combination with RO-treated water could be necessary.

Finally, the use of RO as a polishing final step gave an effluent that could be directly reused in a 100 %, obtaining similar dyeing results than those obtained when using fresh water. Best results were obtained when dyeing PA fibre, even improving K/S value with respect to tap water qualities. It is remarkable that B-dyeing strategy could be considered with both PA and PES, avoiding filtered water in all dyeing process.

In summary, the use of aerobic biological treatment + photo-Fenton + RO is a suitable process combination able to treat wastewater textile effluents, obtaining a final effluent that 100% accomplish specific water reuse normative as well as additional internal requirements for optimum dyeing processes. Contrarily, water without RO final stage treatment could not be used in all different processes in the firm.

Moreover, it should be pointed out that, taking the studied artificial light photo-Fenton process as starting point, more favourable results are expected when using solar light, both in terms of photo-Fenton effectiveness as well as energy consumption.

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Physicochemical and microbiological parameters of real textile wastewater before and after treatment by photo-Fenton alone and by coupled biological-photo-Fenton.

# Table 2

Physicochemical and microbiological limit parameters for textile wastewater reuse, according to RD 1620/2007 and specific requirements of the firm (dyeing stage).

### Table 3

Wastewater characteristics after SBR + photo-Fenton + RO treatments.

Parameter	Raw effluent	Photo-Fenton treated effluent		Coupled biological- photo-Fenton treated effluent	
		Value	% Reduction	Value	% Reduction
рН	7.29	7.50		7.30	
SS (mg·L <sup>-1</sup> )	36.05	< 0.1	99	< 0.1	99
Turbidity (NTU)	66.75	0.21	99	0.31	99
Chloride (mg·L <sup>-1</sup> )	864	864		1324	
Hardness (mg·L <sup>-1</sup> )	500	500		500	
Colour index (cm <sup>-1</sup> )	1485	0.021	98		
$COD (mg \cdot L^{-1} O_2)$	1560	330	79	< 40	97
TOC $(\mathbf{mg} \cdot \mathbf{L}^{-1} \mathbf{C})$	390.4	96.50	75	18	95
Fe (mg·L <sup>-1</sup> )	0.034	0.154		0.095	
UV <sub>254</sub> (Abs units)	3.534	0.060	98	0.0071	88
Escherichia coli	80000	600	99	600	99
(CFU·100 mL <sup>-1</sup> )					
Legionella spp. (CFU·L <sup>-1</sup> )	Absence	Absence		Absence	

Parameter	Raw effluent	Treated effluent (Coupled biological- photo-Fenton)	Limit value
$SS (mg \cdot L^{-1})$	36.5	< 0.1	35
Turbidity (NTU)	65.75	< 0.1	15
Escherichia coli (CFU·100 mL <sup>-1</sup> )	80000	600	10000
Legionella spp. (CFU·L <sup>-1</sup> )	Absence	Absence	100
Chloride (mg·L <sup>-1</sup> )	864	1324	< 300
Hardness (mg·L <sup>-1</sup> )	500	500	53.4
$\mathbf{Fe} \ (\mathbf{mg} \cdot \mathbf{L}^{-1})$	0.034	0.095	< 0.05
рН	7.29	7.30	$7.0 \pm 0.5$

Parameter	Treated effluent	Permeate value	Rejection value
Turbidity (NTU)	0.57	0.55	4.46
TOC ( $\operatorname{mg} \cdot L^{-1} C$ )	9.6	2.8	
$COD (mg \cdot L^{-1} O_2)$	< 40	< 10	
Chloride (mg·L <sup>-1</sup> )	1324	42	
Hardness (mg·L <sup>-1</sup> )	500	< 2	
Fe (mg·L <sup>-1</sup> )	0.034	<0.01	< 0.05
рН	7.3	7.2	7.9

### **Figure Legends**

**Fig. 1.-** TOC evolution at four different temperatures (25, 30, 35 and 45 °C) and optimum photo-Fenton conditions: [Fe (II)] = 216 mg·L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 4950 mg·L<sup>-1</sup>; pH = 2.7.

**Fig. 2.-** TOC evolution with and without 0.45  $\mu$ m pore size filtration at 35 °C and optimum photo-Fenton conditions: [Fe (II)] = 216 mg·L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 4950 mg·L<sup>-1</sup>; pH = 2.7.

**Fig. 3.-** TOC evolution in the pulsed addition of  $[H_2O_2] = 330 \text{ mg} \cdot \text{L}^{-1}$  and optimum photo-Fenton conditions: [Fe (II)] = 216 mg \cdot \text{L}^{-1}; pH = 2.7.

**Fig. 4.-** *Zahn-Wellens* assay. TOC evolution of textile wastewater and the biodegradable standard aniline.

**Fig. 5.-** TOC evolution in biological treatment; HRT = 1 day;  $pH = 7.5 \pm 0.5$ ; T = 25 °C.

**Fig. 6.-** TOC evolution after biological + photo-Fenton treatment; [Fe (II)] = 66.5  $\text{mg} \cdot \text{L}^{-1}$ ; [H<sub>2</sub>O<sub>2</sub>] = 1618 mg \cdot \text{L}^{-1}; pH = 2.7; T = 25 ° C.

Fig. 7.- Appearance of initial (I), rejection (R) and permeate sample (P).

**Fig 8.-** Comparison values of K/S at  $\lambda_{max} = 460$  nm when dyeing PA by using three different dyeing strategies with different water qualities (type A = usually used by the firm (tap water without calcium); type B = reclaimed water after RO filtration used in all dyeing processes; type C = reclaimed water after RO filtration only in dyeing process).

**Fig 9.-** Comparison values of K/S at  $\lambda_{max} = 440$  nm when dyeing PES by using three different dyeing strategies with different water qualities (type A = usually used by the firm (tap water without calcium); type B = reclaimed water, after RO filtration used in all dyeing processes; type C = reclaimed water after RO filtration only in dyeing process).



Fig. 2











Fig. 5







Fig. 7







