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Photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the photo-treated solution

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Abstract

Photo-Fenton process was explored as photochemical pre-treatment to improve the biodegradability of a wastewater coming from a textile industry located in the south of France, which was characterized as very biorecalcitrant by means of Zahn–Wellens biodegradability test. The effect of H_2O_2, Fe(III) and temperature on the photo-mineralization processes have been studied and the optimal conditions were found. Experiments were made to obtain information concerning the evolution of the biodegradability of the treated effluent after 40 and 70% of photo-mineralization. The photo-treated effluent is not biocompatible and its complete mineralization cannot be performed by biological means. UV–VIS and high-performance liquid chromatography (HPLC) analyses show that aromatic intermediates remain in the effluent after the photo-treatment, which have been identified as the principal reason of the biorecalcitrance.

Keywords: Photocatalysis; Textile wastewater; Hydrogen peroxide; Iron salts; Photo-Fenton

1. Introduction

Textile mills are major consumers of water and consequently one of the largest groups of industries causing intense water pollution. According to the US EPA, about (1–2) $\times 10^{-6}$ gal of wastewater per day are generated by average dyeing facility in the US, reactive and direct dyeing generating most of the wastewater. Around 10^6 t and more than 10,000 different synthetic dyes and pigments are produce annually worldwide and used extensively in dye and printing industries. Textile processing employs a variety of chemicals, depending on the nature of the raw material and products. It is estimate that about 10% are lost in industrial wastewater. The wastewater generated by the different production steps (i.e. sizing of fibers, scouring, desizing, bleaching, washing, mercerization, dyeing and finishing) has high pH and temperature [1]. It also contains high concentration of organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulfide, sodas, and alkalinity. In addition, the high salt conditions (typically up to 100 g l^{-1} sodium chloride) of the reactive dyebaths result in high-salt wastewater, which further exacerbates both their treatment and disposal. The fate of these chemicals varies, ranging from 100% retention on the fabric to 100% discharge with the effluent. As a result, textile industry is confronted with the challenge of both color removal (for aesthetic reasons) and effluent salt content reduction. In addition, reactive dyes are highly water soluble and often non-degradable under the typical aerobic conditions found in conventional, biological treatment systems [2,3].

Two main factors have been identified like responsible of the biorecalcitrance in organic compounds: (a) there are no enzymes available in the biocenosis used for biological wastewater treatment, which are suitable for the degradation of the concerned organics; (b) the target organics could be biodegraded, but the wastewater contains (organic or inorganic) substances that severely inhibit the biocenosis or are toxic towards microorganisms. In the first case, biological treatment is possible to remove the biodegradable portion of

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organics, but the biorecalcitrant organics occur in the outlet of the biological wastewater treatment plant as a residual hard chemical oxygen demand (COD). Depending on their quantity and their ecotoxicological behavior in natural environment the biorecalcitrant organics sometimes have to be removed by additional treatment. In the second case, biological treatment is impossible (except dilution of the effluent by recirculating the treated effluent or separation of inhibitory or toxic substances before biological treatment) [4,5].

Advanced oxidation processes (AOPs) have been proposed in recent years as an attractive alternative for the treatment of contaminated ground, surface, and wastewater containing non-biodegradable organic pollutants. The most commonly used AOPs utilized H_2O_2, O_3 or O_2 as the oxidant. Among AOPs, the combined system UV/TiO_2/H_2O_2 and UV/Fe^{3+}/H_2O_2 are considered as the most promising for the remediation of contaminated water [6–9]. These involve the generation of the hydroxyl radical that is a reactive intermediate and has a high oxidation potential. This hydroxyl radical attacks organic molecules by abstracting a hydrogen atom or by adding to the double bonds. Organic molecules are then totally mineralized to carbon dioxide and water. In spite of their effectiveness, the operational costs of these processes are relatively high compared to those of biological treatment [10–12]. However, their use as a pre-treatment step for the enhancement of the biodegradability of wastewater containing recalcitrant compounds, i.e. textile wastewater, can potentially be justified if the intermediate products resulting from the reaction can be readily degraded by microorganisms in a biological treatment plant [13].

In our group, special attention has been given to combining the photo-assisted AOP and aerobic biological processes to degrade biorecalcitrant, non-biodegradable, and/or toxic pollutants. Two kinds of combined systems have been developed using in all cases immobilized activated sludge culture for the biological step and for the photocatalytic pre-treatment Fe^{3+}/H_2O_2/UV [14,15] or TiO_2 supported on glass rings [16]. The treatment of a wide range of biorecalcitrant model compounds and real wastewaters coming from various chemical industries, containing a complex mixture of pollutants have been studied using this coupled systems. More recently, a general strategy for the coupling photo-assisted AOP and biological process was proposed [17].

This study intends to investigate the photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities and its effect in the biodegradability of the photo-treated solution. This effluent is produced in a large-scale plant in the south of France. The following topics are also study in this paper: (a) the wastewater characterization and assessment of biological treatment; (b) the effect and the optimization of Fe^{3+} and H_2O_2 concentration and the temperature in the photo-Fenton pre-treatment; and (c) the biodegradability of the photo-treated wastewater.

2. Experimental

2.1. Materials

All chemicals were used as received without further purification. Textile wastewater and Rapidoprint (product used as anti-reductor) were obtained from a textile plant located in the south of France by means of France Textile Institute. For photo-mineralization experiments, this wastewater was used without dilution. $FeCl_3$, H_2O_2 (30% w/w) analysis grade (per year) and the chemicals for high-performance liquid chromatography (HPLC) analysis are obtained from Fluka. Milli-Q water was used for the preparation of aqueous solutions or as a component of the mobile phase, ammonium acetate–acetonitrile (HPLC grade) in HPLC analysis. pH was adjusted to 3 by means of HCl before photo-Fenton process. The photo-treated solutions were neutralized by means of NaOH.

Neutral pH of the solutions is maintained during the biological tests by adjusting with HCl or NaOH.

2.2. Coiled photochemical reactor

In the coiled photochemical reactor shown in Fig. 1, the pollutant solution circulates through an 8 mm-diameter glass spiral of about 20 m long. A 400 W, 40 cm long, medium-pressure Hg-lamp is positioned in such a way that its center line passes through the axis of the coiled reactor. The pre-dominant radiation is at 366 nm with output equivalent to ∼15 W. The runs are carried out at 30, 45 and 60 °C to study the influence of the temperature in the reaction rate. The pH was adjusted around 3 with HCl. The pollutant solution, H_2O_2, and Fe^{3+} solution are added at the beginning into the mixing-vessel. The solution is in batch mode recirculated at 26 l h^{-1} through the illuminated part of the reactor. In order to prepare the photo-treated water for biological treatment, the solution is neutralized and all experiment were carried out until H_2O_2 was consumed.

2.3. Biological reactor

The fixed bed reactor (FBR) shown on the right-hand side of Fig. 1 consists of a column of 1 l capacity containing biolite colonized by activated sludge from a municipal wastewater treatment plant (Vidy, Lausanne, Switzerland). The pH is controlled and adjusted at 7. The required nutrients N, P, K, and oligoelements for the bacterial activity are also added. The aeration is about 150 l h^{-1} and the O_2 concentration is measured by means of an O_2 probe on the top of the column. This biological reactor was used as supplementary test to measure the biodegradation of the effluent treated.

2.4. Chemical and biological analysis

Dissolved organic carbon (DOC) measurements were performed using a TOC analyzer (Shimadzu, model 5050A)

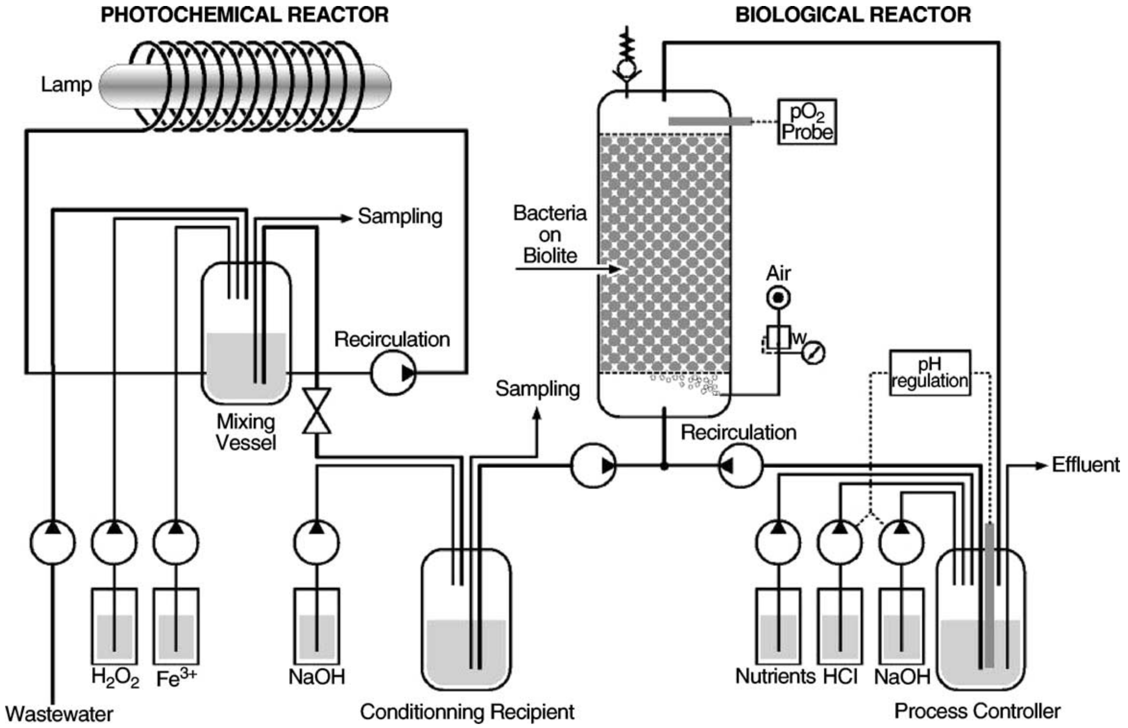

Fig. 1. Scheme of the photochemical-biological flow reactor.

with a solution of potassium phthalate as the calibration standard. COD was carried out via a Hach–2000 spectrophotometer using dichromate solution as the oxidant in strong acid media. HPLC was carried out in a Varian 9065 unit provided with a Varian 9012 solvent delivery system, an automatic injector 9100, and a Varian ProStar variable (200–400 nm) diode array detector 9065 Polychrome. A reverse phase Spherisorb silica column ODS–2 and ammonium acetate–acetonitrile as mobile phase was used to run the chromatography in gradient mode. The additive A signal was detected at 258 nm with a retention time around 3.6 mm. Concentrations of H_2O_2 were determined by the Merckoquant® peroxide analytical test strips. Biological oxygen demand (BOD_5) analysis was made by means of a Hg free WTW 2000 Oxytop unit thermostated at 20 °C. The chloride concentration was determined using a Chlor-o-counter Mark II provided by Flohr-Instrument. The Zahn–Wellens test [18] and the FBR column, which are carried out in conditions similar to those of a wastewater treatment plant using activated sludge were used for determination of inherent biodegradability.

3. Results and discussion

3.1. *Wastewater characterization and assessment of biological treatment*

The composition and physicochemical characteristic of the wastewater under study are summarized in Tables 1 and 2. The effluent exhibits low BOD_5, high COD, high DOC and is highly colored. The BOD_5/COD ratio is 0.045, indicating that this effluent is poorly biodegradable [19]. in addition, this effluent has a high conductivity due the very high salt concentration. The UV–VIS absorption spectrum of this wastewater presents a maximum absorption in the range of 250–340 nm, which is characteristic of aromatics compounds. Another absorption band is observed in the visible range of 400–600 nm. The non-biodegradability of a wastewater have to be confirmed before apply a photochemical treatment, since classical biological treatments are, at the present, the cheapest and most environmentally compatible.

The biodegradability of the textile effluent was tested using the Zahn–Wellens test. Fig. 2 shows that DOC is biorecalcitrant in the tested conditions, since unacclimated bacteria removed only 30% of DOC in 25 days. After 25 days, glucose as co-substrate was added in order to know if the microorganisms are able to eliminate a biodegradable substrate. It was observed that all this biodegradable

Table 1
Composition of the wastewater under study

Industrial name	Concentration	Properties
JE Reverzol 3RS 150	2%	Colorant
RO Everzol 3BS 150	1.88%	Colorant
Rapidoprint	$1\,g\,l^{-1}$	Anti-reductor
Acetic acid	$0.3\,ml\,l^{-1}$	
Salt	$30\,g\,l^{-1}$	
Sodium carbonate	$3\,g\,l^{-1}$	

Table 2
Physicochemical characateristics of the wastewater under study

DOC ($mg\,l^{-1}$)	COD ($mg\ O_2\,l^{-1}$)	BOD_5 ($mg\ O_2\,l^{-1}$)	Conductivity ($ms\,cm^{-1}$)	Cl^- ($mg\,l^{-1}$)	pH
900	4000	180	84.5	31619	11.20

substrate is consumed in only 1 day, demonstrating that the biomass was not inhibited. Afterward, the biomass was concentrated and a new batch of effluent was added to test their biodegradability under acclimated culture conditions. The result was negative, because the DOC removed was close to 30% after supplementary 25 days. These results reveal that the biorecalcitrance of this effluent, in the tested conditions, is associated with the structural stability of compounds towards microbiological attack but no with the toxicity of the solution.

3.2. The photo-Fenton reaction as pre-treatment process

Temperature and both Fe^{3+}, and H_2O_2 concentrations, were optimized for mineralization of the textile effluent by means the photo-Fenton systems. In all following experiments, the mineralization is described assuming a pseudo-first-order reaction (Eq. (1)):

$$\frac{-d(DOC)}{dt} = k(DOC_0), \qquad (1)$$

where k is the pseudo-first-order reaction rate constant Eq. (2) leads to

$$\ln\left(\frac{DOC}{DOC_0}\right) = -kt \qquad (2)$$

From the plot $\ln(DOC/DOC_0)$ versus t (time of irradiation), the pseudo-first-order reaction rate constant, the slope, have been calculated and used to study the effect of different concentrations of Fe^{3+} and H_2O_2 and the temperature.

3.2.1. Effect of the initial Fe^{3+} concentration

To further elucidate the role of Fe^{3+} concentration on the mineralization of the effluent, a series of experiments varying the concentration of iron and keeping fixed the other parameters, were carried out. Fig. 3 shows a plot of the pseudo-first-order rate constant (k_{obs}) as a function of Fe^{3+} concentration. The best mineralization rate was obtained with Fe^{3+} concentration of $1.43\,mmol\,l^{-1}$. It can also be observed that the efficiency of the mineralization attains a plateau when the concentration of Fe^{3+} is between 1.4 and $1.8\,mmol\,l^{-1}$. This may be due to: (a) the increase of a brown turbidity in the solutions during the photo-treatment, which hinders the absorption of the UV light required for the photo-Fenton process; (b) excessive formation of Fe^{2+} (Eqs. (3) and (4)), which can compete with the organic carbon for $OH^\bullet$ radicals (Eq. (5)); (c) the fixed H_2O_2 concentration can become the limiting factor of the oxide-reductive reaction (Eq. (4)) when high concentration of Fe^{3+} is used.

$$Fe^{3+} + h\nu \rightarrow Fe^{2+} + OH^\bullet \qquad (3)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^\bullet + H^+ \qquad (4)$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (5)$$

3.2.2. Effect of the initial H_2O_2 concentration

Another important point to consider in the photo-Fenton oxidation is the amount of H_2O_2 required to obtain the best efficiency of the treatment. Several experiment were performed at optimal Fe^{3+} concentration determined before (Fig. 4).

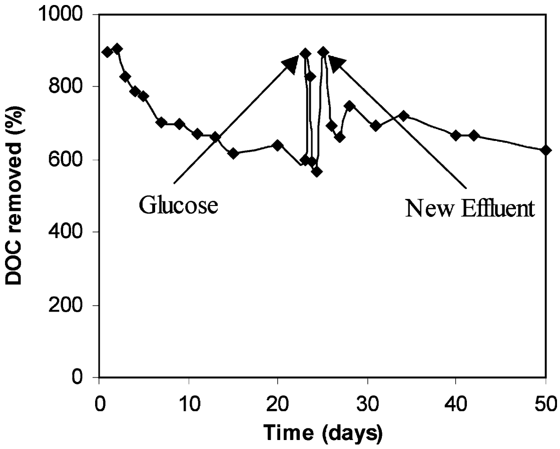

Fig. 2. Zahn–Wellens biodegradability test of the textile effluent. Evolution of DOC as a function of time.

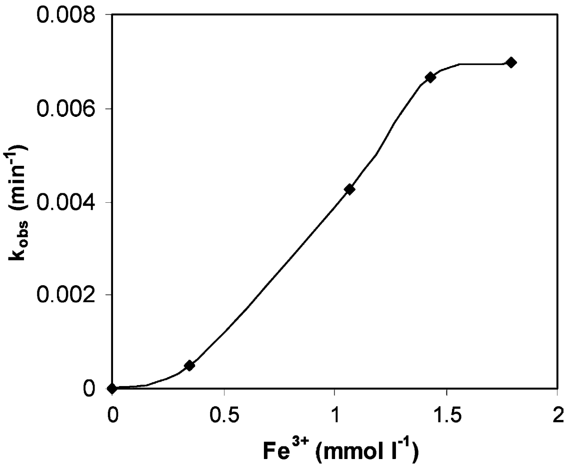

Fig. 3. Initial rate constant of the treated effluent by photo-Fenton oxidation at different Fe^{3+} concentrations.

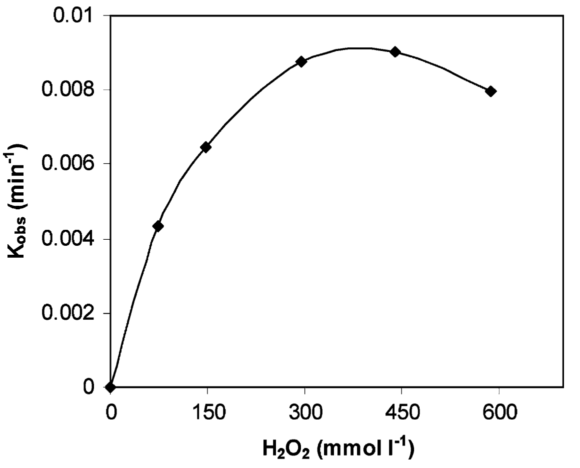

Fig. 4. Initial rate constant of the treated effluent by photo-Fenton oxidation at different H_2O_2 concentration.

As shown in Fig. 4, a significant enhancement of mineralization efficiency was verified when the H_2O_2 concentration was increased from 0 to 441.2 mmol l^{-1}. Above this concentration, the oxidation rate is negatively affected by the progressive increase of H_2O_2 up to 441.2 mmol l^{-1}. This is probably due to both the auto-decomposition of H_2O_2 into oxygen and water (Eq. (6)), and the scavenging of hydroxyl radicals by H_2O_2 (Eq. (7)) as follows;

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (6)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2{}^{\bullet} + H_2O \qquad (7)$$

Excess of H_2O_2 will react with $OH^{\bullet}$ competing with organic reducing the treatment efficiency.

Through this work, we have found that the optimal concentration of H_2O_2 at 60 °C and 1.43 mmol l^{-1} of Fe^{3+} is 441.2 mmol l^{-1} for reach 65% of mineralization.

3.2.3. Effect of the temperature

Normally, the photo-Fenton process is carried out at room temperature. Nevertheless, considering that the waters coming from the textile industry have a temperature between 60 and 90°, we considered very important to assess the effect of the temperature in the mineralization rate. Several experiment were performed at 30, 45 and 60 °C taking into account the optimal Fe^{3+} and H_2O_2 concentrations. As shown in Fig. 5, a significant enhancement of mineralization efficiency was verified when the temperature was increased. The reaction time necessary to achieve 40% of mineralization is 7, 5 and 2 h at 30, 45 and 60 °C, respectively. It is very important to make notice that the final time of reaction is marked by the exhaustion of H_2O_2, key element in the later study of biodegradability of the photo-treated effluent.

The optimal temperature obtained is 60 °C (see insert in Fig. 5). In Fig. 5 is possible to observe that above 60 °C a plateau is reached. The use of a temperature different from room temperature does not imply greater energetic cost because we are simply taking advantage of "natural" temperature of water at the end of the coloring process.

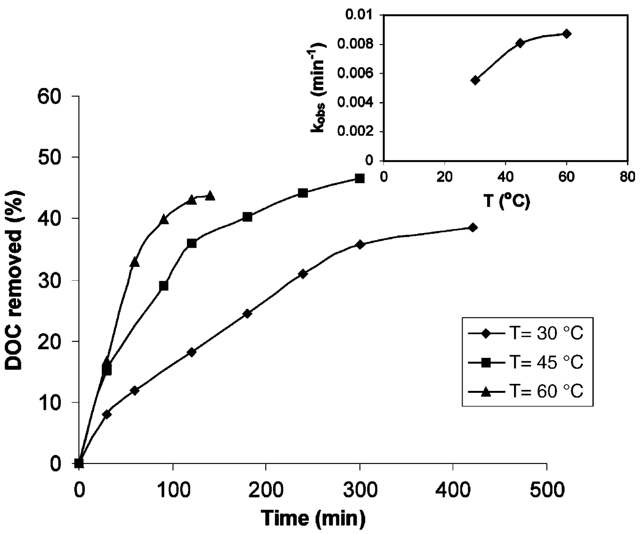

Fig. 5. Percent DOC reduction during the photo-Fenton treatment at different temperatures. The insert represented the initial rate constants of the treated effluent by photo-Fenton.

3.3. Biodegradability evolution of photo-treated wastewater

In order to find out the biocompatibility conditions using the photo-Fenton reaction as a pre-treatment step, the biodegradability of the wastewater after the pre-treatment was evaluated by the Zahn–Wellens test, using unacclimated municipal sludge as initial inoculum. Taking into account previous experiences [15,16,20], 40 and 70% of photo-mineralization have been taking as reference to study the biocompatibility of pre-treated solution, and the results are presented in Fig. 6a and b, respectively. Fig. 6a shows that the elimination of DOC by the microorganisms is very

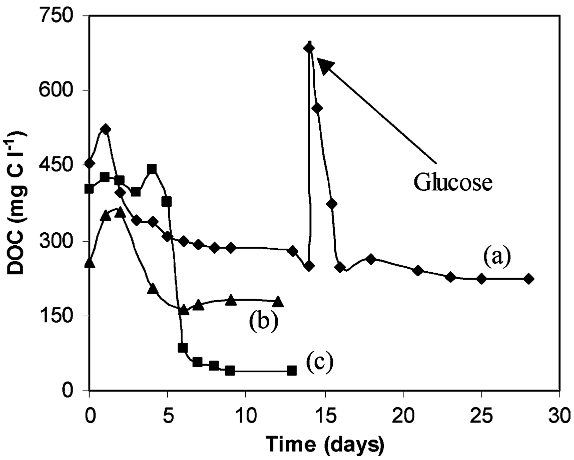

Fig. 6. Zahn–Wellens biodegradability test with non-adapted biomass. Evolution of DOC as a function of time: (a) after 40% of photo-mineralization; (b) after 70% mineralization; and (c) control with diethylenglycol.

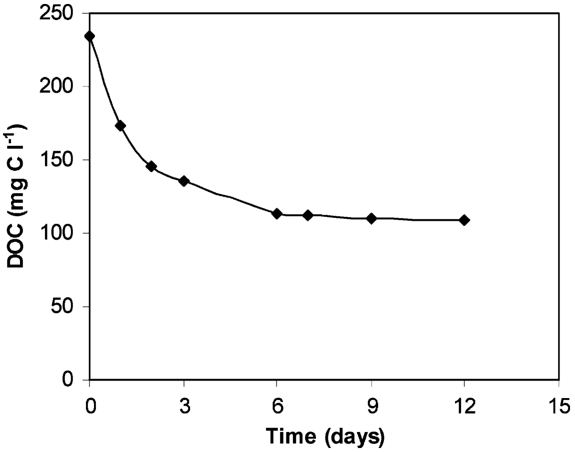

Fig. 7. Biodegradability test of a photo-treated effluent after 70% of mineralization. Evolution of DOC in FBR as function of time.

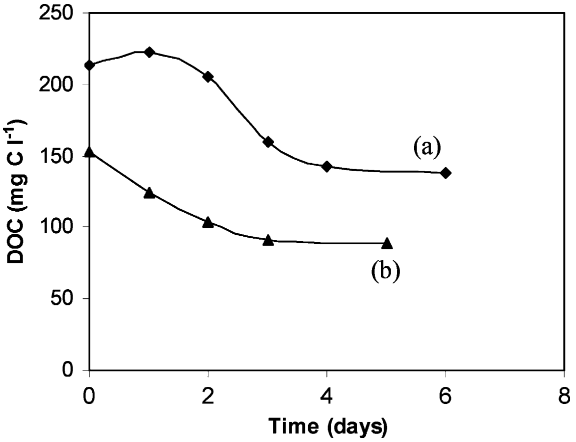

Fig. 8. Zahn–Wellens biodegradability test of effluents two-fold diluted after: (a) after 40% of photo-mineralization; and (b) after 70% of photo-mineralization. Evolution of DOC as a flinction of time using acclimated biomass.

difficult in this case, since only 50% was removed in 28 days. Thus DOC removal of 40% during photo-treatment is no enough to produce an easy biodegradable photo-treated solution. After 15 days of biodegradability test (curve 6a), glucose was added as co-substrate and the biomass response was positive, since all this substrate was consumed very fast. This fact again allows us to confirm that the biorecalcitrance of this treated effluent is due to the absence of bacteria able to degrade it and not to its toxicity. Fig. 6b shows that the DOC eliminated was only 30% in 12 days. It means that even a greater photo-mineralization up to 70% is not enough to render solution easily biodegradable. Fig. 6c. presents a control experiment using diethylenglycol ($400\,\mathrm{mg\,l^{-1}}$) to test the initial activity of the activated sludge. In fact, the biomass is active since the diethylenglycol is degraded up to 90% in 6 days under the same conditions used to test the biodegradability of the photo-treated effluent.

To verify the result shows in Fig. 6b, a supplementary experiment attempting biodegradation of the same sample is carried out in batch mode with the FBR (right-hand side of Fig. 1) and the results are presented in Fig. 7. In this figure, we observe that only 50% of DOC was removed in 12 days, although, this test was carried out under more favorable conditions than the used ones in the Zahn–Wel1ens test (Fig. 6b). The percentage of DOC removed is still very DOC, confirming the biorecalcitrance of the effluent even, after 70% of photo-mineralization.

To conclude this study of biodegradability and to discard a possible inhibiting effect of salt concentration present in the water, the same effluent used in Fig. 6a and b was diluted two-fold and a new Zahn–Wellens test was done for both. The results are presented in Fig. 8a and b, respectively. Even in these cases the weak biodegradability observed confirm once again that the biorecalcitrance is due to the absence of

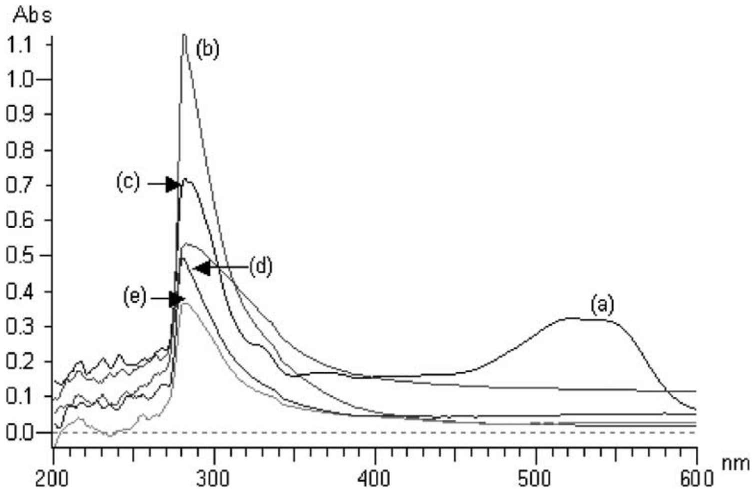

Fig. 9. UV–VIS spectra of the effluent: (a) before photo-Fenton pre-treatment; (b) after 40%; (c) after 50%; (d) after 65%; and (e) after 70% of photo-mineralization.

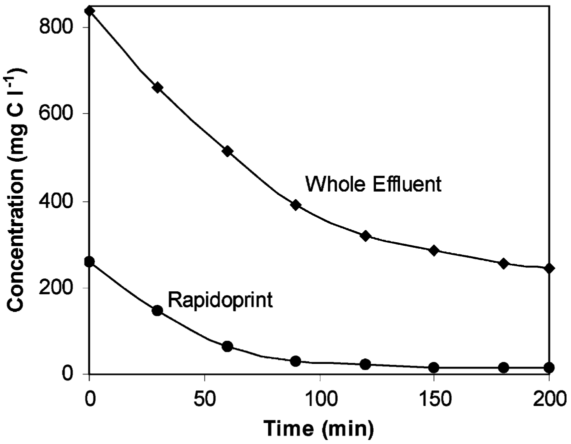

Fig. 10. Concentration evolution ($\mathrm{mg\,C\,l^{-1}}$) during photo-treatment of: (a) whole effluent; and (b) rapidoprint.

bacteria able to degrade the organic matter, as we already observed previously, and not by the osmotic inhibiting effect produced by the high concentration of salts.

3.4. Biorecalcitrance of the photo-treated effluent

In order to attempt an explanation of the strong biorecalcitrance of the photo-treated effluent, UV–VIS spectroscopy (Fig. 9) and HPLC (Fig. 10) analyses have been made to identified and follow the evolution of the main organic substances contained in the effluent.

Fig. 9 shows that initial effluent presents two absorption bands at 280 and 530 mn. The band presents in the visible zone (responsible of color), disappear after 40% of photo-mineralization. The absorption band at 280 nm is partially eliminated. It means that biorecalcitrant aromatic intermediates could still be present in the effluent even after 70% of photo-mineralization. This result can be use in first approximation, to explain the very strong recalcitrance displayed by the photo-treated effluent.

HPLC analyses were carried out and one compound present in the initial effluent was identified and quantified. This compound is the rapidoprint (Table 1), which is used in the textile industry as anti-reductor. Its biodegradability by means Zahn–Wellens test was very weak (not shown here). Its initial concentration is around 1000 $\mathrm{mg\,l^{-1}}$ (300 $\mathrm{mg\,C\,l^{-1}}$). Fig. 10 shows the evolution of concentration of both whole effluent and rapidoprint expressed in $\mathrm{mg\,C\,l^{-1}}$. When 95% of rapidoprint is eliminated, about 30% of the total DOC remains in solution, confirming that there is an important accumulation of intermediates. In this sense, this implies that the biorecalcitrance can be attributed to the aromatic intermediates products and not to the presence of the biorecalcitrant rapidoprint. Unfortunately, the accumulated intermediates (which were no identified) were not easily mineralized by means of photo-Fenton process and neither biodegradable by activated sludge.

4. Conclusions

A textile effluent was determined to be non-biodegradable by the Zahn–Wellens biodegradability test and in a FBR under theoretically favorable conditions.

Through this work, we have found that the optimal concentration of Fe^{3+} and H_2O_2 are 1.43 and 441.2 $\mathrm{mmol\,l^{-1}}$, respectively, for the treatment of the textile effluent. Also, 60 °C was determined as the optimal temperature.

The UV–VIS spectra confirm the elimination of the components responsible for the color in the effluent ($\lambda = 530$ nm) and also the accumulation of aromatics biorecalcitrant intermediates ($\lambda = 280$ nm).

The treated effluent is not biologically compatible and its complete mineralization cannot be performed by biological means.

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References

[1] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, J. Hazard. Mater. 89 (2002) 303.
[2] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Chemosphere 46 (2002) 1173.
[3] S. Rodriguez Couto, A. Dominguez, A. Sanroman, Chemosphere 46 (2002) 83.
[4] P. Pitter, J. Chudoba, Biodegradability of organic, substances in the aquatic environment, CRC Press, Boca Raton, FL, 1990.
[5] H. Gulyas, Water Sci. Technol. 36 (1997) 9.
[6] S. Esplugas, J. Gimenez, S. Contreras, F. Pascual, M. Rodriguez, Water Res. 36 (2002) 1034.
[7] Y. Xu, Chemosphere 43 (2001) 1103.
[8] M. Rodriguez, N. Abderrazik, S. Contreras, F. Chamarro, J. Gimenez, S. Esplugas, Appl. Catal. B 37 (2002) 131.
[9] J. Gimenez, D. Curco, M.A. Queral, Catal. Today 54 (1999) 229.
[10] P.L. Huston, J.J. Pignatello, Water Res. 33 (1999) 1238.
[11] D.F. Ollis, H.A. Ekabi, Photocatalytic purification and treatment of water and air, Elsevier, Amsterdam, 1993.
[12] G.A. Epling, C. Lin, Chemosphere 46 (2002) 561.
[13] L. Bolduc, W.A. Anderson, Biodegradation 8 (1997) 237.
[14] C. Pulgarin, M. Invernizzi, S. Parra, V. Sarria, R. Polania, P. Peringer, Catal. Today 54 (1999) 341.
[15] S. Parra, V. Sarria, S. Malato, P. Peringer, C. Pulgarin, Appl. Catal. B 27 (2000) 153.
[16] S. Parra, S. Malato, C. Pulgarin, Appl. Catal. B 36 (2002) 131.
[17] V. Sarria, S. Parra, N. Adler, P. Péringer, C. Pulgarin, Catal. Today, 2002, in press.
[18] OECD, Guidelines for Testing of Chemicals: Test 302B, Vol. 2, 1996.
[19] A. Marco, S. Esplugas, G. Saum, Water Sci. Technol. 35 (1997) 321.
[20] J. Bandara, C. Pulgarin, P. Peringer, J. Kiwi, J. Photochem. Photobiol. A 111 (1997) 253.