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Technical and Economic Feasibility of Polyester Dyeing Wastewater Treatment by Coagulation/Flocculation and Fenton's Oxidation

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Abstract

This study aims to investigate the efficiency of individual and integrated processes applied to organic matter abatement and biodegradability improvement of a polyester dyeing wastewater, namely: coagulation/flocculation combined with Fenton's reagent (Approach 1), Fenton oxidation alone (Approach 2) and its integration with coagulation/flocculation (Approach 3). The effects of Fe^{2+} dose, initial concentration of the oxidant (H_2O_2) and temperature during Fenton's oxidation were evaluated in Approaches 1 and 2, while in Approach 3 it was also assessed the influence of pH and flocculant dose, during the coagulation/flocculation stage. Toxicity and biodegradability of the final effluent were also evaluated. After oxidation, a slight increase in the specific oxygen uptake rate of the effluent was observed (from 27.0 to 28.5-30.0 $mgO_2/(g_{VSS}\ h)$) and inhibition to *Vibrio Fischeri* was eliminated. An effluent that complies with discharge standards was obtained in all cases; however, Approach 3 revealed to be a promising solution for treating this effluent as it leads to smaller operating costs. Therefore, the use of dissolved iron resulting from Fenton's oxidation as coagulant in the second stage was shown to be an innovative, efficient and economically attractive strategy for treating these effluents.

Keywords: Polyester; Dyeing textile wastewater; Fenton; Coagulation/flocculation; Economic analysis.

1. Introduction

Direct discharge of colored effluents from textile dyeing industry generates important negative impacts in the environment [1]. In order to minimize those impacts it is necessary to implement economical and efficient treatment processes to remove dyes and other toxic and recalcitrant compounds from such wastewaters.

Recently, considerable research effort focused on the treatment of textile wastewaters has been carried out either by physical-chemical processes [2-7] or biological degradation [8-10]. Among those techniques, it is worth referring the coagulation/flocculation and chemical oxidation with Fenton's reagent. The first process is very efficient for removing dyes and colloidal organic matter [11-14], while the second one is promising for dyes and organic compounds degradation [15-17], providing in most cases effluents more biodegradable and less toxic [15-16, 18]. Some works have also been reported addressing integration of coagulation/flocculation with Fenton's oxidation for the treatment of dyes-containing wastewaters [19, 20].

In short, in the coagulation/flocculation a polyelectrolyte or an iron or aluminum salt promotes the destabilization of colloids, then the aggregation of microflocs is achieved by adding a polymer and, finally, the removal of the resulting flocs is done by filtration or sedimentation [21-22]. On the other hand, the Fenton's oxidation originates, at pH values in the range 2-5 [23], the conversion of organics (including dyes) to intermediates or final products (eq. 3) by hydroxyl radicals generated according to eq. 1 [24]; in this simplified scheme, Fe^{2+} acts as catalyst being regenerated by the reaction of Fe^{3+} with H_2O_2 (eq. 2):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \qquad (1)$$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$ (2)

$HO^{\bullet} + RH \rightarrow H_2O$ + intermediates/final products (3)

For minimizing some disadvantages of each individual process [4,25], in particular when one of the treatments per se is not enough efficient to meet discharge limits, the treatability of polyester dyeing effluents by the combination of both techniques was herein evaluated. Besides using the residual iron from coagulation/flocculation as catalyst in Fenton's oxidation, which has been rarely addressed in the literature [26-28], the residual catalyst from the Fenton process was also used as coagulant in the subsequent coagulation step, which is also an innovative approach.

The aim of this study was therefore to find the best integration strategy of the two techniques and optimize the respective operating conditions for obtaining an effluent that meets the discharge standards, at the minimum operating costs associated with chemicals consumption. In the scientific literature just a few works focused on obtaining the maximum removal efficiency employing different integration strategies of these processes for textile wastewaters [19-20]. Moreover, in practical applications it is mandatory to take into account the treatment costs and this has been often ignored; this is also an innovative aspect of this work.

2. Materials and Methods

2.1 Synthetic Polyester Dyeing Wastewater

A synthetic wastewater with a composition similar to that of a real effluent was prepared taking into account the quantity of dyes (Dianix Blue K-FBL and Dianix Orange K3G – see chemical structures in Figure S1 of the Supplementary Material section) and auxiliaries used in dyeing baths, the percentage of these products unfixed by the polyester fibers (i.e., that are rejected by the fibers and therefore remain in the dyeing bath) and the water used in washing operations. Such information is given in Table S1.

2.2. Experimental Procedure

2.2.1. Coagulation/Flocculation

All coagulation/flocculation experiments were performed in an Isco jar-test apparatus at room temperature (22-25 ºC), because in a previous study no improvement on color and dissolved organic carbon (DOC) removals was observed at higher temperatures [29].

When combining coagulation/flocculation with the Fenton's process the first stage was carried out in the optimized conditions already determined in a previous work [30]: the pH of the effluent was adjusted to 9.4, 300 mL of simulated wastewater was transferred into a 800 mL beaker, the ferric sulfate (coagulant) was added ($[Fe^{3+}]$=500 mg/L) and the rapid mixing stage (150 rpm) started, after readjusting the pH, if necessary. After 3 minutes the stirring rate was changed to 20 rpm, the flocculant (Superfloc C-573) was added (1 mg/L) and the agitation proceeded for 15 minutes; the addition of the coagulant (or coagulant aid) aimed at obtaining macroflocs from the microflocs formed in the coagulation stage to further facilitate the sedimentation. It is noteworthy that a pH value ≥ 9.0 has also been recommended for coagulation/flocculation by other authors [31] when using ferric sulfate as coagulant. In such conditions $Fe(OH)_3$ is formed, so that the dominant mechanism for coagulation is the inclusion of colloids in iron hydroxide precipitate [32]. The supernatant was collected after 30 minutes of sedimentation and acidified with HNO_3 68% (Merck) to pH ≈3.5 to keep the remaining iron dissolved for further use as catalyst in the Fenton's reaction. When the coagulation/flocculation was performed after the Fenton's oxidation, the operating conditions were similar, except for the following issues: i) no coagulant was added, because the dissolved iron resulting from the Fenton's process was employed (as detailed below), and ii) the supernatant was not acidified. The collected samples were centrifuged at 13400 rpm during 2 minutes (Mini Spin Eppendorf) and some parameters measured for process optimization.

2.2.2. Fenton Oxidation

Fenton's oxidation was studied in a 1 L-capacity jacketed reactor connected to a thermostatic water bath (Grant Y6) to maintain the temperature inside the reactor in the range 10-70 ºC. In all runs, 500 mL of synthetic wastewater or pre-treated effluent was loaded into the reactor and after temperature stabilization, the pH was adjusted to 3.5 with 0.5 M H_2SO_4 or 1 or 10 M NaOH; this pH was found to be the optimum in similar works [4, 9, 33]. When required, ferrous sulfate heptahydrate (Merck) was added and the reaction started with the addition of H_2O_2, 30% (w/v) (Merck).

The oxidation reaction proceeded under constant stirring, using a magnetic bar and a stir plate (Falc). Experiments lasted 2 h, but periodically samples were taken from the reactor and the reaction stopped, by the addition of excess sodium sulfite, before measuring the dissolved organic carbon (DOC) as described below. As regards other parameters, firstly the residual H_2O_2 was eliminated and the iron precipitated by raising the pH to 12.3 with 10 M NaOH, heating the sample at 80 °C for 10 minutes and adjusting the pH to ~7.0 with conc. H_2SO_4. The toxicity was assessed in samples neutralized with HCl 1 M, instead of H_2SO_4, as proposed by the analytical methodology.

In this case sodium sulfite was not used because it leads to inhibition of *V. fischeri* and decay in the luminescence.

2.3. Analytical methods

The biodegradability was evaluated by measuring the specific oxygen uptake rate (k') at 20 ºC [34, 35]. The samples were inoculated with biomass from the activated sludge tank of a WWTP treating textile effluents, and the dissolved oxygen (DO) measured for 30 min (YSI Model 5300 B biological oxygen monitor), a period necessary to reach a DO value close to 1 mg/L; in such a period DO concentration decreased linearly along time. The specific oxygen uptake rate was calculated as the ratio between the oxygen decay rate and the initial volatile suspended solids (VSS) concentration (700 mg/L). The inhibition of *V. fischeri* was performed according to standard DIN/EN/ISO 11348-3 [36], i.e. incubation at 15 ºC and bioluminescence measurement after a contact time of 5, 15 and 30 minutes (model 500 Microtox analyzer). Most analytical parameters were determined according to Standard Methods [35] or ASTM Standards [37]. Details about determinations are presented as Supplementary Material. Chloride, nitrate and dissolved phosphorus were measured by ion chromatography (Dionex DX 120) using a Dionex Ionpac AS9-HC 4 mm (10-32) column and sodium carbonate 9 mM as eluent.

The intermediates formed during oxidation were analyzed by HPLC (VWR, Elite Lachrom model), using a Purospher Star RP-18 (5 μm) column at 30 ºC and a DAD detector (200 nm) in the conditions described in the Supplementary Material section. The concentration of hydrogen peroxide was measured from the intensity of the yellow-orange color resulting from the reaction of hydrogen peroxide with titanium oxalate, using a Helios α Unicam spectrophotometer, as described by Sellers [38]. The samples were previously filtered through nylon filter membranes with pore diameter of 0.45 μm.

All analytical determinations were performed in duplicate and the coefficients of variation were less than 2% for DOC, 14% for BOD_5, 8% for COD, 10% for k', 3% for inhibition of *V. fischeri* and 7% for the other parameters. Error bars and standard derivations at 95% confidence level are included in Figures and Tables, respectively.

3. Results and Discussion

The more relevant characteristics of the effluent under study are reported in Table 1. It is noteworthy that the textile effluent is colorless, due to the reductive washing employed in the dyeing process. Several parameters such as BOD_5, DOC, k', N, P and ecotoxicity were analyzed to decide on the possibility of directly applying a biological treatment to this kind of effluent, which would be cheaper than the chemical processes. Considering the low values of BOD_5/COD (<0.4), k', nitrogen and phosphorus concentrations, and the high toxicity to *V. fischeri*, a biological process was excluded. The effluent does not comply with limits for BOD_5 and COD, as established in the Portuguese legislation (Ordinance No. 423 of June 25, 1997, for discharge of textile wastewaters – cf. Table 1). So, different approaches have been attempted, as described below.

3.1. Combination of Coagulation/Flocculation and Fenton Reagent (Approach 1)

The effluent was firstly treated by coagulation/flocculation under the better operating conditions found in a previous work (pH=9.4, $[Fe^{3+}]$=500 mg/L, $v_{coagulation}$ = 150 rpm, $t_{coagulation}$= 3 min, T =

T_{amb} = 23-25 ºC, $v_{flocculation}$ = 20 rpm, $t_{flocculation}$ = 15min, [Superfloc C-573] = 1 mg/L) [30]. At pH=9.4 the coagulation mechanism is mainly by incorporation of colloids in $Fe(OH)_3$ precipitate [32]. It stands out that after coagulation/flocculation an additional treatment must be implemented because COD is still above the discharge limit (cf. Table 1). Considering the biodegradability and toxicity values, the subsequent treatment cannot be biological. Alternatively, Fenton's reagent, using part of the dissolved iron coming from the chemical coagulation/flocculation stage (8.7 mg Fe/L) as catalyst, was employed.

A parametric study was carried out aiming at finding the best amount of Fe^{2+} salt to be added, the dose of H_2O_2 required and the operating temperature that maximized the DOC removal.

3.1.1. Influence of Fe^{2+} added in the chemical oxidation stage

To evaluate the influence of Fe^{2+} concentration in DOC removal, five experiments were performed by changing the supplementary dose of Fe^{2+} in the range 0-241.3 mg/L. The iron dose was successively increased from the residual concentration (dissolved iron) coming from coagulation/flocculation up to 250 mg/L. This maximum concentration corresponds to the situation where a decrease in process performance was observed for the first time, as detailed below.

Figure 1a presents the DOC removal along time for different runs. It is very fast in the first 15 minutes of reaction (time after which most of the hydrogen peroxide has been consumed – cf. Fig. 1b), but then it slows down till 60 minutes of reaction, and presents a negligible increase in the range 60-120 minutes. A very similar pattern was observed for the consumption of H_2O_2 (Fig. 1b). On the other hand, DOC removal increased with the added dose of Fe^{2+} up to 191.3 mg/L (total iron load of 200 mg/L), leading to a mineralization of ~45% with a H_2O_2 consumption of 96%. The efficiency of the process declined for a Fe^{2+} dose of 241.3 mg/L (~41% of DOC removal) and also decreased the H_2O_2 consumption (90-91%).

In the literature concerning either dyes or organic matter removal by Fenton's oxidation optimum doses of ferrous ion are often reported [4, 17, 39, 41], which is explained by the detrimental effect of excessive catalyst dosages leading to competitive reactions ($Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-}$) that reduce the amount of available radicals.

The optimal dose of Fe^{2+} (200 mg/L) required for Fenton's oxidation of the polyester dyeing pre-treated effluent is between those obtained for cotton (100 mg/L) [42] and acrylic (350 mg/L) [33] dyeing effluents, both pre-treated by coagulation/flocculation. Azbar et al. [39] achieved 96% and 94% of COD and color removal, respectively, using an optimum concentration of Fe^{2+}=184 mg/L for treating a mixture of polyester and acetate dyeing effluents (COD=930 mg/L and BOD_5=375 mg/L) and Blanco et al. [43] found 64% TOC removal when treating a textile wastewater by Fenton's oxidation using 216 mg/L of Fe^{2+}.

3.1.2. Effect of the initial H_2O_2 concentration on the chemical oxidation stage

The hydrogen peroxide dose has a significant impact on the operating costs of wastewater treatment by the Fenton process. On the other hand, when using an excess of H_2O_2 the parallel and undesirable $HO^{\bullet}$ scavenging reaction may occur ($HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$) [44]. Therefore, it is necessary to optimize this parameter to increase the process efficiency and reduce operating costs. The minimum tested dose of hydrogen peroxide is around the stoichiometric theoretical value (587 mg/L), and was further increased to compensate side reactions.

For H_2O_2 in the range 500-1500 mg/L, Figures 1c and 1d evidence that the DOC was mostly removed in the first 30-40 minutes of reaction, leading in the same period to a high consumption of H_2O_2. For reaction times between 30 and 60 min only a slight increase in the DOC removal (and H_2O_2 consumption) was observed; for t > 60 minutes a plateau was reached in both cases. The DOC removal increases with the H_2O_2 concentration up to 1000 mg/L, and decreases for higher doses. The existence of an optimal H_2O_2 dose was also observed by others authors [4, 45-46], which is usually attributed to the fact that reaction between H_2O_2 with $HO^\bullet$ occurs when there is an excess of oxidant. For the optimum H_2O_2 dose (1000 mg/L) the mineralization is ~53% after 60 minutes of reaction. This value is close to those obtained by other authors, namely by Blanco et al. [43] whom achieved an optimum H_2O_2 dose of 1650 mg/L for treating a textile wastewater, and by Wu and Wang [17] whom reported an optimum of 1500 mg/L to treat a mixture of printing and dyeing wastewaters.

3.1.3. Effect of the temperature during the chemical oxidation stage

The influence of temperature on the mineralization of the dyeing polyester effluent was assessed by a series of experiments varying this parameter in the range 10-70 ºC. This range takes into account that textile dyeing processes are carried out at elevated temperatures (50-70 °C or even higher), but on the other hand the effluent is often sent to an open air equalization tank for homogenization. In this case the effluent temperature can strongly decrease when the ambient temperature is low, depending on the region and the time of the year.

Results of DOC removal and percentage of H_2O_2 consumed are shown in Figs. 1e and f, respectively. Organics oxidation rises considerably when T increases from 10 to 30 ºC. A similar effect is noticed in the peroxide consumption. DOC removal still slightly increases with the temperature up to 50 ºC, but at 70 ºC a negative effect was observed. The consumption of H_2O_2 increases with temperature, but beyond 40-50 ºC there is also its thermal decomposition into oxygen and water [40], as well as the fast hydroxyl radicals "scavenging" reactions. This explains the results shown in Fig. 1e, where maximum mineralization is reached at 50 ºC.

At this temperature 56% of DOC removal was achieved after 60 min. An optimum value was also reported in other Fenton's oxidation studies with textile effluents [4, 9, 23, 33, 41, 42, 44].

3.1.4. Optimized integrated coagulation/flocculation plus Fenton's treatment

After determining the conditions that maximize DOC removal by the Fenton's process (pH=3.5, T=50 ºC, $[Fe^{2+}]_{added}$=191.3 mg/L and $[H_2O_2]$=1000 mg/L), an additional experiment was performed in those conditions, using the effluent pre-treated by coagulation/flocculation.

Samples were taken during 60 minutes of reaction for measuring the toxicity (*V. fischeri* inhibition - see Fig. S2a in Supplementary Material) and registering HPLC chromatograms (Fig. S2b in Supplementary Material). After 30 minutes the effluent does not present any negative effect on *V. fischeri*; a similar behavior was observed for acrylic dyeing wastewater [30]. The changes in the HPLC chromatograms (Fig. S2b in Supplementary Material) prove the formation and disappearance of intermediates responsible for the above-described change in effluent's toxicity.

Table 1 presents the results of pH, COD, BOD_5, DOC, and visible color (after 1:40 dilution) for the treated effluent. The organic matter removal in the Fenton's process (61.0% for COD, 44.5% for BOD_5 and 56.0% for DOC) was higher than in the previous coagulation/flocculation stage. The overall efficiencies of the combined treatment were 79.2%, 61.9% and 75.7% for COD, BOD_5 and

DOC, respectively. It is important to remark that now the characteristics of the final effluent comply with the discharge standards (cf. Table 1).

3.2. Fenton's Oxidation (Approach 2)

The treatability study of the polyester dyeing effluent also included the application of the Fenton's reagent alone. A parametric study was performed to evaluate the effect of ferrous ion, initial H_2O_2 concentration and temperature on DOC removal and biodegradability.

3.2.1. Influence of ferrous ion concentration

The effect of Fe^{2+} dose was evaluated in the range 275-400 mg/L. It was decided to start with the same range of ferrous ion dose that was applied in the treatment of an acrylic effluent by Fenton's oxidation [33]. DOC removal occurs rapidly in first 15-20 minutes (Fig. 2a) and at the same time there is a faster H_2O_2 consumption (Fig. 2b). Then the increase of DOC removal and H_2O_2 consumption proceeded at a slower rate until ca. 60 min, and afterwards remained nearly constant.

DOC removal raises with Fe^{2+} concentration up to 350 mg/L but greater doses do not result in increased mineralization. For that dose ~43% of DOC removal was achieved at the end of the reaction.

The biodegradability (k') decreased after 2 minutes of reaction (as compared to raw synthetic wastewater), but it tended afterwards to remain nearly constant whatever the load of catalyst (Fig. 2c).

The optimum dose of ferrous iron (350 mg/L) is within the range obtained by Rodrigues et al. [9] for maximizing color and DOC removals and biodegradability improvement of a cotton dyeing effluent.

3.2.2. Effect of the initial H_2O_2 concentration

To minimize the operating costs of the Fenton's process, H_2O_2 concentration must be optimized. Four runs were performed varying this parameter between 1 and 10 g/L (this range was established considering its relation with COD of the raw effluent), at pH = 3.5, T = 30 ºC and $[Fe^{2+}]$ = 350 mg/L.

Figure 2d) shows the variation of DOC removal with initial H_2O_2 dosage; once again, the removal is much faster in the first 15-20 min, when a faster consumption of hydrogen peroxide is also observed (Fig. 2e). However, DOC removal and H_2O_2 consumption continue to increase till 60 min of reaction.

The DOC removal increased with the H_2O_2 concentration up to 2.5 g/L and decreased for higher doses. The optimum reagent dose is justified by the occurrence of parallel reactions between excess of H_2O_2 and the hydroxyl radical (scavenging effect), generating radicals like $HO_2^{\bullet}$ with a lower oxidation potential.

The percentage of oxidant consumed is maximal for initial doses of 1.0-2.5 g/L (Fig. 2e); above this value hydrogen peroxide is not effectively consumed to generate hydroxyl radicals and part remains in solution.

The effect of initial H_2O_2 dose in the biodegradability (k') is shown in Fig. 2f. There is a decrease in k' upon 2 minutes of reaction in all runs as compared to raw wastewater. However, as the oxidation proceeds, k' increases up to 60 min and then remains nearly constant.

The optimal oxidant dose (2.5 g/L) is very different from that required for treating cotton and acrylic dyeing effluents (10 g/L for cotton [42] and 20 g/L for acrylic [33]), which is related to the organic load (DOC) of each effluent (350, 500 and 828.1 mg/L for cotton, polyester and acrylic, respectively) but also to the nature of the organics in each one and to other compounds that impair the organics oxidation (for example chlorides). Tantak and Chaudhari [47] obtained the maximum reduction of organic matter for reactive black 5, reactive blue 13 and acid orange 7 solutions using 2.45 g/L of hydrogen peroxide. Shrivastava and Rao [48] achieved maximum dyes and COD removals by using 2.1 g/L of hydrogen peroxide in the Fenton's oxidation of a synthetic effluent containing reactive blue 4 and reactive orange 16. Other authors [49] found 3.06 g/L as the better dose of H_2O_2 for treating a dry-spun acrylic fiber effluent, and Rodrigues et al. [33] found a value of 3.5 g/L for the oxidation of an acrylic dyeing effluent previously treated by coagulation/flocculation (DOC=334.1 mg/L, COD=828.1 mg/L and BOD_5<1.0 mg/L).

3.2.3. Effect of the temperature

To determine the effect of temperature on DOC removal and biodegradability, various experiments were conducted by varying this parameter from 10 ºC to 70 ºC (Figs. 2g, 2h and 2i). As above-mentioned, this range was selected taking into account the ambient temperature in Portugal, that can be ~10 ºC or even lower in some times of the year, and the temperature of the wastewater at the outlet of the drainage system (usually in the range 50-70 ºC or even higher). It can be seen that:

i) DOC reduction is low at 10 ºC (21.9% after 120 min), and a small percentage of H_2O_2 was consumed; ii) the mineralization improved at higher temperatures, mostly in the first 45 min, and the H_2O_2 consumption also increased; iii) the maximum DOC removal was reached at 50 ºC (56.3% after 45 min), but the H_2O_2 consumption increased until 70 ºC, due to the thermal decomposition of H_2O_2 into water and oxygen at $T > 50$ ºC, as mentioned previously, and by the increased kinetics of "scavenging" reactions.

It was again observed a small decrease of the biodegradability (inferred from k' – see Fig. 2i) for short reaction times, in all runs, but then it increases, in some cases with slight oscillations. In the runs at 50 and 70 ºC, k' increases up to 60 min, and then remains nearly constant. The decrease of biodegradability can probably be associated to the generation of less biodegradable intermediates. Maximum k' values were obtained at 50 ºC (30.0 $mgO_2/(g_{VSS}.h)$) after 60 min of reaction), the same temperature that led to maximum mineralization.

The optimum value of temperature was the same found in the pre-treatment of either cotton [42] or acrylic dyeing wastewaters [33], dyes and textile dyeing wastewaters [4, 9, 23, 33, 41,42, 44] by the Fenton's process.

3.2.4. Optimized Fenton treatment

A Fenton's oxidation run was carried out under the conditions that maximize DOC removal and biodegradability ($[Fe^{2+}]$= 350 mg/L, $[H_2O_2]$= 2.5 g/L, T=50 ºC at pH 3.5). Along 60 minutes (corresponding to the maximum biodegradability – as inferred from k'), samples were collected to follow up the toxicity (inhibition of *V. fischeri*) and HPLC chromatograms (data not shown). *V. fischeri* toxicity decreases up to 30-45 minutes for all contact times (5, 15 or 30 min) and then the inhibition percentage is null, indicating that the effluent is no longer toxic. HPLC chromatograms confirm the formation and disappearance of intermediates responsible for the decreased effluent's toxicity.

The treated effluent was analyzed after 60 minutes of reaction (Table 2). A considerable organic matter removal was obtained (57.3% for COD, 55.7% for DOC and 52.0% for BOD_5) and the effluent is no longer toxic (0.0% of *Vibrio fischeri* inhibition); the ratio of BOD_5:COD slightly increased from 0.26 to 0.28 and k' from 27.0 to 30.0 mg O_2/(g_{VSS} h). Again, the final effluent meets the discharge limits. However, as the value of COD is very close to the maximum allowable value (Table 2), a subsequent treatment such as coagulation/flocculation, using the dissolved iron from the Fenton's process as coagulant, is recommended.

3.3. Fenton's Oxidation followed by Coagulation/Flocculation (Approach 3)

To increase the removal of organics and aiming at obtaining an effluent with COD values much lower than maximum allowable values, the effluent from the Fenton's process was treated by coagulation/flocculation. The results from the parametric study of the 2nd process stage, in which the effect of pH and dose of flocculant on DOC removal was evaluated, are presented in this section. The Fenton's stage included three experiments: run #3 corresponding to the conditions that maximized DOC removal and biodegradability; runs #2 and #1 where the H_2O_2 and Fe^{2+} doses were reduced to ½ and ¼, respectively. The main goal behind this strategy was to reduce the operating costs associated with chemicals consumption. In the coagulation/flocculation stage the coagulant used was the dissolved iron resulting from the previous oxidation step (64.8, 88.5 and 222 mg/L of Fe in run#1, run#2 and run#3, respectively).

3.3.1. Influence of pH in the coagulation process

The influence of pH was assessed by carrying out six runs in which this parameter varied between 3.5 and 10.4, using as coagulant the residual dissolved iron from the previous Fenton's reaction. This range is the same used in previous studies concerning the treatment of textile dyeing wastewaters by coagulation/flocculation employing iron salts as coagulants [29-30].

Figure 3 shows the results of DOC removal for different pH levels. The performances slightly improved when the pH was varied from 3.5 to 5.0 and worsened for higher pH (for instance, in run #1, for a hydrogen peroxide dose of 0.625 g/L in the Fenton's stage, the DOC removal increased from 35.8% to 38.5%, while in run #3, where the highest dose of oxidant was employed in the chemical oxidation stage, the removal raised from 41.6% to 55.0%). In these circumstances, the dominant coagulation mechanism is charge neutralization, because at pH < 5 the iron species in solution are mainly $Fe(OH)_2^+$, Fe^{3+} and $Fe(OH)^{2+}$.

The optimal pH in the acidic zone is in accordance with literature reporting the use of ferric sulfate as coagulant (from 3.5 to 7.0) [31]. Besides, the value is similar to those determined in other works. In particular, Joo et al. [50] obtained an optimum pH between 4 and 7 for treating a textile wastewater. Aziz et al. [51] and Liang et al. [52] achieved the maximum removal at pH=4 for a landfill leachate and a molasses effluent treatment, respectively.

3.3.2. Effect of the Superfloc C-573 dose

The selection of Superfloc C-573 (cationic polymer) as flocculant (or coagulant aid) takes into account the results obtained in preliminary studies using synthetic textile wastewaters [29-30]. Indeed, this flocculant shows better performance when using ferric ion salt as coagulant.

The effect of the flocculant dose, in the range 0.1 to 5 mg/L, on DOC removal was evaluated. The results obtained (cf. Supplementary Material - Fig. S3) show a small increment in efficiency when the flocculant was used (0 vs. 0.1 mg/L dose), because the removal of organic compounds mainly occurs in the coagulation step. In all experiments (i.e., whatever the dose of chemicals in the oxidation stage) the DOC removal slightly increased with the flocculant dose up to 0.5 mg/L, and for this optimum dose the performances reached were 42.0, 51.1 and 60.5% for run #1, run #2 and run #3, respectively. The optimum dose obtained is equal to that found when treating simulated cotton dyeing wastewater by coagulation/flocculation using ferric sulfate as coagulant [30]. Besides, it is similar to those reported in literature, even with other flocculants [51-53].

3.3.3. Optimized integrated Fenton's plus coagulation/flocculation treatment

After determining the operating conditions that maximize DOC removal in the coagulation/flocculation stage, three runs were carried out, as previously described – treating the effluent by the Fenton's process using different hydrogen peroxide doses (0.625, 1.25 and 2.5 g/L – runs #1 to #3), and subsequently submitting it to coagulation/flocculation under the better conditions determined before. Table 3 presents the results of the effluent characterization after each stage, together with the respective removal efficiencies and the overall treatment performance. The results indicate that the removal of organic compounds is higher in the coagulation/flocculation stage if low doses of chemicals are employed in the Fenton's process (run #1); for higher doses, the performances are similar in each stage. It is also noteworthy that values below the maximum COD and BOD discharge limits were reached in all runs. In run#3, where higher removal efficiencies were attained, the global efficiencies were 78.9, 73.3 and 82.9% for COD, BOD_5 and DOC, respectively.

3.4. Operating Costs

The selection of the best treatment process, besides considering efficiency and ability to comply with legislation, should also take into account the treatment costs. Thus, an economic analysis was made, focused in the total costs of reagents given by Quimitécnica S.A.: H_2O_2 (49.5% (w/v), density at 25 ºC = 1.2 g cm^{-3}) – 365 €/ton; $FeSO_4.7H_2O$ (93 wt.% of purity) – 233.7 €/ton; $Fe_2(SO_4)_3$ (solution with 44% (w/w)) – 240 €/ton; and Superfloc C-573 – 2500 €/ton. The costs of acids and base were not considered as they are almost negligible compared to the other chemicals.

Figure 4 shows the influence of the reagents doses on the treatment cost, for the different strategies mentioned above. In particular, are shown the effects of the Fe^{2+} and H_2O_2 doses during the Fenton's stage when the effluent was previously treated by coagulation/flocculation (Fig. 4a), Approach 1, including in the costs those of the coagulant and flocculant, or when directly applied to the raw wastewater - Approach 2 (Fig. 4b). It turns out, as expected, that the cost increases with increasing concentrations of either reagent but the major contribution comes from the hydrogen peroxide, being far most notorious in Approach 2.

When treating the synthetic wastewater by combining coagulation/flocculation and Fenton´s oxidation under the best conditions, the operating costs amount to 3.1 €/m^3, slightly above the costs of applying directly the Fenton's reagent to the raw simulated wastewater (2.7 €/m^3). Besides, the two strategies allowed reaching global efficiencies that would permit to meet the discharge limits, but in Approach 2 (Fenton's reagent alone) the final COD value (221.1 mgO_2/L) is close to the legislated one (250 mg O_2/L).

Figure 4c shows the influence of Superfloc C-573 and hydrogen peroxide costs upon the integration of chemical oxidation followed by coagulation/flocculation. The operatory costs increased with the doses of reagents, however, this increase is more notorious for hydrogen peroxide. In fact, the effect of flocculant in the global cost is almost negligible because the doses used are small. Thus, the total cost of the treatment according to Approach 3 is almost entirely due to the consumption of reagents in the oxidation stage (that amounts to ca. 0.7, 1.3 and 2.7 €/m^3 in runs #1, #2 and #3, respectively). The three experiments allowed obtaining an effluent that can be discharged, but given the low differences of the operating costs of runs #1 and #2 and the COD value obtained in run #1, which is close to the maximum allowable value, the conditions of run #2 for treating the simulated wastewater by Fenton's oxidation plus coagulation/flocculation are recommended. In this case, it was possible to reduce the cost from 3.1-2.7 €/m^3 in previous Approaches to only 1.3 €/m^3 due to the better integration strategy of the treatment stages.

4. Conclusions

i) The integration of coagulation/flocculation and Fenton's process (using the dissolved iron resulting from the coagulation stage as catalyst in the second one) leads to high organic matter removals (79.2% for COD, 61.9% for BOD_5 and 75.7% for DOC) and generates a nontoxic effluent meeting the discharge limits at an operating cost of around 3.1 €/m^3;

ii) The Fenton's oxidation per se allows obtaining slightly smaller removal efficiencies (57.3% for COD, 52.0% for BOD_5 and 55.7% for DOC), yielding also a nontoxic effluent and a small improvement of the biodegradability. The treated effluent meets the discharge limits although the COD value is near the maximum allowable value. The estimated costs associated to chemicals consumption in this process are 2.7 €/m^3;

iii) The combination of Fenton's process plus coagulation/flocculation in optimized conditions provided an effluent that meets the discharge limits, with high global organic matter removals (78.9% for COD, 73.3% for BOD_5 and 82.9% for DOC). Considerable organic matter removals (62.7% for COD, 59.3% for BOD_5 and 73.4% for DOC) are also reached when reducing the H_2O_2 dose to one-half (run #2), the effluent still complying with the maximum legislated values at a much smaller operating cost (1.3 €/m^3).

iv) The operating costs can be further decreased (0.7 €/m^3) using a smaller dose of H_2O_2 (run #1), but in this case the final COD value is close to the discharge limit. However, we propose not to reduce further the amount of reagents used in the Fenton reaction to ensure that the final COD values do not exceed 250 mg/L (legal limit), specially when the COD of the raw wastewater slightly increases due to daily or seasonal variations.

v) The use of the dissolved iron resulting from the Fenton's process as coagulant in the subsequent treatment step revealed to be an innovative and promising strategy to considerably decrease operating costs.

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Appendix A. Supplementary Material

Supplementary material associated with this article is attached.

References

[1] P.K. Malik, S.K. Saha, Oxidation of Direct Dyes with Hydrogen Peroxide Using Ferrous Ion Catalyst, Sep. Purif. Technol. 31 (2003), pp. 241-250.

[2] T.-H. Kim, C. Park, J. Yang, S. Kim, Comparison of Disperse and Reactive Dye Removals by Chemical Coagulation and Fenton Oxidation, J. Hazard. Mater. B112 (2004), pp. 95-103.

[3] B. Shi, G. Li, D. Wang, C. Feng, H. Tang, Removal of Direct Dyes by Coagulation: The Performance of Preformed Polymeric Aluminum Species, J. Hazard. Mater. 14 (2007), pp. 567-574.

[4] C.S.D. Rodrigues, L.M. Madeira, R.A.R Boaventura, Optimization of the Azo Dye Procion Red H-EXL Degradation by Fenton's Reagent Using Experimental Design, J. Hazard. Mater. 164 (2009) pp. 987-994.

[5] E. Errais, F. Darragi, Textile Dye Removal by Natural Clay – Case Study of Fouchana Tunisian Clay, Environ. Technol. 31 (2010) pp. 373-380.

[6] Y. Wang , B-Y. Gao , Q-Y. Yue , J-C. Wei , W-Z. Zhou, R. Gu, Color Removal from Textile Industry Wastewater Using Composite Flocculants, Environ. Technol. 28 (2007), pp. 629-637.

[7] S.H. Lin, C.F. Peng, A continuous Fenton's Process for Treatment of Textile Wastewater, Environ. Technol. 16 (1995), pp. 693-699.

[8] P. Niren, P. Jigisha, Textile Wastewater Treatment using a UF Hollow-Fibre Submerged Membrane Bioreactor (SMBR), Environ. Technol. 32 (2011), pp. 1247-1257.

[9] C.S.D. Rodrigues, L.M. Madeira, R.A.R. Boaventura, Treatment of Textile Effluent by Chemical (Fenton's Reagent) and Biological (Sequencing Batch Reactor) Oxidation, J. Hazard. Mater. 172 (2009), pp. 1551-1559.

[10] S.J. You, D.H. Tseng, S.H. Ou, W.K. Chang, Performance and Microbial Diversity of a Membrane Bioreactor Treating Real Textile Dyeing Wastewater, Environ. Technol. 28 (2007), pp. 935-941.

[11] S. Meriç, H. Selçuk, V. Belgiorno, Acute Toxicity Removal in Textile Finishing Wastewater by Fenton's Oxidation, Ozone and Coagulation-Flocculation Processes, Water Res. 39 (2005), pp. 1147-1153.

[12] I. Khouni, B. Marrot, P. Moulin, R.B. Amar, Decolourization of the reconstituted textile effluent by different process treatments: Enzymatic catalysis, coagulation/flocculation and nanofiltration processes. Desalination 268 (2011), pp. 27-37.

[13] A.Y. Zahrim, C. Tizaoui, N. Hilal, Evaluation of several commercial synthetic polymers as flocculant aids for removal of highly concentrated C.I. Acid Black 210 dye. J. Hazard. Mater. 182 (2010), pp. 624-630.

[14] B. Merzouk, B. Gourich, K. Madani, Ch. Vial, A. Sekki, removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study. Desalination 272 (2011), pp. 246-253.

[15] J. Li, Z. Luan, L. Yu, Z. Ji, Pretreatment of acrylic fiber manufacturing wastewater by Fenton process, Desalination 284 (2012), pp. 62-65.

[16] J. Wei, Y. Song, X. Tu, L. Zhao, E. Zhi, Pretreatment of Dry-Spun Acrylic Fiber Manufacturing Wastewater by Fenton Process: Optimization, Kinetics and Mechanisms, Chem. Eng. J. 218 (2013), pp. 319-326.

[17] H. Wu, S. Wang, Impacts of Operating Parameters on Oxidation-Reduction Potential and Pretreatment Efficacy in the Pretreatment of Printing and Dyeing Wastewater by Fenton Process, J. Hazard. Mater. 243 (2012), pp. 86-94.

[18] K. Ntampegliotis, A. Riga, V. Karayannis, V. Bontozoglou, G. Papapolymerou, Decolorization Kinetics of Procion H-ELX Dyes from Textile Dyeing Using Fenton-like Reactions, J. Hazard. Mater. 136 (2006) pp. 75-86.

[19] A. Yadav, S. Mukherji, A. Garg, Removal of Chemical Oxygen Demand and Color from Simulated Textile Wastewater Using a Combination of Chemical/Physicochemical Processes, Industrial & Engineering Chemistry Research 52 (2013), pp. 10063−10071.

[20] A. Dulov, N. Dulova, and M. Trapido, Combined Physicochemical Treatment of Textile and Mixed Industrial Wastewater, Ozone: Science & Engineering 33 (2011), 285–293.

[21] P. Cañizares, C. Jiménez, F. Martínez, M.A. Rodrigo, C. Sáez, The pH as a Key Parameter in the Choice Between Coagulation and Electrocoagulation for the Treatment of Wastewaters, J. Hazard. Mater. 163 (2009), pp. 158-164.

[22] Y. L. Pang, A. Z. Abdullah, Current Status of Textile Industry Wastewater Management and Research Progress in Malaysia: A Review, Clean – Soil, Air, Water (2013), doi: 10.1002/clen.201000318.

[23] I.A. Alaton, S. Teksoy, Acid Dyebath Effluent Pretreatment Using Fenton's Reagent: Process Optimization, Reaction Kinetics and Effects on Acute Toxicity, Dyes Pigm. 73 (2007), pp. 31-39.

[24] C. Walling, Fenton's reagent revisited, Accounts Chem. Res. 8 (1975), pp. 125-131.

[25] K.A. Flaherty, C.P. Huang, Continuous Flow Applications of Fenton´s Reagent for the Treatment of Refractory Wastewater, In: Proceedings of the Second International Symposium on Chemical Oxidation-Technologies for the Nineties, Nashville, Tennessee, U.S.A., 1992, pp. 58-77.

[26] J.A. Peres, J.B. de Heredia, J.R. Domínguez, Integrated Fenton's reagent—coagulation/flocculation process for the treatment of cork processing wastewaters, J. Hazard. Mater. 107 (3) (2004), pp. 115-121.

[27] J.A. Perdigon-Melon, J.B. Carbajo, A.L. Petre, R. Rosal, E. Garcia-Calvo, Coagulation–Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater, J. Hazard. Mater. 181 (2010), pp. 127-132.

[28] Z.-P. Xing, D.-Z. Sun, Treatment of antibiotic fermentation wastewater by combined polyferric sulfate coagulation, Fenton and sedimentation process, J. Hazard. Mater. 168 (2009), pp. 1264-1268.

[29] C.S.D. Rodrigues, L.M. Madeira, R.A.R. Boaventura, Treatment of Textile Dye Wastewaters Using Ferrous Sulphate in a Chemical Coagulation/Flocculation Process, Environ. Technol. 34 (6) (2013), pp. 719-729.

[30] C.S.D Rodrigues, L.M.P. Madeira, R.A.R. Boaventura, Use of Ferric Sulphate to Treat Textile Synthetic Wastewaters by Coagulation/Flocculation, Proceedings of the 11th International Chemical and Biological Engineering Conference, Lisbon, Portugal, 2011, pp. 455-456.

[31] F. Edeline, L´Épuration Physico-Chimique des Eaux – théorie & technologie, 2e édition, Editions CEBEDOC, 1992.

[32] J. Duan, J. Gregory, Coagulation by Hydrolysing Metals Salts. Advances Adv. Colloid. Interfac. 100-102 (2003), pp. 475-502.

[33] C.S.D. Rodrigues, R.A.R. Boaventura, L.M.P. Madeira, Application of Fenton´s Reagent for Acrylic Dyeing Wastewater Decolorization, Organic Matter Reduction and Biodegradability Improvement, J. Adv. Oxid. Technol. 15 (2012), pp. 78-88.

[34] R.S. Ramalho, Introduction to Wastewater Treatment Processes, Academic Press, New York, USA, 1977.

[35] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington DC, 1998.

[36] International Organization for Standardization, Water Quality - Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio Fischeri (luminescent Bacteria Test) - Part three: Method Using Freeze-dried Bacteria, 2005.

[37] Annual Book of ASTM Standards, Water; Atmospheric Analysis, Part Twenty three, American Society for Testing and Materials, Philadelphia, 1973.

[38] R.M. Sellers, Spectrophotometric Determination of Hydrogen Peroxide Using Potassium Titanium (IV) Oxalate, Analyst 105 (1980), pp. 950-954.

[39] N. Azbar, T. Yonar, K. Kestioglu, Comparison of Various Advanced Oxidation Processes and Chemical Treatment Methods for COD and Color Removal from a Polyester and Acetate Fiber Dyeing Effluent, Chemosphere 55 (2004), pp. 35-43.

[40] J.H. Ramirez, C.A. Costa, L.M. Madeira, Experimental Design to Optimize the Oxidation of Orange II Dye Solution Using a Clay-Based Fenton-Like Catalyst, Industrial Ind. Eng. Chem. Res. 47 (2008), pp. 284-294.

[41] Í. Gulkaya, G.A.Surucu, F.B. Dilek, Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater, J. Hazard. Mater. B136 (2006), pp. 763-769.

[42] C.S.D. Rodrigues, R.A.R. Boaventura, L.M.P. Madeira, Combination of Coagulation/Flocculation and Chemical Oxidation Processes for Treating a Cotton Dyeing Wastewater – Comparison of Performances and Cost Analysis, Proceedings of the Sixteenth International Water Technology Conference, Istanbul, Turkey, 2012, pp. 156-157.

[43] J. Blanco, F. Torrades, M. de la Varga, J. García-Montãno, Fenton and Biological-Fenton Coupled Processes for Textile Wastewater Treatment and Reuse, Desalination 286 (2012), pp. 34-399.

[44] J.H. Ramirez, C.A. Costa, L.M. Madeira, Experimental Design to Optimize the Degradation of the Synthetic Dye Orange II Using Fenton´s Reagent, Catal. Today 107-108 (2005), pp. 68-76.

[45] K. Swaminathan, S. Sandhya, A.C. Sophia, K. Pachhade, Y.V. Subrahmanyam, Decolorization and Degradation of H-Acid and Other Dyes Using Ferrous-Hydrogen Peroxide System, Chemosphere 50 (2003), pp. 619-625.

[46] A.E. Papadopoulos, D. Fatta, M. Loizidou, Development and Optimization of Dark Fenton Oxidation for the Treatment of Textile Wastewaters With High Organic Load, J. Hazard. Mater. 146 (2007), pp. 558-563.

[47] N.P. Tantak, S. Chaudhari, Degradation of Azo Dyes by Sequential Fenton's Oxidation and Aerobic Biological Treatment, J. Hazard. Mater. B 136 (2006), pp. 698-705.

[48] S. Shrivastava, S.N. Rao, Pickling Waste as an Inexpensive Iron Source for Fenton Oxidation of Synthetic Dye Bath Waste, Clean – Soil, Air, Water 39 (2011), pp. 996–1000.

[49] J. Wei, Y. Song, X. Tu, L. Zhao, E. Zhi, Pretreatment of Dry-Spun Acrylic Fiber Manufacturing Wastewater by Fenton Process: Optimization, Kinetics and Mechanisms, Chem. Eng. J. 218 (2013), pp. 319-326.

[50] D.J. Joo, W.S. Shin, J.-H. Choi, S.J. Choi, M.-C. Kim, M.H. Han, T.W. Ha, Y.-H. Kim, Decolorization of Reactive Dyes Using Inorganic Coagulants and Synthetic Polymer, Dyes Pigm. 73 (2007), pp. 59-64.

[51] H.A. Aziz, S. Alias, M.N. Adlan, Faridah, A.H.; Assari, M.S. Zahari, Colour Removal from Landfill Leachate by Coagulation and Flocculation Processes, Bioresource Technol. 98 (2007), pp. 218-220.

[52] Z. Liang, Y. Wang, Y. Zhou, H. Liu, Z. Wu, Hydrolysis and Coagulation Behavior of Polyferric Sulfate and Ferric Sulfate, Water Sci. Technol. (2009), pp. 1129-1135.

[53] F. El-Gohary, A. Tawfik, Decolorization and COD Reduction of Disperse and Reactive Dyes Wastewater Using Chemical-Coagulation Followed by Sequential Batch Reactor (SBR) Process, Desalination 249 (2009), pp. 1159-1164.

Table 1 - Characteristics of the synthetic wastewater, after coagulation/flocculation and after coagulation/flocculation followed by Fenton's oxidation (percent removal efficiencies for each stage are indicated within brackets), and global removal for the combined process (Approach 1). Legislated discharge limits are also shown.

Parameter	**Raw wastewater**	**Coagulation & flocculation**	**Fenton**	**Global removal (%)**	**Discharge limits***
pH	8.3	7.3	7.02	-	5.5-9.0
Total nitrogen (mg N/L)	15.9±0.4	14.2±0.3 (10.4)	n.d.	-	
Nitrates (mg NO_3^{2-}/L)	7.5±1.5	6.7±0.3 (10.1)	n.d.	-	
Total phosphorus (mg P/L)	3.0±0.4	2.3 ±0.3 (22.0)	n.d.	-	
Dissolved phosphorus (mg P/L)	2.7±0.4	2.4 ±0.3 (9.4)	n.d.	-	
Chemical oxygen demand (mg O_2/L)	517.9±7.3	276.2±7.9 (46.7)	108.1±8.2 (61.0)	79.2	250
Biochemical oxygen demand (mg O_2/L)	130.7±2.8	89.7±1.0 (31.3)	49.7±2.8 (44.5)	61.9	100
Dissolved organic carbon (mg C/L)	143.1±0.7	78.9±0.2 (44.8)	34.7±1.8 (56.0)	75.7	
Chlorides (mg Cl^-/L)	17.3±1.3	15.3±0.3 (11.3)	n.d.	-	
Specific oxygen uptake rate (k') (mg O_2 (g_{VSS} h))	27.0±2.0	28.5±0.3	n.d.	-	
BOD:COD ratio	0.26±0.3	0.32±0.1	0.46±0.3		
Visible color after dilution 1:40	not visible	not visible	not visible	-	not visible
Vibro fischeri Inhibition 5 min (%)	74.5±5.0	43±3.3	0.0±1.7	-	
Vibro fischeri Inhibition 15 min (%)	82.5±5.0	62±1.7	0.0±4.5	-	
Vibro fischeri Inhibition 30 min (%)	84.5±5.0	67±1.7	0.0±1.6	-	

n.d. – not determined

* Ordinance No. 423 of June 25, 1997, for discharge of textile wastewaters.

Table 2 - Characteristics of the synthetic polyester dyeing wastewater after Fenton's oxidation and respective removals (Approach 2). Legislated discharge limits are also shown.

Parameter	**Fenton**	**Removal (%)**	**Discharge limits***
pH	7.05	-	5.5-9.0
Total nitrogen (mg N/L)	15.1±1.2	5.0	
Total phosphorus (mg P/L)	2.8±0.4	6.7	
Chemical oxygen demand (mg O_2/L)	221.1±1.5	57.3	250
Biochemical oxygen demand (mg O_2/L)	62.8±9.7	52.0	100
Dissolved organic carbon (mg C/L)	63.4±2.0	55.7	
Specific oxygen uptake rate (k') (mg O_2 (g_{VSS} h))	30.0±0.3	-	
BOD:COD ratio	0.28±0.3	-	
Visible color after dilution 1:40	not visible	-	not visible
Vibro fischeri Inhibition 5 min (%)	0.0±2	-	
Vibro fischeri Inhibition 15 min (%)	0.0±1.8	-	
Vibro fischeri Inhibition 30 min (%)	0.0±1.7	-	

* Ordinance No. 423 of June 25, 1997, for discharge of textile wastewaters.

Table 3 - Characteristics of the synthetic wastewater after Fenton's oxidation and coagulation/flocculation – Approach 3 (percent removal efficiencies within brackets) and global removal for the combined process; runs #1 to #3 correspond to different dosages of hydrogen peroxide in the Fenton's stage. Legislated discharge limits are also shown.

Parameter	**Run #1**			**Run #2**			**Run #3**			**Discharge limits***
	Fenton	**Coagulation & flocculation**	**Global removal (%)**	**Fenton**	**Coagulation & flocculation**	**Global removal (%)**	**Fenton**	**Coagulation & flocculation**	**Global removal (%)**	
pH	1.21	7.10	-	1.22	7.09	-	1.10	7.15	-	5.5-9.0
Chemical oxygen demand (mg O_2/L)	403.4± 0.5 (19.3)	207.8±0.4 (48.5)	58.4	301.5±8.2 (39.7)	186.3±0.4 (38.2)	62.7	230.4± 6.9 (53.9)	105.4±8.2 (54.3)	78.9	250
Biochemical oxygen demand (mg O_2/L)	105.1±8.2 (24.8)	60.7±0.7 (42.2)	56.6	85.5±4.8 (38.8)	56.9±1.5 (33.5)	59.3	67.0±8.3 (52.1)	37.3±3.1 (44.3)	73.3	100
Dissolved organic carbon (mg C/L)	115.9±5.5 (24.1)	67.3±3.2 (41.9)	56.0	83.1±3.9 (45.6)	40.6±1.9 (51.1)	73.4	65.7±3.1 (57.0)	26.1±1.2 (60.3)	82.9	
BOD:COD ratio	0.26±0.3	0.29±0.4	-	0.28±0.1	0.31±0.3	-	0.29±0.2	0.35±0.3	-	
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

* Ordinance No. 423 of June 25, 1997, for discharge of textile wastewaters.

Captions of Figures

Figure 1 – Effect of Fe^{2+} dose (a and b), H_2O_2 concentration (c and d) and temperature (e and f) on DOC removal and percentage of H_2O_2 consumption along time, during the 2nd stage – Fenton's oxidation in Approach 1 (initial pH=3.5, T=30 ºC, initial $[H_2O_2]_{a)\text{ and }b)}$= 500 mg/L, $[H_2O_2]_{e)\text{ and }f)}$= 1000 mg/L and $[Fe^{2+}]_{c)-f)}$=191.3 mg/L).

Figure 2 – Effect of Fe^{2+} dose (a-c), H_2O_2 concentration (d-f) and temperature (g-i) on DOC removal, percentage of H_2O_2 consumption and k' along time, during Fenton's reaction in Approach 2 (initial pH=3.5, T=30 ºC, initial $[H_2O_2]_{a)-c)}$= 5.0 g/L, $[H_2O_2]_{g)-i)}$ 2.5 g/L and $[Fe^{2+}]_{d)-i)}$=350 mg/L).

Figure 3 – Variation of DOC removal with pH during the coagulation stage – Approach 3 – for the different doses of hydrogen peroxide employed in the previous Fenton's process in runs #1, #2 and #3 ($v_{coagulation}$=150 rpm, $t_{coagulation}$=3 min, $[Fe]_{\text{dissolved run \#1}}$ = 64.8 mg/L, $[Fe]_{\text{dissolved run \#2}}$=88.5 mg/L, $[Fe]_{\text{dissolved run \#3}}$=222 mg/L and T =$T_{ambient}$=22-24 ºC).

Figure 4 – Effect of Fe^{2+} and H_2O_2 doses on the operating cost of wastewater treatment by: coagulation/flocculation plus Fenton's processes – Approach 1 (a) or Fenton's reagent – Approach 2 (b), and influence of [Superfloc C-573] and $[H_2O_2]$ on the operating cost of Fenton's process followed by coagulation/flocculation – Approach 3 (c).

Fig. 1

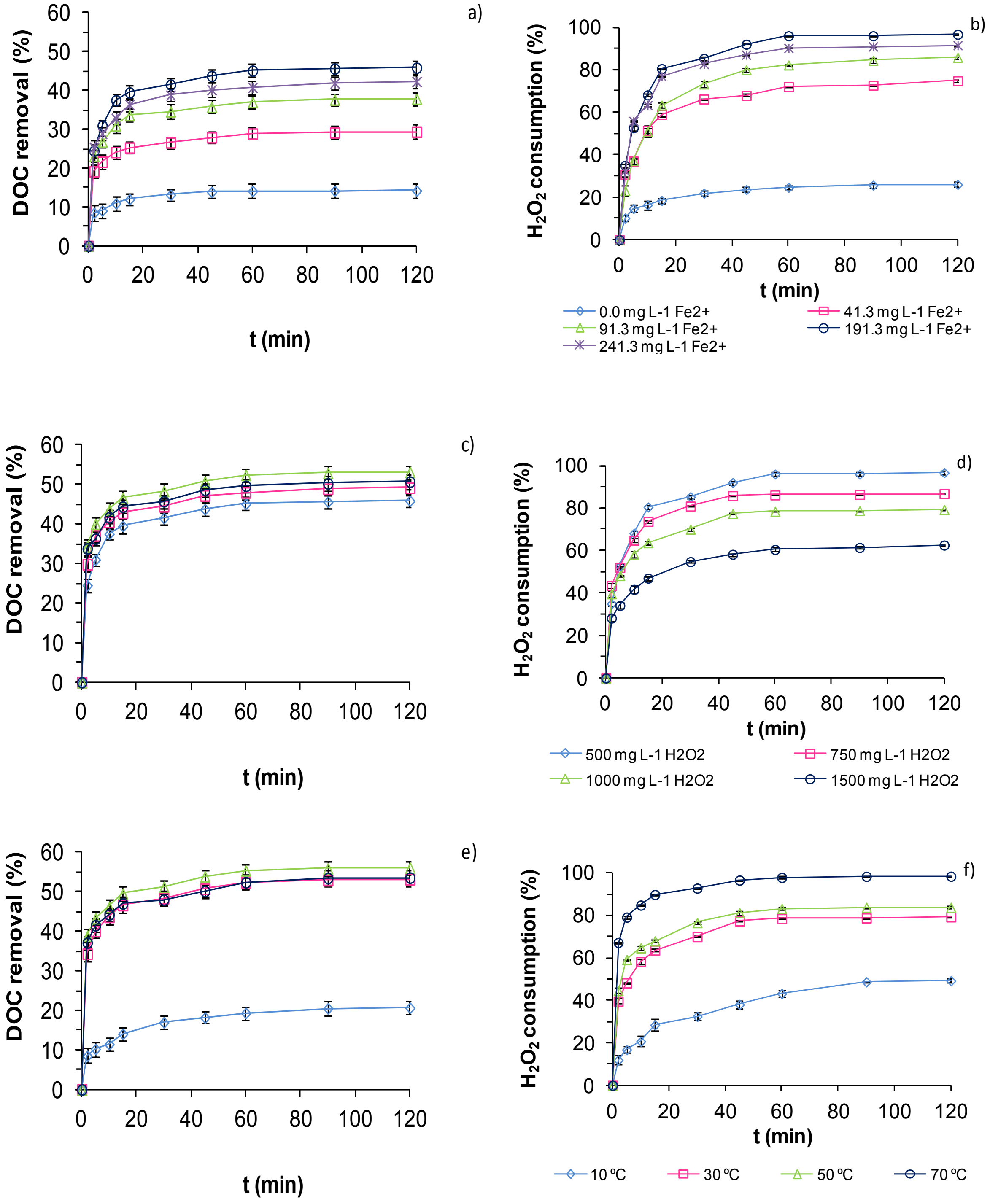

a)
DOC removal (%)
t (min)
b)
H_2O_2 consumption (%)
t (min)
0.0 mg L-1 Fe2+
41.3 mg L-1 Fe2+
91.3 mg L-1 Fe2+
191.3 mg L-1 Fe2+
241.3 mg L-1 Fe2+
c)
DOC removal (%)
t (min)
d)
H_2O_2 consumption (%)
t (min)
500 mg L-1 H2O2
750 mg L-1 H2O2
1000 mg L-1 H2O2
1500 mg L-1 H2O2
e)
DOC removal (%)
t (min)
f)
H_2O_2 consumption (%)
t (min)
10 ºC
30 ºC
50 ºC
70 ºC
0
20
40
60
80
100
120

Fig. 2

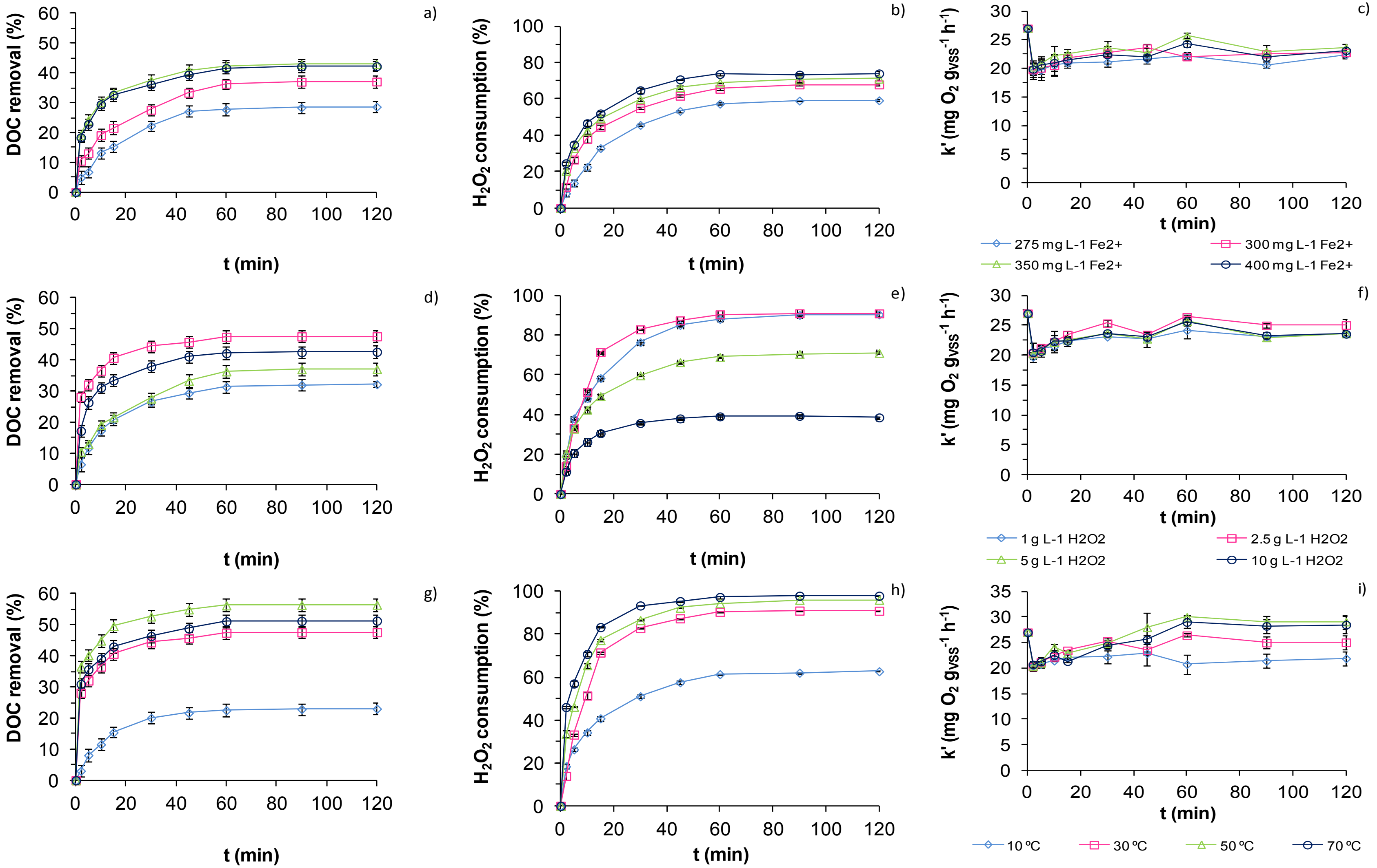

a)
DOC removal (%)
t (min)
b)
H_2O_2 consumption (%)
t (min)
c)
k' (mg O_2 g_{VSS}^{-1} h^{-1})
t (min)
275 mg L-1 Fe2+
300 mg L-1 Fe2+
350 mg L-1 Fe2+
400 mg L-1 Fe2+
d)
DOC removal (%)
t (min)
e)
H_2O_2 consumption (%)
t (min)
f)
k' (mg O_2 g_{VSS}^{-1} h^{-1})
t (min)
1 g L-1 H2O2
2.5 g L-1 H2O2
5 g L-1 H2O2
10 g L-1 H2O2
g)
DOC removal (%)
t (min)
h)
H_2O_2 consumption (%)
t (min)
i)
k' (mg O_2 g_{VSS}^{-1} h^{-1})
t (min)
10 ºC
30 ºC
50 ºC
70 ºC

Fig. 3

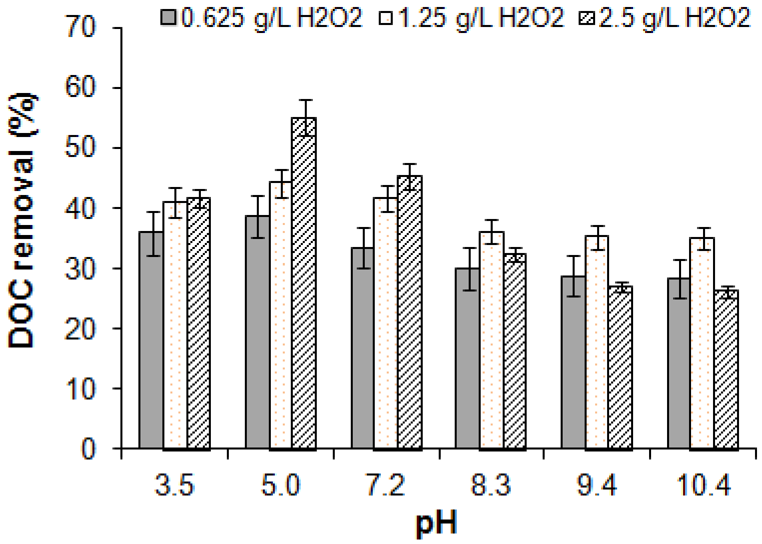
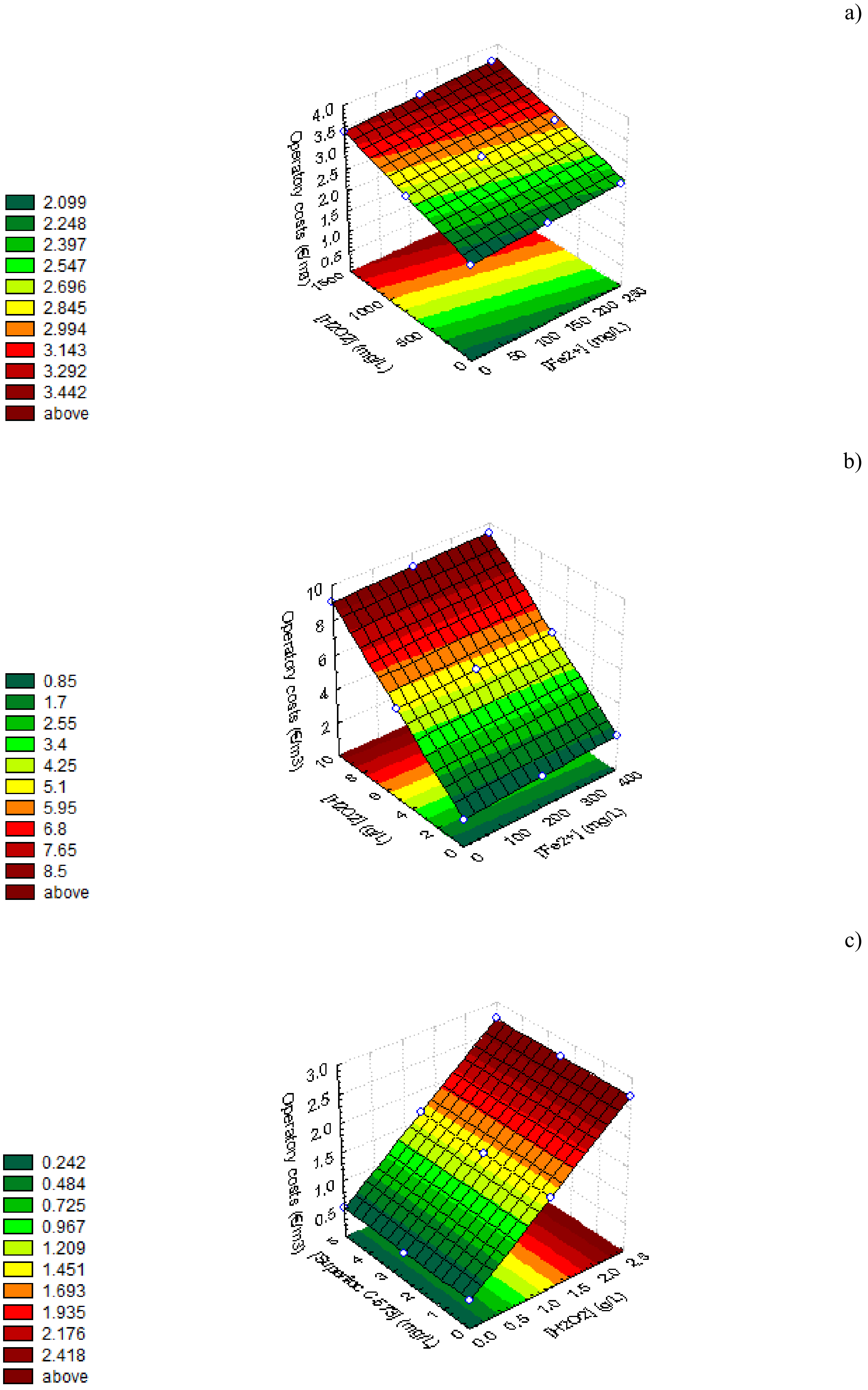

0.625 g/L H2O2
1.25 g/L H2O2
2.5 g/L H2O2
DOC removal (%)
70
60
50
40
30
20
10
0
3.5
5.0
7.2
8.3
9.4
10.4
pH

Fig. 4


a)
2.099
2.248
2.397
2.547
2.696
2.845
2.994
3.143
3.292
3.442
above
Operatory costs (€/m3)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
[H2O2] (mg/L)
0
500
1000
1500
[Fe2+] (mg/L)
0
50
100
150
200
250
b)
0.85
1.7
2.55
3.4
4.25
5.1
5.95
6.8
7.65
8.5
above
Operatory costs (€/m3)
2
4
6
8
10
[H2O2] (g/L)
0
2
4
6
8
10
[Fe2+] (mg/L)
0
100
200
300
400
c)
0.242
0.484
0.725
0.967
1.209
1.451
1.693
1.935
2.176
2.418
above
Operatory costs (€/m3)
0.5
1.0
1.5
2.0
2.5
3.0
[Superfloc C-573] (mg/L)
0
1
2
3
4
5
[H2O2] (g/L)
0.0
0.5
1.0
1.5
2.0
2.5