This article was published in Environment and Waste Management, 14 (3), 232-255, 2014
http://dx.doi.org/10.1504/ijewm.2014.064583

A New Strategy for Treating a Cotton Dyeing Wastewater – Integration of Physical-Chemical and Advanced Oxidation Processes

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Abstract

New strategies were herein applied for treating a cotton dyeing wastewater: coagulation/flocculation followed by Fenton's oxidation - Approach 1, Fenton process *per se* - Approach 2, and Fenton followed by coagulation/flocculation -Approach 3, aiming reducing chemicals consumption. Regarding the cost analysis, which is crucial for deciding on the best strategy to implement, it was found that in Approach 1 and Approach 2 the hydrogen peroxide has a major influence on the total costs as compared to ferrous ion. In Approach 3, the total costs are again mostly related to the consumption of reagents in the oxidation stage. The integration of the Fenton's process followed by coagulation/flocculation provided an effluent that meets the discharge limits, with global organic matter removals of 55.6% for COD, 42.7% for BOD and 70.4% for DOC, and almost complete color reduction (99.6%). However, the combined treatment of coagulation/flocculation followed by Fenton's oxidation exhibits also high overall efficiencies (61.7%, 25.8% and 71.2% for COD, BOD_5 and DOC removal, respectively, with almost complete decolorization) but simultaneously smaller operating costs associated with chemicals consumption (0.82 €/m^3), putting into evidence the usefulness of the novel strategy implemented: use of the residual dissolved iron employed as coagulant in the first stage as catalyst in the subsequent Fenton's oxidation.

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

1. Introduction

Textile dyeing is the most chemically intensive process among all textile industry steps, which include textile preparation, dyeing, washing and finishing. Wastewaters resulting from textile dyeing contain significant concentrations of unfixed dyestuff and considerable quantities of auxiliary products (Grau, 1991). Unfortunately, many of the chemicals and dyes used in textile dyeing are recalcitrant; they are often not biodegradable and eventually toxic (Anouzla et al., 2009). As such substances remain in the effluent they create negative impacts on the receiving water bodies, even when the wastewater is treated together with domestic effluents in WWTPs (Alaton, 2007).

In order to minimize the environmental impacts caused by the effluents generated in the dyeing of fibers and fabrics, it is necessary to implement efficient and effective processes for the removal of toxic and recalcitrant compounds. The coagulation/flocculation process is a versatile technique that has been used for removal of suspended solids, organic compounds and color (Meriç et al., 2005). This technique involves a series of physical-chemical interactions: electrostatic attraction, sorption, bridging (related to high molecular weight polymers) and inclusion in metal precipitates, which are responsible for the pollutants removal. However, the pollutants are transferred to another phase or simply concentrated, not being destroyed.

Another promising technique that can be used in dyeing textile wastewater treatment for organic matter removal, dyes degradation and often effluent biodegradability improvement, is the Fenton's process. This method is based on the generation of hydroxyl radicals (species with a very high oxidation potential - 2.8V (Papadopoulos, 2007)) by the decomposition of hydrogen peroxide, in acidic conditions, catalyzed by ferrous ions (eq. 1), followed by the organics (including dyes) oxidation by such radicals, according to eq. 2 (Walling, 1975; Kuo, 1992):

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

$$HO^{\bullet} + RH \rightarrow H_2O + \text{intermediates} \quad (2)$$

Of course, the intermediates can be also oxidized and ultimately mineralized.

In this work it was evaluated the treatability of a synthetic cotton dyeing effluent by combining coagulation/flocculation and Fenton's oxidation processes for reducing the disadvantages of each treatment when used alone. Besides, by using an iron salt as coagulant in the first stage, the amount of catalyst added in the chemical oxidation step is reduced, thus decreasing the overall treatment cost. The same also applies if coagulation is preceded by Fenton's oxidation. A synthetic wastewater with a composition similar to that of a real effluent was used, for minimizing the experimental problems that result from the seasonal variations in real effluents from this type of industries. The main objective was therefore to find the best treatment approach and adjust the operating conditions in order to obtain an effluent that can be discharged into water bodies, i.e., an effluent that accomplishes the maximum allowable limits imposed by legislation for discharge, while simultaneously reducing the operating costs. An economic analysis was thus accomplished, taking into account the operating costs

associated to the consumption of chemicals in each stage. The approaches herein considered are only scarcely addressed in the scientific literature, are almost always focused in processes efficiencies only and, up to the authors' knowledge, were never integrated with costs assessment. In fact, different combinations of these types of treatments allow reaching very good performances, which makes the operating costs associated with each process a key factor to be considered.

2. Materials and Methods

2.1 Synthetic Cotton Dyeing Wastewater Preparation

As mentioned above, a real wastewater was not used in this work because its characteristics change dramatically from day to day. So, a synthetic effluent was prepared in accordance with the information presented elsewhere (Rodrigues et al., 2012 a). Basically, it was taken into account the quantity of dyes (Procion yellow H-EXL gran and Procion deep red H-EXL gran) and of auxiliary products used in the dyeing baths, and the percentage of these products unfixed in the fibers (rejection percentage). Such information was supplied by the dye-house Erfoc – Acabamentos Têxteis S.A. (Famalicão, Portugal), allowing thus estimating the concentration of each species in the effluent.

2.2. Experimental Procedure

2.2.1. Coagulation/Flocculation

In Approaches 1 and 3 (cf. Figure 1) the coagulation/flocculation process was followed or preceded by the Fenton's oxidation, respectively. The coagulation/flocculation experiments were conducted in a *Jar-test* (ISCO). In all experiments, 300 mL of effluent was employed. For Approach 1, the pH of the raw wastewater was adjusted to a previously established value (between 3.5 and 10.4) and the solution transferred into a beaker (800 mL capacity). The coagulant (ferrous sulfate) was added with rapid stirring (150 rpm) and the pH readjusted, if necessary. After 3 min rapid mixture the stirring rate was reduced to 20 rpm, the flocculant added (Magnafloc 155 at a dose of 0.5 mg/L) and the agitation proceeded during 15 minutes. These were the optimal conditions determined in a previous work (Rodrigues et al., 2012 a)).

After 30 min of sedimentation the supernatant was collected and acidified with HNO_3 (68%, from Merck) to pH 1 to keep the iron dissolved (so that it could be used as a catalyst in Fenton's reaction). In Approach 3 the supernatant from the Fenton's process was previously subjected to centrifugation at 13400 rpm for 2 min (Mini Spin Eppendorf), and then acidified with HNO_3 (68%, from Merck) to pH 1 to keep the iron dissolved for the coagulation/flocculation stage. Before the coagulation experiments the pH was then adjusted to predefined values in the range 3.5-10.4. The conditions used in Approach 3 were the same as in Approach 1. All coagulation/flocculation experiments were conducted at room temperature (21-23 ºC).

2.2.2. Fenton's Oxidation

In Fenton's oxidation runs 500 mL of synthetic dyeing wastewater (pre-treated by coagulation/flocculation – Approach 1; or the raw effluent – Approaches 2 and 3) was put into an 1 L-capacity batch jacketed reactor, connected to a water thermostatic bath (Grant Y6) to maintain the temperature inside the reactor at the desired value (between 10 and 70 ºC). After temperature stabilization, the pH was adjusted to 3.5 with 1N H_2SO_4 (from Merck) since this was the optimal value found in the treatment of similar effluents (Rodrigues et al., 2009 a); 2009 b); 2012 b)). The catalyst ($FeSO_4$, $7H_2O$, from Merck) was then added (if required – e.g. in Approach 1 a null catalyst dose was attempted, using only the remaining dissolved iron – 0.29 mg/L) and the reaction started with addition of H_2O_2 30% (w/v) (Merck); the oxidant was added in a single step because preliminary results have evidenced almost no improvement through several additions (data not shown). During the reaction the solution was constantly stirred by using a magnetic bar and a magnetic stirrer (from Falc).

Along the reaction, samples were collected for further analyses, particularly for quantifying the DOC and absorbance at 520 nm (wavelength corresponding to the maximum absorbance in the visible region, as described below). The reaction was stopped by addition of excess sodium sulfite, which immediately reacts with the remaining hydrogen peroxide.

Because sodium sulfite affects the determination of other parameters, e.g. COD, in Approaches 1 and 2, H_2O_2 elimination was accomplished, with simultaneous iron precipitation, by raising the pH to 12.3 through addition of 10 M NaOH (from Merck) and heating the samples at 80 °C for 10 minutes. After this the effluent was neutralized (to pH ~7.0) with concentrated H_2SO_4, although for samples aiming measuring the inhibition of *V. fischeri* neutralization was carried out with HCl, as proposed by the analytical methodology. This procedure was adopted for determination of k' (see section 2.4) along Fenton's reaction and other parameters imposed by legislation for the final effluent as well as for toxicity assessment (inhibition of the bacterium *Vibrio fischeri*). Such parameters include chemical oxygen demand (COD), biochemical oxygen demand after 5 days (BOD_5), pH and visible color at naked eye after a dilution of 1:40. In Approach 3 the effluent after the oxidation stage was acidified to pH 1 to keep the iron dissolved for the coagulation/flocculation study, which simultaneously slows down or inhibits Fenton's reaction; analyses of the effluent were done immediately.

2.3. Research Strategy

The methodology adopted involved three different approaches depending on the type and sequence of the treatment processes applied (see Figure 1). Because the pre-treatment of the raw wastewater by coagulation/flocculation did not allow obtaining an effluent that can be discharged into water bodies (the value of COD was slightly above the maximum allowable discharge limit – cf. Table 1) (Rodrigues et al., 2012 a), it was necessary to use a further treatment. However, the BOD/COD ratio of the resulting effluent is too low (0.28 – Table 1) for considering a biological treatment. The application of Fenton's technique is an attractive alternative

to the biological process because one can use the dissolved iron resulting from the coagulation/flocculation stage (0.29 mg/L) as catalyst in the chemical oxidation, reducing the cost with reagents. So, integration of coagulation/flocculation with chemical oxidation by Fenton's reagent was attempted (Approach 1 – Figure 1). In the chemical oxidation stage performed, a parametric study was carried out where it was individually varied the dose of Fe^{2+} added, the initial concentration of hydrogen peroxide and the temperature, to better understand the effect of each variable in color and DOC removal. Then, an experiment was carried out to assess if the final effluent had characteristics that allowed discharging it into the environment, and the operating costs assessed.

In Approach 2 Fenton's oxidation was directly applied to the effluent. The objective was to assess if the chemical oxidation per se would be able to produce an effluent meeting legal standards. This treatment will be analyzed in section 3.2 and, again, and a parametric study was implemented to better comprehend the effect of each variable (Fe^{2+} concentration, initial H_2O_2 concentration and temperature) in the process efficiency.

In Approach 3, the Fenton's reagent (under the previously determined optimum conditions of Approach 2) was followed by coagulation/flocculation (because it was concluded that chemical oxidation alone is not effective enough). For the coagulation stage it was also analyzed the effect of the most relevant conditions (pH and flocculant dose), using as coagulant the dissolved iron resulting from Fenton's oxidation. Because for this strategy the costs revealed to be quite high, further runs were carried out in which the dose of chemicals (H_2O_2 and Fe^{2+}) was progressively reduced in the Fenton's stage: first by 1/2, and subsequently to 1/4; as detailed below, no further runs were done because the effluent was no longer meeting legislation standards.

2.4. Analytical Methods

The UV–Vis spectrum of the effluent was recorded from 200 to 800 nm using an UV–Vis spectrophotometer (Pye Unicam Model Heyios α). Color removal was then assessed at 520 nm, the maximum absorbance wavelength (λ_{max}) in the visible range. In the case of samples collected after treatment, the pH was adjusted to the initial value, because absorbance reading varies with pH.

The biodegradability was evaluated by measuring the specific oxygen uptake rate (k) at 20 ºC. The samples were inoculated with biomass from the activated sludge tank of a WWTP treating textile effluents, and the dissolved oxygen concentration measured for 30 min (using a YSI Model 5300 B biological oxygen monitor). The specific oxygen uptake rate (k') was calculated as the ratio between the oxygen concentration decay rate (which was linear in the above-mentioned period) and the volatile suspended solids (VSS) concentration after the addition of the inoculum (700 mg VSS/L).

The inhibition of *Vibrio fischeri* test was performed according to the standard DIN/EN/ISO 11348-3 (International Organization for Standardization 2005). The bacterium was 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.

Other analytical determinations were carried out according to Standard Methods (APHA 1998): dissolved organic carbon (DOC) was measured in a TC/TOC analyzer (Shimadzu 5000A) - 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); and total phosphorus by Method 4500P - E. Total nitrogen was determined by colorimetry according Method D992-71 ASTM Standards (ASTM 1973) after previous digestion (Method 4500 - N C) while chlorides, nitrates and dissolved phosphorus were measured by ion chromatography (Dionex DX 120) using a Dionex Ionpac AS9-HC 4 mm (10-32) column.

The dissolved iron was measured by flame atomic absorption spectrometry (Method 3111 B), using an AAS GBC spectrophotometer (model 932 AB Plus), in samples previously filtered through cellulose nitrate membranes (Albert) with 0.45 μm of pore size.

All analytical determination were performed in duplicate, with exception of absorbance at 520 nm, and the coefficients of variation were less than to 2% for DOC, 17% for BOD_5, 6% for COD and k', 3% for inhibition of *V. fisheri* and 5% for the other parameters.

3. Results and Discussion

The more relevant characteristics of the synthetic cotton dyeing wastewater used in this study are reported in Table 1. It is a colored effluent presenting high values of pH and chlorides, moderate concentration of organic matter (DOC and COD) and low biodegradability (BOD:COD ratio <0.4) but is not toxic for *Vibrio fischeri* .

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

Section 2.3 presents a brief explanation about: i) the need of a subsequent process after the coagulation/flocculation stage and ii) the reasons for choosing the Fenton's reagent. So, a detailed parametric study was carried out, analyzing the effect of the most important variables in the Fenton's process, aiming choosing the best ones that lead to higher color and DOC removals. Among the variables studied, the concentration of catalyst (ferrous iron salt) was considered, in addition to the dose resulting from the coagulation stage (0.29 mg Fe/L); the effect of the initial concentration of hydrogen peroxide and temperature on color and DOC removal was also analyzed. In the following subsections are presented the results obtained for each variable studied during the Fenton's stage. The pre-treatment of the raw wastewater by coagulation/flocculation was performed under the optimum conditions determined in a preliminary work (Rodrigues et al., 2012 a)): $v_{coagulation}$ = 150 rpm, $t_{coagulation}$= 3 min, $[Fe^{2+}]$ = 200 mg/L, pH = 9.4, T = T_{amb} = 21-23 ºC, $v_{flocculation}$ = 20 rpm, $t_{flocculation}$ = 15min, [Magnafloc 155] = 0.5 mg/L.

3.1.1. Influence of ferrous ion concentration added

To study the effect of the dose of ferrous ion added in color and DOC removal, the following range was considered: from 0 up to 199.7 mg/L; higher doses did not lead to improved performances, as shown below. The H_2O_2 concentration and temperature were fixed at 500 mg/L and 30±0.5 ºC, respectively.

In general, and as can be seen in Figure 2a), color removal is very rapid in the first 15 minutes, remaining practically constant for longer reaction times. DOC removal is also fast in the first 15 minutes of reaction, then slows down till 60 minutes of reaction, and presents a negligible increase for t > 60 minutes.

The two responses considered (color and dissolved organic carbon removal) increased with the dose of iron added up to 99.7 mg/L (meaning a total iron load of ~100 mg/L), and the reaction rate is also higher. However, if the amount of Fe^{2+} added is increased up to 199.7 mg/L, both the rate of reaction and process performance are detrimentally affected, either in terms of color or DOC removal. The existence of an optimum iron dose is also reported in others works that evaluated either dyes or organic compounds removal (Malik and Saha, 2003; Meriç, 2004; Rodrigues et al., 2009 a); Sun et al., 2007) and is explained by the scavenging reaction of the hydroxyl radicals by excess of iron ions ($HO^{\cdot} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$), thereby decreasing the concentration of radicals available and limiting the oxidation of the organic compounds. With 99.7 mg/L of Fe^{2+} added it was obtained ~81% of color removal (as long as t > 15 minutes), and 46.8% for DOC reduction after 120 min of reaction. It is noteworthy that if no iron was added in the Fenton's process, making use of the dissolved iron proceeding from the coagulation/flocculation stage, it is possible to degrade the dyes, but at a slow rate. However, mineralization was insignificant. This evidences the need of adding further iron in the Fenton's step.

The optimum dose of ferrous iron found is similar to that reported in other studies. For instance, Kim et al. (2004) obtained the optimum concentration of ferrous ion of 90.2 mg/L for removing the reactive dye blue 49 and also for COD abatement (initial COD=300 mg/L and $[dye]_o$=500 mg/L).

3.1.2. Effect of the initial hydrogen peroxide concentration

The reaction of hydrogen peroxide with Fe^{2+} in acidic conditions generates hydroxyl radicals (eq. 1), and thus the H_2O_2 concentration influences the decomposition of the dyes and organic matter by Fenton's oxidation. In this study the dose of oxidant was varied between 250 and 750 mg/L (this range was established taking into account the organic load, in terms of COD present in solution after the coagulation/flocculation step). The other parameters were kept constant at 30±0.6ºC for temperature and 99.7 mg/L for the amount of ferrous ion added.

The results of color removal during 120 minutes of reaction are presented in Figure 2 d), showing again that its removal occurs, preferentially, in the first 5-15 minutes of reaction (depending on the initial concentration of hydrogen peroxide). It is notorious the influence of the hydrogen peroxide dose in this period, leading to ~80% of color removal for $[H_2O_2]$ = 500 mg/L and t ~ 15 min, without any significant increase for longer reaction times. In Figure 2 c) are shown the results of DOC removal. It can be see that most of the organic carbon is removed in the first 30-40 minutes, but continues to slightly increase till 60 or 120 min. The DOC removal increases with the H_2O_2 concentration up to 500 mg/L, and slightly decreases for a higher dose. For this optimum dose the DOC removals are 40.1 and 46.8%, respectively, after 30 and 120 minutes of reaction. It is noteworthy that the same optimum dose of peroxide was observed in the color removal (Fig. 2d).

The existence of an optimum H_2O_2 concentration was also observed by other authors (Azbar et al., 2004; Ramirez et al., 2005; Alaton and Teksoy, 2007; Rodrigues et al., 2009 a)) and is explained by the fact that a parallel reaction

between H_2O_2, in excess, with the hydroxyl radicals occurs, generating $HO_2^{\bullet}$ species with a lower oxidation potential ($HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$).

In the literature there are various studies dealing with the treatment of dye-containing solutions or effluents through Fenton's oxidation where optimum H_2O_2 concentration, similar to that obtained in this study, have been reported. In particular, Swaminathan et al. (2003) studied the degradation of three different dye solutions with 250 mg/L of Red M5B (initial COD=142 mg/L), of an H-acid (initial COD=215 mg/L) and of Blue MR (initial COD=180 mg/L) and obtained the optimum dose of hydrogen peroxide in the range of 400-500 mg/L. Meriç et al. (2004) obtained 98% color removal and 76% of COD reduction in a solution with 100 mg/L of RB5 dye (initial COD=75 mg/L) when using 500 mg/L of H_2O_2 (optimum dose) through the Fenton's process. Later on, Meriç et al. (2005) tested the treatment of a synthetic dyeing wastewater (BOD=150 mg/L, COD=560 mg/L) and found an optimum hydrogen peroxide concentration of 800 mg/L.

3.1.3. Effect of the temperature

The temperature is a key variable that has to be taken into account because has an important influence in the efficiency and rate of the Fenton's reactions. In order to determine the effect of this parameter in color and COD removal, a series of experiments were conducted by varying the reaction temperature between 10 and 70 ºC while fixing the other variables in the optimum values determined before.

Figure 2 e-f) presents the results obtained and show that temperature exerts a strong effect in the mineralization of the organic compounds and color removal. These removals are accelerated when the temperature increased up to 50 ºC, but at 70 ºC the color removal was not improved, and the DOC removal inclusively slightly decreased as compared to performances reached at 50 ºC.

At the optimum temperature of 50 ºC, a very high color removal was obtained in only 2 minutes of reaction (95.9%), which was nearly the same as that reached after 120 minutes of reaction (97.3%). For mineralization, after 30 min a value of 45.5% was achieved, but it continued to increase slowly (50.4% and 53.8% for 60 and 120 min of reaction, respectively). This optimum value for temperature was also reported in other studies that evaluated the removal of total organic carbon and dyes (Ramirez et al., 2005; Gulkaya et al., 2006; Sun et al., 2007; Rodrigues et al., 2009 a); 2012 a)).

The reason for obtaining an optimum temperature has been attributed to the fact that, on one hand, the rate of reaction and inherently the performance increases, because the kinetic constants also increase with the temperature (Arrhenius law), but on the other hand, for higher temperatures (T>40-50 ºC) the hydrogen peroxide decomposes into oxygen and water (Ramirez et al., 2008).

3.1.4. Optimized treatment performance

After having carrying out the parametric study, which allowed to establish the optimal conditions for the Fenton process ($[Fe^{2+}]_{added}$= 99.7 mg/L, $[H_2O_2]$= 500 mg/L and T= 50±0.5 ºC), an additional run was performed using

these operating conditions for 60 minutes of reaction only (because for longer reaction times oxidation performance is almost not improved, as shown in the previous figures). Under such optimized conditions, the inhibitory effect of the effluent on *Vibrio fischeri* was analyzed. It was observed that the inhibition remained at 0%, meaning that the organic intermediates generated in the Fenton's process show no toxicity to these bacteria. The treated effluent, after 60 minutes of reaction, was analyzed and the results (upon neutralization) of DOC, BOD_5, COD, visible color after 1:40 dilution and absorbance at 520 nm are presented in Table 1. The organic matter removal reached in the Fenton process (48.8% for COD, 22.5% for BOD_5 and 50.4% for DOC) was higher than in the coagulation/flocculation stage (25.2% for COD, 4.3% for BOD_5 and 41.9% for DOC); the overall removal efficiencies obtained with the combination of these two treatments were 61.7, 25.8, 71.2 and 99.8% for COD, BOD_5, DOC and color, respectively. The wastewater biodegradability, as inferred from the BOD/COD ratio, increased slightly with the coagulation/flocculation process, from 0.22 to 0.28. A more significant increase was observed with the chemical oxidation, the final effluent being biodegradable (BOD/COD=0.43). However, it is important to highlight that the wastewater, after being submitted to the combined treatment of coagulation/flocculation and Fenton's oxidation (Approach 1), can be discharged into water bodies because it exhibits values below the maximum allowable limits (according to Portuguese legislation for the textile sector – cf. Table 1). Such limits are not reached by the coagulation/flocculation process alone.

3.2. Fenton Oxidation (Approach 2)

In Approach 2 it was evaluated the treatability of the synthetic cotton dyeing wastewater by Fenton's oxidation *per se*. A parametric study was performed, being evaluated the influence of initial ferrous salt and hydrogen peroxide concentrations and temperature in color and DOC removal. The effects in the effluent biodegradability (assessed by measuring k' – specific oxygen uptake rate) were also determined, aiming assessing the possibility of integrating subsequently a biological treatment.

3.2.1. Influence of ferrous ion concentration

For evaluating the effect of the catalyst dose four runs were carried out wherein this parameter was varied between 100 and 350 mg/L. The other variables were fixed at 5 g/L for H_2O_2, 3.5 for pH and 30±0.4 ºC for temperature. In Figure 3 b) are shown the results obtained for color removal. It can be concluded that: i) for 100 and 275 mg/L of Fe^{2+} color abatement proceeded at a slower rate as compared to the other runs, where higher concentrations of catalyst were employed; ii) for the first two concentrations the color removal reaches its maximum (and then remains nearly constant) within 10-15 minutes of reaction while for 300 and 350 mg/L of Fe^{2+} only 5 minutes were required to reach that point; iii) for 300-350 mg/L of Fe^{2+} a color removal of ~90% was reached.
The organic carbon removal (see Figure 3 a)) occurs more rapidly in the first 20-30 minutes of reaction, and after this time the rate of mineralization slows down, whatever the load of catalyst employed. The mineralization at the

end of the experiments increased from 30.7 to 41.4% when the dose of ferrous ion increased from 100 to 300 mg/L, but further increasing the dose of catalyst do not result in any improvement in DOC removal.

The biodegradability, expressed in terms of the specific oxygen uptake rate - k', decreased after 2 minutes of reaction as compared to the raw wastewater, but tended to increase up to 60 min of reaction (Figure 3c); afterwards an inversion of the k' value was noticed. A possible explanation for the k' profiles is related to the formation of more recalcitrant compounds at the earlier stages of the reaction (responsible for the lowest k' values), which are further converted into more biodegradable compounds as reaction proceeds. These intermediates in turn revert into less biodegradable substances for very long reaction times. A similar pattern was also observed in a previous work, with a similar effluent (Rodrigues et al., 2012 b)). The maximum biodegradability, corresponding to k' of 10.8 mg $O_2/(g_{VSS}.h)$, was achieved after 60 minutes of reaction and when using 300 mg/L of ferrous ion.

Again, as in section 3.1.1., it was observed an optimum dose of catalyst (which is the same in the different responses considered), what can be attributed to the scavenging reaction between excess of ferrous ion with the hydroxyl radicals.

The optimum dose of ferrous iron achieved is similar to that obtained in other studies. For example, Rodrigues et al. (2009 b)) obtained an optimum concentration of ferrous ion for maximizing the color and DOC removal of 404 mg/L and 325 mg/L, respectively, when treating a synthetic cotton dyeing effluent (initial DOC=161.4 mg/L).

3.2.2. Effect of the initial hydrogen peroxide concentration

For selecting the optimum hydrogen peroxide concentration to treat a cotton dyeing wastewater by Fenton oxidation, which is quite important when assessing the costs of this process, four experiments were carried out wherein this variable was varied in the range 2.5-20 g/L (while fixing the ferrous ion concentration in the optimum value determined before – 300 mg/L – and the temperature in 30±0.7 ºC). The high concentrations of H_2O_2 employed are justified by the oxidation of the high amount of chloride present in the effluent (around 8 g/L), which is used as electrolyte (9 g/L) in the cotton dyeing bath. The chlorides act as scavengers of the hydroxyl radicals, thus requiring the use of high oxidant doses.

Figure 3 e) shows the variation of the color removal with the initial H_2O_2 dose; it can be seen that, in general, color was quickly removed (in only 2-5 minutes of reaction) whatever the oxidant concentration, and that removals of ~ 90% were reached.

The DOC removal (Figure 3 d)) does not proceed so quickly, as in the previous experiments. The mineralization degree increased with the hydrogen peroxide concentration, in the range tested. However, we will consider 10 g/L as the more suitable dose of hydrogen peroxide because when doubling it (till 20 g/L), increase in DOC removal is almost negligible. For a concentration of 10 g/L the DOC reduction was 36.2% at 15 minutes and 44.2% at 120 minutes of reaction.

The effluent biodegradability (assessed through k') along reaction time for different H_2O_2 concentrations is presented in Figure 3 f). Although there are slight oscillation in k' at the earlier stages of reaction, a maximum was obtained again at t= 60 min. As stated before, the reduction of k' for longer reaction times may be related to

the formation of less biodegradable organics during the oxidative process. The H_2O_2 concentration influences the biodegradability of the final effluent, a maximum value of k' of 14.1 mg $O_2/(g_{VSS}.h)$ being obtained when using an oxidant dose of 10 g/L, after 60 minutes of reaction.

The optimum dose of oxidant obtained was similar to that achieved in other works reported in literature. Namely, Rodrigues et al. (2009 b)) found an optimal H_2O_2 dose of 5 g/L for maximizing the biodegradability increase of a simulated dyeing cotton wastewater (COD = 428 mg O_2/L and TOC = 161 mg C/L.

3.2.3. Effect of the temperature

In Figure 3 h) is presented the variation of the color removal with temperature, along the reaction time. Again, color removal was very fast (only ca. 2 min were required to reach levels of ~90% that were maintained constant for longer times). DOC removal histories (Figure 3 g) are similar to those reported previously, the temperature exhibiting in this case a more notorious effect. Best results were obtained in the run at 50 ºC (42.8% of mineralization after 15 min, which increased up to 52.2% after 120 min of reaction).

In what concerns biodegradability (k' – c.f. Figure 3 i)), it is noteworthy that it remained constant at T=10 ºC, but clearly improves for higher temperatures. Higher values of k' were obtained at 50 ºC, with the maximum being again observed after 60 min of reaction (15.5 mg$O_2/(g_{VSS}.h)$).

The higher performances obtained at 50 ºC can be due to the thermal decomposition of hydrogen peroxide in water and oxygen at higher temperatures. The optimum value achieved was equal to that obtained when applying the Fenton process to the pre-treated effluent (Approach 1) and similar to that reported in other works ((Ramirez et al., 2005; Gulkaya et al., 2006; Sun et al., 2007; Rodrigues et al., 2009 a); 2012 a)).

3.2.4. Optimized treatment of the raw synthetic cotton dyeing wastewater

After evaluating the influence of each variable on the efficiency of the Fenton's process, a further run was carried out under the more suitable conditions previously identified (those maximizing color and DOC removal, and also biodegradability): $[Fe^{2+}]$= 300 mg/L, $[H_2O_2]$= 10 g/L and T=50±0.7 ºC. The run lasted only 60 minutes (time after which it was obtained the maximum biodegradability - k' value); besides, after such time no further improvement was observed in color reduction, and DOC removal only slightly increased. Samples were collected and taken to follow up the toxicity (inhibition of *Vibrio fischeri*). At all times of reaction and contact with bacterium the effluent exhibited no toxic behavior, i.e. the percentage of inhibition was 0.0% (value equal to that obtained for the raw wastewater – Table 2).

The treated effluent was analyzed in terms of several legislated parameters and the results are shown in Table 2. With the Fenton's process alone a high color removal (89.9%) was obtained but the organic matter removal was inferior (25.1% for COD and 48.8% for DOC). Besides, it allowed to make the effluent more biodegradable because i) the BOD_5 value increased, ii) the BOD_5:COD ratio was increased (from 0.22 to 0.52) and iii) k' was also considerably increased from 0.7 to 15.5 mg $O_2/(g_{VSS}$ h).

However, the effluent obtained upon treatment by the Fenton's reaction alone is not suitable to be discharged because the values of COD and BOD were slightly higher than the maximum allowable discharge limits (Table 2). So, it is necessary to apply a subsequently treatment that can be: i) coagulation/flocculation, for instance using as coagulant the quantity of dissolved iron resulting from the Fenton's process – study presented in section 3.3 – or ii) biological oxidation (since the effluent can be considered as biodegradable after the Fenton's process); this later topic will be the aim of future work.

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

To increase the removal of organic compounds and aiming obtaining a wastewater with characteristics that would allow its discharge or disposal in the environment, the coagulation/flocculation technique was applied to the effluent previously treated by the Fenton process. So, in the following sections are presented the results of the parametric study, in which it was evaluated the effect of pH and dose of flocculant in the removal of DOC and color. The effect of coagulant was not evaluated, because it was only employed the dissolved iron resulting from Fenton's oxidation (to reduce costs).

As above mentioned, different conditions were attempted in the Fenton's stage: one experiment was performed in conditions that maximized DOC removal and biodegradability increase, as determined in Approach 2 (run #3); in the other runs the doses of H_2O_2 and Fe^{2+} were reduced for 1/2 and 1/4, respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively). In the coagulation/flocculation stage the coagulant used is the dissolved iron resulting from the previous oxidation (52.1, 85.6 and 167 mg/L of Fe in run#1, run#2 and run#3, respectively).

3.3.1. Influence of pH

In order to evaluate the influence of pH in the coagulation/flocculation step, six experiments were carried out in which this parameter was varied between 3.5 and 10.4. Figure 4 a) and b) show the results of DOC and color removal obtained, respectively, for different hydrogen peroxide doses previously employed in Fenton's oxidation. It can be seen that, in all cases, the performances slightly increased when the pH was varied from 3.5 to 5.0 (for instance, in run #1, for a hydrogen peroxide dose of 2.5 g/L in the Fenton's stage, the DOC and color removal increased from 20.5 to 21.2% and from 77.7 to 83.7%, respectively, while in run #3, where the highest dose of oxidant was employed in the oxidation stage, performances raised from 30.9 to 42.3% and from 93.3 to 94.7%, respectively for DOC and color). At pH above 5 there is a slight decrease in the removal performances, becoming more pronounced for increased pH values.

In accordance with Duan and Gregory (2003), in the optimum range obtained (pH= 5) the coagulation probably occurs by charge neutralization and inclusion in a precipitate, because at this pH value the species that are present in solution are Fe^{3+} ions and some hydrolysable species ($Fe(OH)^{2+}$ and $Fe(OH)_3$).

The optimal pH found is in the acidic zone, which is in accordance with literature reports when ferric sulfate is used as coagulant (from 3.5 to 7.0) (Edeline, 1992). Besides, the value herein determined is equal to the optimum pH value obtained in a preliminary work where ferric sulfate was employed as coagulant (Rodrigues et al., 2011), and also within the range found by Joo et al. (2007) that obtained an pH optimum between 4 to 7 for treating a textile wastewater. Additionally, Aziz et al. (2007) and Liang et al. (2009) obtained the maximum removal at pH 4 when treating a landfill leachate and molasses effluents, respectively. So, in subsequent runs the optimum pH value of 5.0 was used.

3.3.2. Effect of the Magnafloc 155 dose

The selection of Magnafloc 155 (anionic polymer) as flocculant takes into account the results obtained in preliminary studies with the raw wastewater (Rodrigues et al., 2011; 2012 a)). It was thus evaluated the effect of flocculant dose in both color and DOC removal, varying the concentration of Magnafloc 155 in the range 0.25 to 5 mg/L. Figure 5 a) and b) present the results obtained, where it and can be seen that both responses only slightly increased when the flocculant was used vs. simple coagulation (null concentration of Magnafloc). The very small increment in efficiency is justified by the fact that the removal of dyes and organic compounds occur, in general, in the coagulation step. The flocculation stage has the objective to aggregate the flocs, yielding larger particles that are more prone to suffer sedimentation.

Figure 5a) also shows that the COD removal increased with the dose of flocculant up to 2.5 mg/L, and for this optimum dose performances reached are 26.6, 32.9 and 45.7% for run #1, run #2 and run #3, respectively (i.e., when different doses of hydrogen peroxide were employed in the previous Fenton's process). In what concerns decolorization (Fig. 5b), results are not too different when the dose of Maganafloc is changed, being however apparent that the optimum dose is in the range 1.0-2.5 mg/L. Thus, the optimum dose considered for subsequent experiments was 2.5 mg/L, a value that is similar to those reported in literature, even with other flocculants (Beas-Piá, 2002; Joo et al., 2007; El-Gohary and Tawfik, 2009).

3.3.3. Overall process efficiency

After determining the operating conditions that maximize color and DOC removal in the coagulation/flocculation stage, further tests were carried out using the effluent previously treated by the Fenton's process (but with different hydrogen peroxide doses – runs #1 to #3) to assess the overall efficiency of the integrated treatment. The first experiment was performed in conditions that maximized DOC removal and biodegradability increase (run #3); in the other runs the doses of H_2O_2 and Fe^{2+} were reduced for 1/2 and 1/4, respectively, with the objective of reducing the operating costs (runs #2 and #1, respectively).

Table 3 presents, for the three experiments, the results of the characterization of the effluent resulting from Fenton's oxidation and from coagulation/flocculation, and the removal efficiencies obtained for each treatment

technique; the global efficiency of the overall treatment is also reported. The results obtained allow concluding that, in all runs, higher organic matter removals were reached in the coagulation/flocculation step than in Fenton's oxidation. Decolorization performances were similar in both processes. It is also noteworthy that values below the maximum legislated limit values of COD and BOD were only reached in runs#2 and #3, where higher H_2O_2 doses were employed. In run#3, where higher removal efficiencies were attained, the global efficiencies obtained with the combination of the two treatment techniques were 55.6, 42.7, 70.4 and 99.6% for COD, BOD_5, DOC and color, respectively.

3.4. 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 wastewater, as well as the configuration of the reactors. In this study, we considered only the costs with the chemicals, i.e., the costs of reagents obtained from Quimitécnica S.A. and Rivaz Química S.A. 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 and Magnafloc 155 – 3850 €/ton). The prices of acid (H_2SO_4) and base (NaOH) were not considered, because the quantities consumed are insignificant.

Figure 6 shows the influence of doses of reagents in the total cost of the processes, for the different strategies mentioned above. In Figure 6 a) and b) 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. 6a) or when directly applied to the raw wastewater (Fig. 6b). It turns out, as expected, that the cost increases with increasing concentrations of either chemical; however, this increase is far more pronounced for the hydrogen peroxide dose than for the ferrous salt one. So, it is concluded that hydrogen peroxide is the chemical that has a greater contribution to the total cost of operation, particularly in the latter case (Fig. 6b). Besides, it is noteworthy that in Approach 1 (coagulation/flocculation + Fenton's oxidation) the costs are below 1.2 €/m^3, while in Approach 2 (Fenton´s process alone) they are considerably higher as a consequence of requiring much higher consumption of those chemicals. The use of the dissolved iron resulting from the coagulation in the subsequent catalytic oxidation step revealed therefore to be a very promising strategy to considerably decrease the operating costs. In the optimal conditions of operation, as determined in previous sections, the cost to perform the treatment by coagulation/flocculation followed by Fenton's oxidation is 0.82 €/m^3 while it amounts to 9.2 €/m^3 when the Fenton's process is applied per se. Besides, only the first strategy allowed reaching global efficiencies that would permit to meet the discharge limits.

Figure 6c shows the influence of the hydrogen peroxide and the Magnafloc 155 cost upon combination of Fenton's process with coagulation/flocculation. It appears that overall cost increases with increasing concentrations of either reagent; however, this increase is clearly more pronounced for the hydrogen peroxide dose than for the Magnafloc 155 one. In fact, the flocculant contribution to the overall cost is almost negligible, because the doses used for the treatment are small (one should remark that the cost of this reagent is very high). Thus, the total cost

of the treatment by Fenton's reagent followed by coagulation/flocculation (Approach 3) is almost entirely due to the consumption of hydrogen peroxide (and iron) in the Fenton reaction (that amounts to ca. 2.3, 4.6 and 9.2 €/m^3 in runs #1, #2 and #3, respectively). Run #2 seems therefore to be the best choice for this strategy, because the effluent produced complies the discharge limits (cf. Table 3) and allows reducing the overall cost, as compared to run #3 (which was carried out in the optimum conditions determined in the parametric study). Even so, the cost is much higher than in Approach 1.

4. Conclusions

The present study demonstrated the applicability of integrating coagulation/flocculation and Fenton's process in the treatment of a synthetic cotton dyeing wastewater. It was found that:

i) The coagulation/flocculation per se did not allowed to obtain an effluent that meets discharge limits;

ii) The application of the combined treatment (coagulation/flocculation followed by Fenton's reagent) under optimized conditions allows to achieve high efficiencies of color (99.8%) and organic matter removal (61.7% for COD, 71.2% for DOC, and 25.8% for BOD_5). This combination allowed to obtain an effluent that can be discharged into the environment;

iii) The application of the Fenton's process *per se* in oxidation of the raw wastewater allows obtaining high color removal (89.9%), with considerable efficiencies in reduction of organic compounds (25.1% for COD and 48.8% for DOC), yielding a non-toxic effluent (0.0% for inhibition of *Vibrio fischeri*) and significant improvement of the effluent biodegradability (both k' and BOD_5:COD increased). However, the wastewater resulting from this treatment cannot be discharged, according to Portuguese legislation; the treatment could, nonetheless, be complemented by a biological process.

iv) The integration of Fenton's process followed by coagulation/flocculation in optimized conditions of both processes provided an effluent that can be discharged into the environment, with global organic matter removals of 55.6% for COD, 42.7% for BOD and 70.4% for DOC, and almost complete color reduction (99.6%); the costs can however be decreased by reducing the H_2O_2 dose, the effluent still complying with the discharge limits.

v) The treatment of the dyeing wastewater by coagulation/flocculation followed by Fenton's reagent allowed obtaining an effluent that meets the discharge limits with the smaller operating costs (0.82 €/m^3). So, the use of the dissolved iron resulting from the coagulation process in the subsequent chemical oxidation stage revealed to be a very promising strategy to considerably decrease operating costs.

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Table 1 - Characteristics of the synthetic cotton 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). Maximum allowable values for legislated parameters are also shown.

Parameter	**Raw wastewater**	**Coagulation & flocculation**	**Fenton's oxidation**	**Global removal (%)**	**Maximum Allowable Value***
pH	11.4	9.4	7.05	-	5.5-9.0
Total nitrogen (mg N/L)	3.9	3.8 (2.6)	n.d.	-	
Nitrates (mg NO_3^{2-}/L)	4.25	4.22 (0.0)	n.d.	-	
Total phosphorus (mg P/L)	5.9	4.5 (24.3)	n.d.	-	
Dissolved phosphorus (mg P/L)	0.1	< 0.06 (100)	n.d.	-	
Chemical oxygen demand (mg O_2/L)	350.0	261.9 (25.2)	134.0 (48.8)	61.7	250
Biochemical oxygen demand (mg O_2/L)	77.5	74.1 (4.3)	57.4 (22.5)	25.8	100
Dissolved organic carbon (mg C/L)	117.5	68.2 (41.9)	33.9 (50.4)	71.2	
Chlorides (mg Cl^-/L)	7981.8	8030 (0.0)	n.d.	-	
Specific oxygen uptake rate (k') (mg O_2/(g_{VSS} h))	5.6	8.0	n.d.	-	
BOD:COD ratio	0.22	0.28	0.43	-	
Absorbance at λ_{max} (abs. units)	0.437	0.034 (92.2*)	0.0015 (97.3**)	99.8	
Visible color after dilution 1:40	not visible	not visible	not visible	-	not visible
Vibro fischeri Inhibition 5 min (%)	0.0	0.0	0.0	-	
Vibro fischeri Inhibition 15 min (%)	0.0	0.0	0.0	-	
Vibro fischeri Inhibition 30 min (%)	0.0	0.0	0.0	-	

n.d. – not determined

* calculated from the absorbance of wastewater at pH 9.4 (0.3875 abs. units)

** calculated from the absorbance after coagulation/flocculation at pH 3.5 (0.0564 abs. units)

*** Portuguese legislation for discharge of textile wastewaters

Table 2 - Characteristics of the synthetic cotton dyeing wastewater after Fenton oxidation and respective removal efficiencies (Approach 2).

Parameter	**Fenton's oxidation**	**Removal (%)**	**Maximum Allowable Limit****
pH	6.99	-	5.5-9.0
Chemical oxygen demand (mg O_2/L)	262.1	25.1	250
Biochemical oxygen demand (mg O_2/L)	135.7	0.0	100
Dissolved organic carbon (mg C/L)	60.2	48.8	
Chlorides (mg Cl^-/L)	8017	-	
Specific oxygen uptake rate (k') (mg O_2/(g_{VSS} h))	15.51	-	
BOD:COD ratio	0.52	-	
Absorbance at λ_{max} (abs. units)	0.0331	89.9*	
Visible color after dilution 1:40	Not visible	-	not visible

* calculated from the absorbance at pH 3.5 (0.3267 abs. units)

** Portuguese legislation for discharge of textile wastewaters

Table 3 - Characteristics of the synthetic cotton dyeing wastewater after Fenton 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.

	Run #1			**Run #2**			**Run #3**			
Parameter	**Fenton's oxidation**	**Coagulation & flocculation**	**Global removal (%)**	**Fenton's oxidation**	**Coagulation & flocculation**	**Global removal (%)**	**Fenton's oxidation**	**Coagulation & flocculation**	**Global removal (%)**	**Maximum Allowable Value*** **
pH	-	7.14	-	-	7.10	-	-	7.25	-	5.5-9.0
Chemical oxygen demand (mg O_2/L)	324.2 (7.4)	261.8 (19.2)	25.2	286.8 (18.1)	187.0 (34.8)	46.6	266.6 (23.8)	155.3 (41.7)	55.6	250
Biochemical oxygen demand (mg O_2/L)	89.2 (0.0)	70.7 (20.7)	20.7	113.2 (0.0)	76.0 (32.9)	32.9	135.4 (0.0)	77.6 (42.7)	42.7	100
Dissolved organic carbon (mg C/L)	103.9 (11.6)	76.8 (26.1)	34.6	96.2 (18.1)	64.45 (33.0)	45.1	65.4 (44.4)	34.8 (46.7)	70.4	
BOD:COD ratio	0.28	0.27	-	0.39	0.41	-	0.51	0.50	-	
Absorbance at λ_{max} (abs. units)	0.0256 (92.2*)	0.00195 (89.5**)	99.2	0.0235 (92.8*)	0.0013 (92.7**)	99.5	0.0340 (89.6*)	0.0005 (95.9**)	99.6	
Visible color after dilution 1:40	not visible	not visible	-	not visible	not visible	-	not visible	not visible	-	not visible

* calculated from the absorbance of wastewater at pH 3.5 (0.3267 abs. units)

** calculated from the absorbance after Fenton at pH 5.0 (0.0190, 0.0177 and 0.0123 abs. units for run #1, #2 and #3, respectively)

*** Portuguese legislation for discharge of textile wastewaters

Captions of Figures

Figure 1 – Schematic diagram of process configurations adopted.

Figure 2 – Effect of Fe^{2+} dose (a and b), H_2O_2 concentration (c and d) and temperature (e and f) on DOC and color removals along time, during the 2nd stage – Fenton's oxidation in Approach 1 (for a and b: initial pH=3.5, T=30±0.5 ºC, initial $[H_2O_2]$) = 500 mg/L; for c and d: (initial pH=3.5, T=30±0.5 ºC, $[Fe^{2+}]_{added}$=99.7 mg/L; for e and f: initial pH=3.5, $[Fe^{2+}]$added=99.7 mg/L and $[H_2O_2]_o$=500 mg/L).

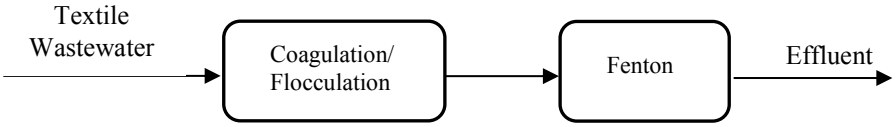
Figure 3 – Effect of Fe^{2+} dose (a-c), H_2O_2 concentration (d-f) and temperature (g-i) on DOC and color removals and k' along time, during Fenton's reaction in Approach 2 (for a-c: initial pH=3.5, T=30±0.5 ºC, initial $[H_2O_2]_o$= 5.0 g/L; for d-f: initial pH=3.5, T=30±0.5 ºC, $[Fe^{2+}]_o$=300 mg/L; for g-i: initial pH=3.5, $[Fe^{2+}]_o$=300 mg/L, $[H_2O_2]_o$ =10 g/L).

Figure 4 – Variation of DOC (a) and color (b) removals with pH during the coagulation stage – Approach 3 – for 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, $[Fe\ dissolved]_{run\ \#1}$ =52.1 mg/L, $[Fe\ dissolved]_{run\ \#2}$=85.6 mg/L, $[Fe\ dissolved]_{run\ \#3}$=167 mg/L and T =$T_{ambient}$=23-25 ºC).

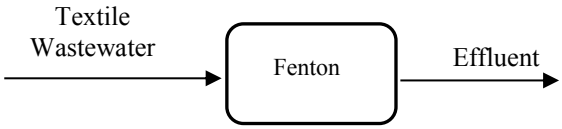
Figure 5 – Variation of DOC (a) and color (b) removals with the flocculant concentration during the flocculation step – Approach 3 – for the different doses of hydrogen peroxide employed in the previous Fenton's process in runs #1, #2 and #3 ($v_{coagulation}$=150 rpm, $t_{coagulation}$=3 min, T=Tambient=23-25 ºC, pH=5.0, $[Fe\ dissolved]_{run\ \#1}$ =52.1 mg/L, $[Fe\ dissolved]_{run\ \#2}$=85.6 mg/L, $[Fe\ dissolved]_{run\ \#3}$=167 mg/L, $v_{flocculation}$=20 rpm and $t_{flocculation}$=15 min).

Figure 6 – 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).

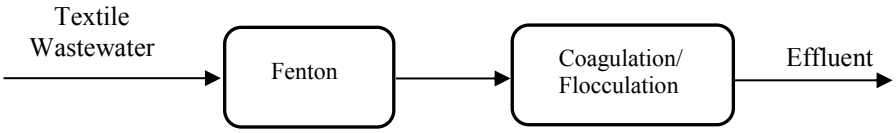
Figure 1



Approach 1: Integration of coagulation/flocculation followed by Fenton's reaction



Approach 2: Fenton's oxidation alone



Approach 3: Combination of Fenton's oxidation followed by coagulation/flocculation

Figure 2

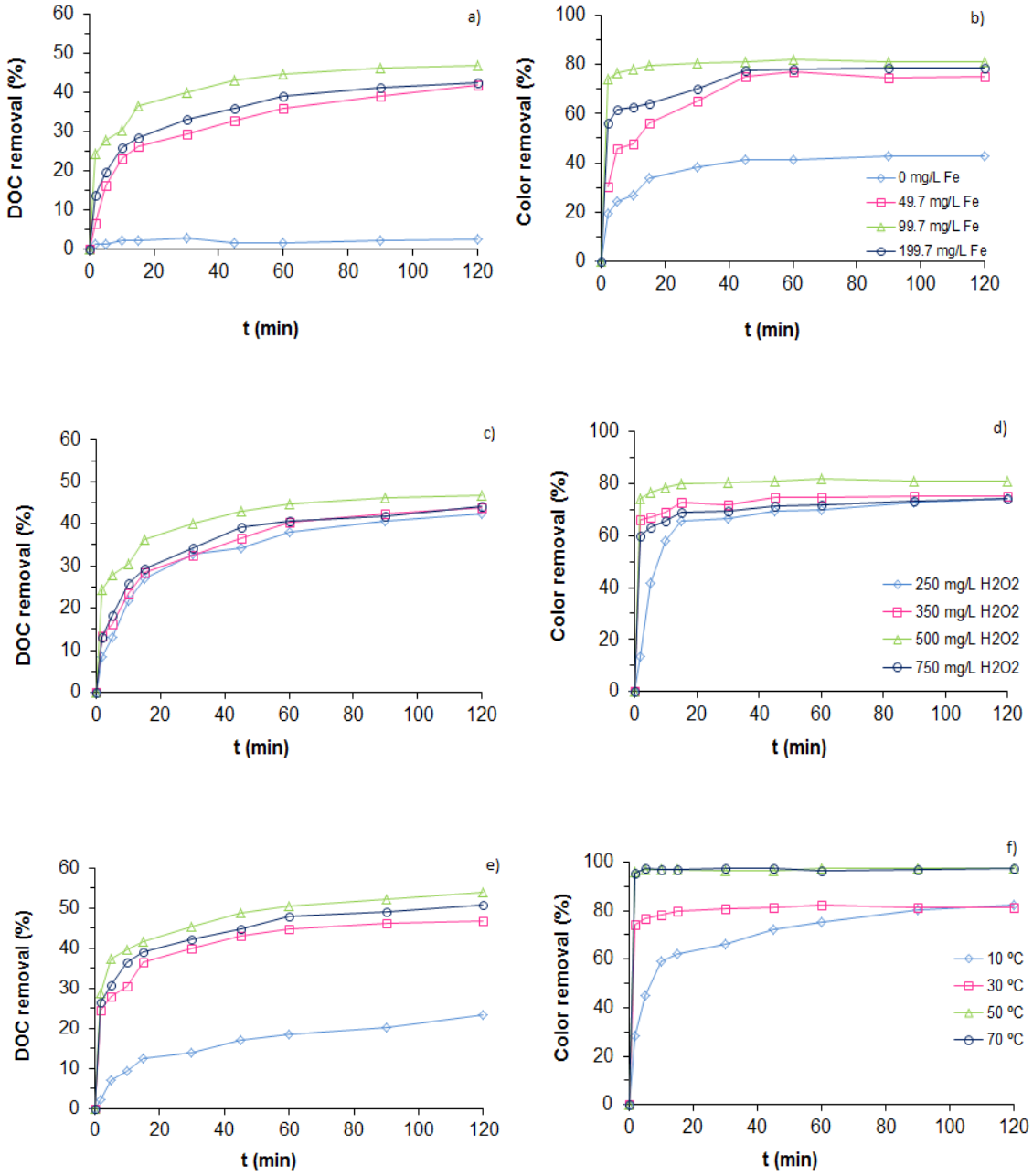

a)
DOC removal (%)
t (min)
b)
Color removal (%)
0 mg/L Fe
49.7 mg/L Fe
99.7 mg/L Fe
199.7 mg/L Fe
t (min)
c)
DOC removal (%)
t (min)
d)
Color removal (%)
250 mg/L H2O2
350 mg/L H2O2
500 mg/L H2O2
750 mg/L H2O2
t (min)
e)
DOC removal (%)
t (min)
f)
Color removal (%)
10 ºC
30 ºC
50 ºC
70 ºC
t (min)

Figure 3

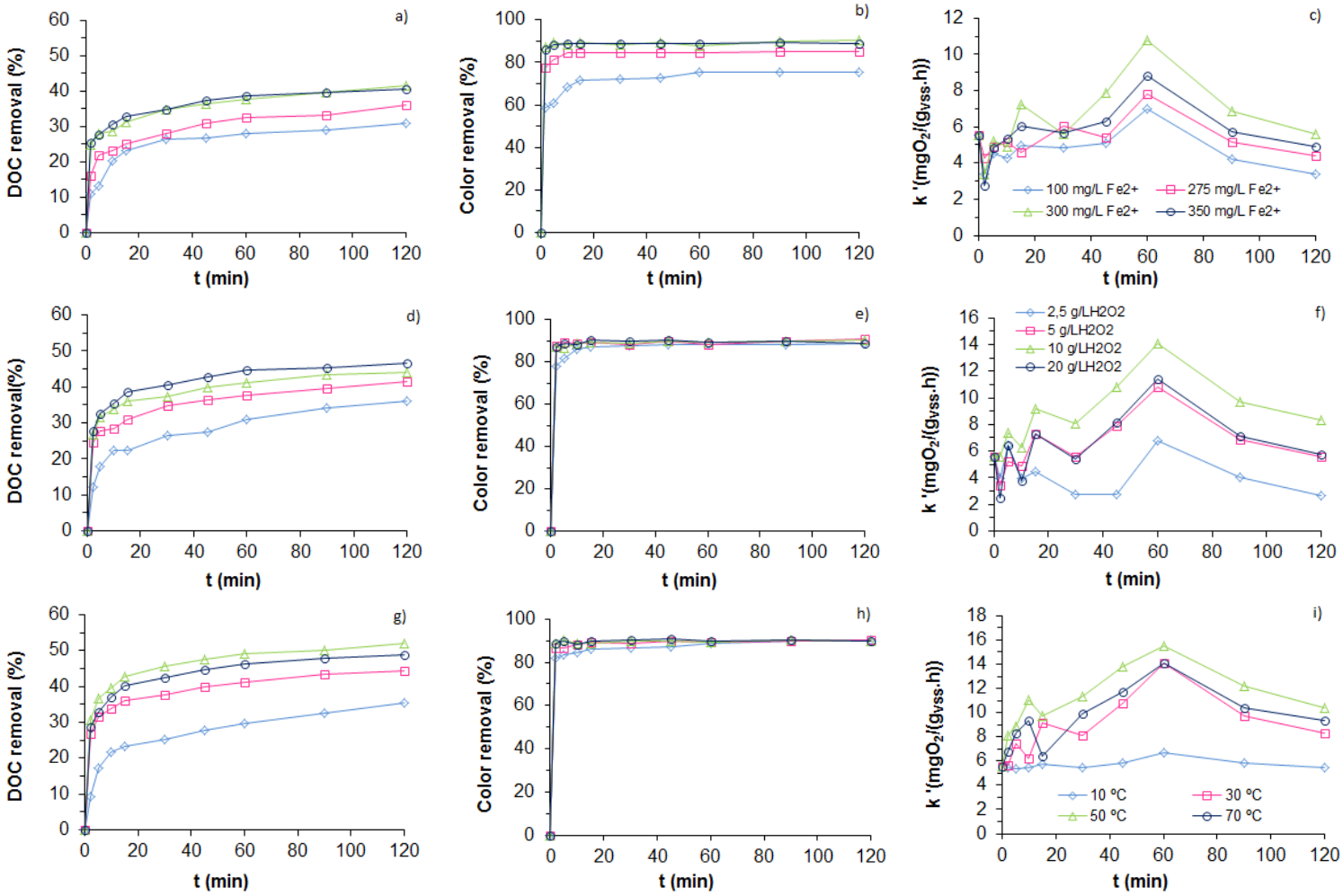

a)
DOC removal (%)
t (min)
b)
Color removal (%)
t (min)
c)
k '(mgO2/(gvss.h))
100 mg/L Fe2+
275 mg/L Fe2+
300 mg/L Fe2+
350 mg/L Fe2+
t (min)
d)
DOC removal(%)
t (min)
e)
Color removal (%)
t (min)
f)
2,5 g/LH2O2
5 g/LH2O2
10 g/LH2O2
20 g/LH2O2
k '(mgO2/(gvss.h))
t (min)
g)
DOC removal (%)
t (min)
h)
Color removal (%)
t (min)
i)
k '(mgO2/(gvss.h))
10 ºC
30 ºC
50 ºC
70 ºC
t (min)

Figure 4

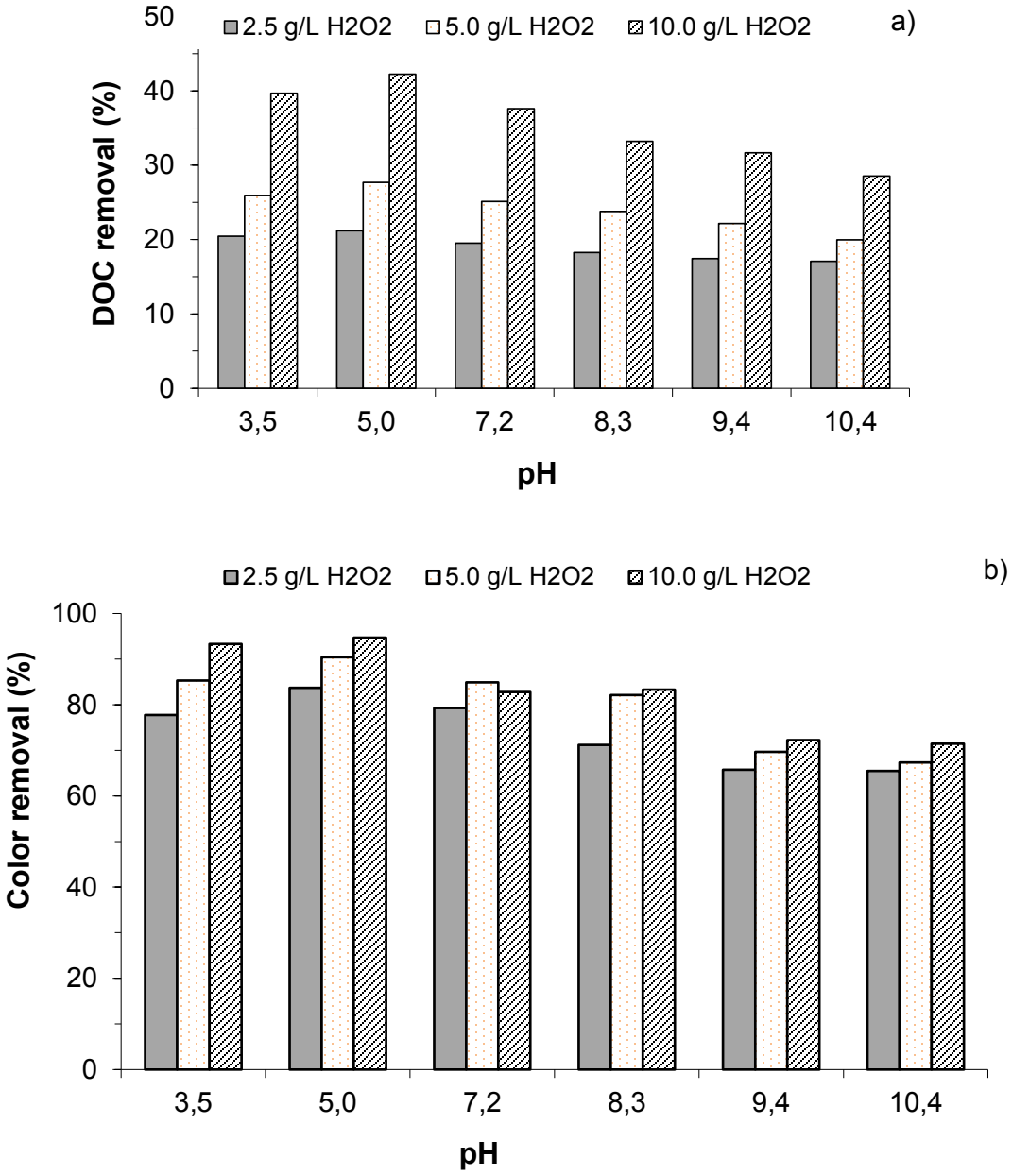

a)
2.5 g/L H2O2
5.0 g/L H2O2
10.0 g/L H2O2
DOC removal (%)
0
10
20
30
40
50
3,5
5,0
7,2
8,3
9,4
10,4
pH
b)
2.5 g/L H2O2
5.0 g/L H2O2
10.0 g/L H2O2
Color removal (%)
0
20
40
60
80
100
3,5
5,0
7,2
8,3
9,4
10,4
pH

Figure 5

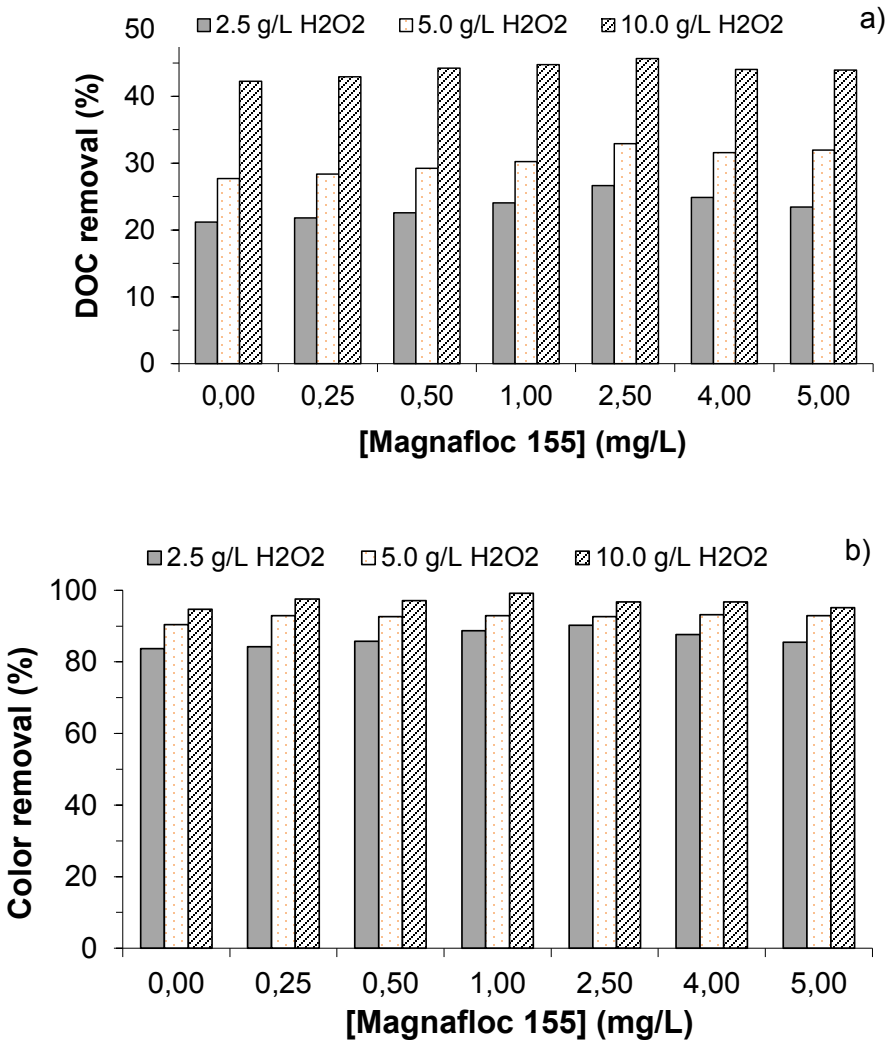
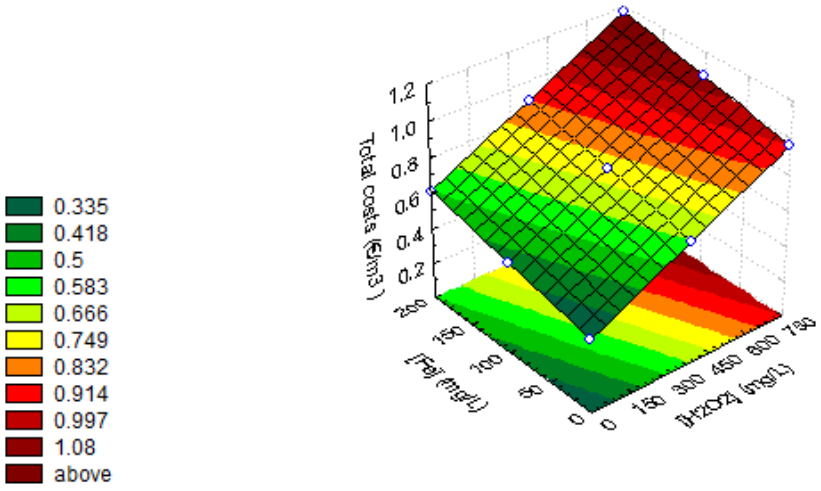
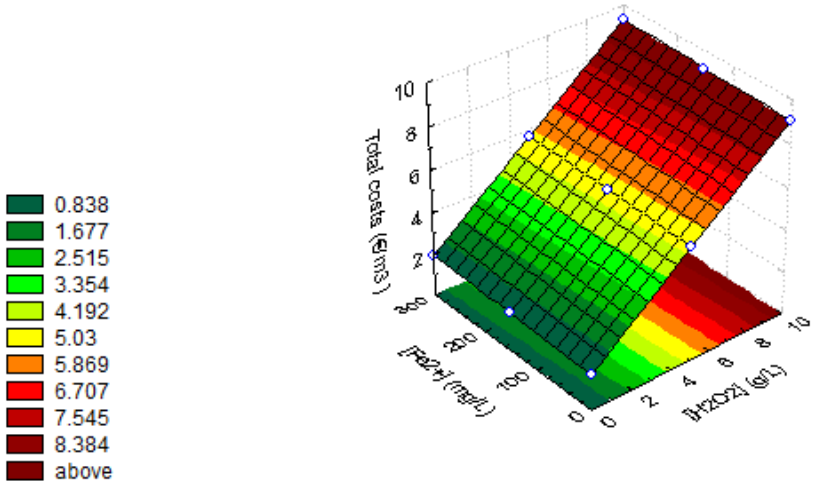

a)
2.5 g/L H2O2
5.0 g/L H2O2
10.0 g/L H2O2
DOC removal (%)
50
40
30
20
10
0
0,00
0,25
0,50
1,00
2,50
4,00
5,00
[Magnafloc 155] (mg/L)
b)
2.5 g/L H2O2
5.0 g/L H2O2
10.0 g/L H2O2
Color removal (%)
100
80
60
40
20
0
0,00
0,25
0,50
1,00
2,50
4,00
5,00
[Magnafloc 155] (mg/L)

Figure 6

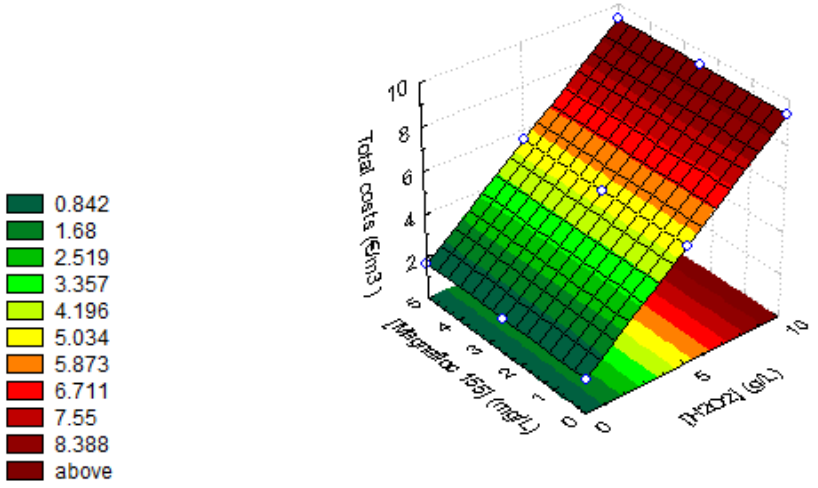
a)


0.335
0.418
0.5
0.583
0.666
0.749
0.832
0.914
0.997
1.08
above
Total costs (€/m3)
[Fe] (mg/L)
[H2O2] (mg/L)

b)


0.838
1.677
2.515
3.354
4.192
5.03
5.869
6.707
7.545
8.384
above
Total costs (€/m3)
[Fe2+] (mg/L)
[H2O2] (g/L)

c)


0.842
1.68
2.519
3.357
4.196
5.034
5.873
6.711
7.55
8.388
above
Total costs (€/m3)
[H2O2] (g/L)