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Degradation of azo dye mixtures through sequential hybrid systems: Evaluation of three advanced oxidation processes for the pre-treatment stage

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ABSTRACT

Homogeneous (Fenton and photo Fenton) and heterogeneous (TiO_2-anatase) advanced oxidation process were applied to decolorize a mixture of azo dyes consisted of acid red 151, acid orange 7 and acid blue 113. Under the selected conditions the photo-Fenton process allowed up to 97% decolorization of the model mixture (150 mg/L, 50 mg/L of each dye) in 45 min. Although, Fenton process also provided high decolorization percentages (86%), the presence of residual peroxide and recalcitrant by-products affected the aerobic biodegradability of the pre-treated effluent. The major drawbacks for the TiO_2-anatase heterogeneous process were the higher reaction times (4 h) and the lower decolorization percentages. Under the tested conditions, the photo-Fenton process produced a biodegradable (86%) effluent during the pre-treatment of mixtures of 150 mg/L (50 mg/L of each dye) and 600 mg/L (200 mg/L of each dye). The biodegradability was not significant affected due to the change of concentration of the dyes suggesting the feasibility of coupling a photochemical process to biological one.

1. Introduction

Nowadays alternatives such as biological, chemical, physicochemical, photochemical and electrochemical processes have been tested successfully for the treatment of dyes [1,2]. The development of robust technologies is a matter of interest for the degradation of textile effluents due to the variability observed in composition and biodegradability of this type of wastewaters [1–3]. Although biological processes can degrade dyestuffs and dye intermediates through an anaerobic–aerobic strategy [4,5], the concentration changes and the presence of several dyes frequently reduced its robustness [4–6]. The advanced oxidation processes, AOPs, which are based on the generation of highly oxidizing species such as $HO^{\bullet}$ radical, have demonstrated its advantages to mineralize recalcitrant compounds [7,8]. Although $HO^{\bullet}$ radical can be efficiently produced by several AOPs, Fenton and TiO_2 processes have been raised recently as an important alternative to deal with synthetic colored wastewaters [3,7–12]. Despite its versatility, operative factors such as irradiation source, pH, reagent concentration, type of catalyst, presence of additional oxidants, reactor configuration and pollutant concentration, among others can affect the performance of the aforementioned processes [7,12–16]. The generation $HO^{\bullet}$ radicals through Fenton's reagent (Eq. (1)) is performed efficiently at acidic conditions (pH: 2.8–3.0), however in absence of photons the accumulation of Fe^{3+} and its complexation with carboxylate species appears to be main drawback in Fenton processes due to the reduction of degradation rates [7,11,13]. Nonetheless, solar radiation and UV-light can induce the photo-reduction (Eq. (2)) and photo-decarboxylation of Fe^{3+} species (Eq. (3)) allowing catalyst regeneration and producing additional radicals [11,13].

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

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad (2)$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (3)$$

TiO_2-based photocatalytic processes also have been reported as a good alternative for the generation of $HO^{\bullet}$ radical (Eqs. (4)–(6)), because of its photocatalytic activity, chemical stability, availability, low cost and non-toxic nature [13,15–18].

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{BC} + h^+_{BV}) \quad (4)$$

$$TiO_2(h^+_{BV}) + H_2O \rightarrow TiO_2 + H^+ + HO^{\bullet} \quad (5)$$

$$TiO_2(e^-_{BC}) + O_2 \rightarrow TiO_2 + O^{\bullet}{}_2{}^- \quad (6)$$

The advantages of TiO_2 and Fenton processes to deal with the decolorization of textile effluents has been well documented [3,7,12]. Nevertheless, the degradation of complex effluents by AOPs may result complicated due to operative factors such as the presence of inorganic ions [19,20], chemical auxiliaries [20,21], reagent concen-

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tration [7,11], iron source [7,11,22] and dye concentration changes that may affect its performance [3,7,11].

On this regard, the catalyst load (Fe or TiO_2) and dye concentration reduces the optical path length of the photo-reactor due to the solution becomes turbid and thus blocks radiation [13,15]. Also, the competitive absorption of photons may lead to a reduction in the pre-treatment's efficiency and will be needed longer treatment time to overcome the aforementioned drawbacks [15–18]. Gaya and Abdullah [18] indicates that the degradation rate of dye mixtures was always lower than in the case of one-dye at a time. The observed effect may be connected with the competition of dyes in mixtures to access to the active centers of catalyst and the reduction of the radiation intensity reaching to the TiO_2 surface.

It has been found that the value for k in the pseudo-first order reaction rate decreased in the presence of other dyes; nevertheless, the oxidation process maintains an acceptable reaction rate [23,24]. In those studies, the effect of concentration changes in process performance as well as effluent's biodegradability was not tested. The last fact it is actually a key-issue in AOPs because in many cases the improvement of the biodegradability, instead of total mineralization, may allow a cost reduction [3,13,25,26].

In general, fixed and operative costs have limited AOPs feasibility at industrial scale as an stand-alone treatment [3,7]. It is possible to take advantage of AOPs and biological processes for the development of robust and economic alternatives to remove biorecalcitrant compounds [3,25,26]. In a combined AOP and biological process, the oxidative stage is frequently used to improve its biodegradability. Then, using an aerobic pos-treatment stage may be feasible the economic degradation of the residual organic carbon. Up to date, several AOPs-aerobic sequential strategies have been assessed to degrade dyes [3,10,27–29]. However, that studies focused mainly on the degradation of one dye at a time and no much information about the effect of concentration changes in the performance of the coupled process is available. Taking into consideration the wide variability of wastewater parameters in textile effluents, it is necessary to consider simultaneously both the effect of the presence of dye mixtures and the concentration changes in the pre-treatment performance.

The objective of this work was to assess the feasibility of a sequential AOPs-biological systems for the degradation of a synthetic mixture of three sulphonated dyes: a mono azo (acid orange 7, AO7), a disazo (acid red 151, AR151) and a trisazo dye (acid blue 113, AB113). The performance of three AOPs (Fenton, photo-Fenton and TiO_2-anatase) was assessed considering the decolorization of the dyes' mixture and its capability to generate a biodegradable effluent.

2. Materials and methods

2.1. Reagents

The azo dyes AO7 (C.I.: 15510, $C_{16}H_{11}N_2NaO_4S$, M.W.: 350 g/mol, λ_{max}: 484 nm, Fig. 1a) and AR151 (C.I. 26900, $C_{22}H_{15}N_4NaO_4S$, M.W.: 454 g/mol, λ_{max}: 514 nm, Fig. 1b) were commercial grade (Clariant S.A. de C. V.). AB113 (C.I. 26360, $C_{32}H_{21}N_5Na_2O_6S_2$, M.W.: 681 g/mol, λ_{max}: 567 nm, dye content 50%, Fig. 1c) was purchased from Sigma–Aldrich. $FeSO_4{\cdot}7H_2O$ (Sigma–Aldrich, ACS, 97%). Other reagents utilized were TiO_2-anatase (powder, 99.8%, Sigma–Aldrich); H_2O_2 (50%, w/v, Reproquifin S.A. de C.V.); NH_4VO_3 (Sigma–Aldrich, ACS, 99%); H_2SO_4 (Sigma–Aldrich, ACS, 96%); NaOH (Sigma–Aldrich, ACS, 96%). The stock solutions of AR151, AO7, AB113 and reagents were prepared dissolving the appropriate reagent in deionized water (Elix 3 Water Purification System-MILLIPORE®). The dye mixtures used in this work 150 (50 mg/L each dye) and 600 (200 mg/L each dye) were prepared from dye stock solutions (1 g/L) and then diluted with tap water. The effect of tap on the model mixture was evaluated and no significant differences in process performance after the photo-Fenton process were found compared with the use of deionizer water.

2.2. Analytical determinations

All measurements were done at least in duplicate. Carbon removal was monitored by measuring the DOC (Dissolved Organic Carbon) by injection of filtered samples (Whatman GFA 1820-025) into a Shimazu-5050A TOC analyzer (Japan). Short chain carboxylic acids were analyzed using reverse-phase liquid chromatography (20 μL, flow 1 mL/min, 40 °C) with UV detector in an HPLC-UV (Agilent Technologies, series 1010) with C-18 column (Grace Prevail Organic 5 μm, 250 μm × 4.6 μm).

The identification of intermediate aromatic products was performed by combining a dispersive liquid–liquid micro-extraction (DLLME) technique with GC/MS. In the DLLME extraction method [30], 0.50 mL of methanol and 0.50 mL of dichloroethane were rapidly injected by syringe into a 5 mL pre-treated sample containing the analyte, forming a turbid solution. After phase separation by centrifugation (2 min at 4000 rpm), the enriched analyte in the settled phase was analyzed by GC/MS. The GC/MS (GC: Agilent technologies 6890N, USA; MS: Agilent Technologies 5975, USA) was equipped with a column (HP 5MS, 30 m × 0.25 mm × 0.25 μm). The GC/MS analyses were carried out according to [31] in a splitless mode using Helium as carrier gas (1 mL/min measured at 150 °C). The injector temperature was maintained at 250 °C and the oven temperature program was 40 °C for 5 min, 40–290 °C (at 12 °C/min), and then held at 290 °C for 3 min and finally 290–325 °C (at 20 °C/min), and then held at 325 °C for 5 min. Before HPLC, DOC and GC/MS analyses the samples were treated with $NaOH–Na_2S_2O_3$ solution to prevent further oxidation. Hydrogen peroxide concentration was determined by the ammonium-metavanadate (NH_4VO_3) spectrophotometric method at a 454 nm wavelength according to [32].

The decolorization rate of the dye mixture was assessed on the basis of changes in the maximum absorbance of the mixture at 506 nm using an UV–vis spectrophotometer (bandwidth: 1 nm, 10 mm cuvettes, PerkinElmer UV-25, USA). Prior to UV–vis analysis, the samples were withdrawn from the photo-reactor and quenched with a methanol–water solution (200 mM) to prevent further degradation. Because of it is expected a large number of aromatic compounds from the degradation of the dye mixture, UV absorption at 254 and 310 mm was used as a surrogate measure for the aromatic compounds [33]. Total dissolved solids (TDS) and total solids (TS) were measured according to Standard Methods [34].

2.3. Biodegradability assays

The biodegradability assays was performed in 0.75-L-flasks aerated by diffused air using the Zahn–Wellens test [35]. The inoculum was obtained from an activated sludge treatment plant of Queretaro (Mexico). The assays were started and monitored for 28 days and the reactors (750 mL, 0.75 g VSS/L) were kept at 28 ± 2 °C. The samples were withdrawn at frequent intervals and centrifuged at 3000 rpm for 5 min, subsequently the DOC of the supernatant liquid was analyzed in the carbon analyzer. The DOC removal was used to quantify de biodegradability of the photo-treated samples as indicated in [35]. The biodegradability (B_t, %) at time t was evaluated by means of Eq. (7), where C_A is DOC of the pre-treated azo dye mixture (measured 3 h after the beginning of the test, mg/L), C_t is DOC in the test mixture at time t, C_B is DOC of the blank at time t and

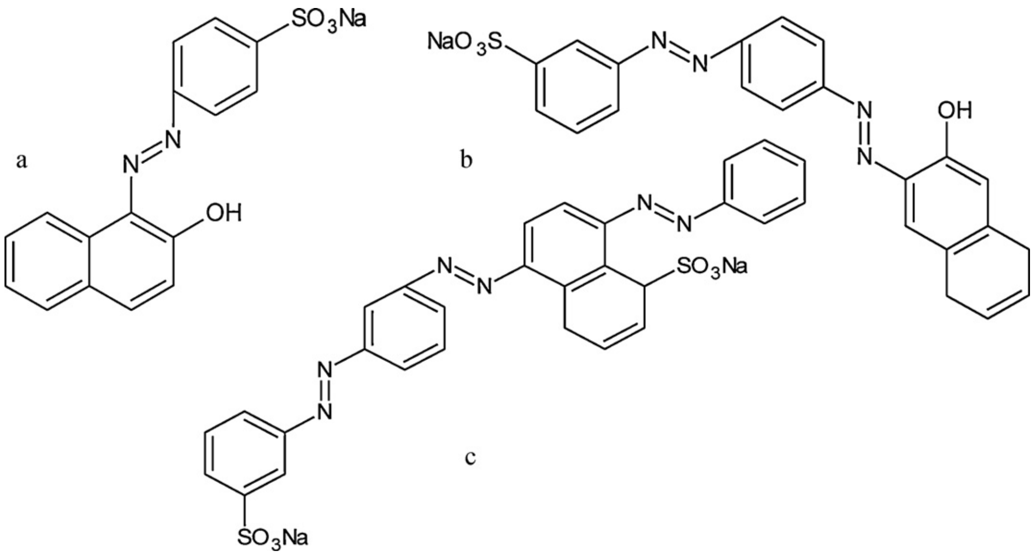

Fig. 1. Chemical structures of the studied azo dyes. (a) AO7, (b) AR151 and (c) AB113.

C_{BA} is DOC of the blank (measured three hours after the beginning of the test).

$$B_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100 \quad (7)$$

2.4. Experimental setup

The photo-Fenton and TiO_2-anatase assays were carried out in a CPC solar-based reactor. The experimental setup shown in Fig. 2 (total volume: 0.6 L) consisted of a tank, tubing and fittings, solar collector (0.043 m^2; concentration factor: 1.06; 1 pyrex-glass tube: OD: 30 mm, ID: 2.85 mm, length: 46 cm) a peristaltic recirculation pump (7553-70 Masterflex) with speed control (7553-71 Masterflex). In all cases, the volumetric flow was fixed at 1.2 L/min and the reactor volume was composed of: irradiated volume (V_{IRR}: 42%) and the dead volume (V_D: 57%). Incident radiation (W/m^2) was measured every minute with a pyranometer (Davis Instruments Vantage Pro2^{TM} Weather Stations, spectral range 300–1100 nm). The reactor was held fixed in an aluminium frame tilted 20° in Queretaro (Mexico).

The experiments were carried out in a fixed schedule span from 11:00 AM to 4:00 PM when the highest irradiation is present. It is important to indicate in photo-Fenton and TiO_2-anatase experiments temperature evolves freely (between 28 ± 2 up to 41 ± 4 °C) along the treatment. Comparisons between the experiments were always done under similar irradiation conditions in order to reduce the effect of the temperature in the process performance.

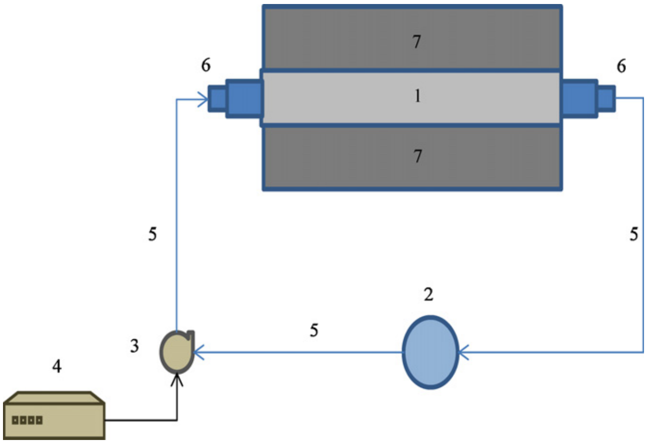

Fig. 2. Photocatalytic reactor scheme. (1) Pyrex tube, (2) tank, (3) pump, (4) speed control, (5) tubing, (6) fittings, (7) involute.

2.5. Experimental design

2.5.1. TiO_2-anatase experiments

Heterogeneous phase experiments were carried out using TiO_2-anatase as the photo-catalyst and an azo model mixture of 150 mg/L (50 mg/L each dye). Before irradiation, the model mixture was premixed for 30 min under dark conditions in order to achieve the maximum adsorption of the dyes onto the TiO_2 surface. In order to evaluate the effects of the selected factors (pH and TiO_2) a Design of Experiments (DOE) was used. Three initial TiO_2 concentrations (0.25, 0.5 and 1.0 g/L) and three pH conditions (3, 5 and 7) were selected as independent variables meanwhile decolorization was chosen as dependent variable (response). The decolorization was assessed on the basis of changes in the absorbance at 506 nm after 4 h of solar photo-assisted treatment in the CPC reactor. Again, the photocatalytic process was conducted for 4 h and 2 mL aliquots of the mixture were withdrawn over regular intervals of time for spectrophotometric analysis.

The independent variables and their operative range were selected taking into consideration the literature [9,16–18]. Due to acidic (pH < 3) and alkaline conditions (7 < pH < 11) negatively affect the degradation rate of sulphonated dyes, the star points of the experimental design were substituted by center of edges experiments [9,15–18]. In order to avoid an unnecessary excess of catalyst and ensure the efficient absorption of the photons, the catalyst load were within the 0.25–1.0 g/L range. The proposed DOE consists of three types of points: vertices (4), center of edges (4) and center points (5), with 13 experiments. The levels of the independent variables and its corresponding natural values are shown in Table 1. Low and high levels are represented by (−1) and (+1), respectively, while central points are denoted as (0). The DOE and ANOVA tests were carried out in Design-Expert 8.0.1 (Stat-Ease, Inc, USA). Later, the effect of H_2O_2 in TiO_2-assited process was investigated at 290 and 580 mg/L, which represent an excess of 40 and 280%, respectively of the peroxide dose required to decolorize 97% the model mixture (150 mg/L) by means of photo-Fenton Process (see Section 2.5.2).

Table 1
Experimental ranges of the selected independent variables in TiO_2 process.

Run	Coded variable		Natural variable	
	TiO_2, x_1	pH, x_2	TiO_2, g/L	pH
1	1	0	1.0	5
2	−1	0	0.25	5
3	0	1	0.5	7
4	−1	−1	0.25	3
5	−1	1	0.25	7
6	0	0	0.5	5
7	1	1	1.0	7
8	0	−1	0.5	3
9	1	−1	1.0	3
10	0	0	0.5	5
11	0	0	0.5	5
12	0	0	0.5	5
13	0	0	0.5	5

2.5.2. Photo-Fenton experiments

In a previous study [36], a Central Composite Design (CCD) was applied for determine the reagent dose for maximizing the decolorization of AO7, AR151 and AB113 through a photo-Fenton process. The experimental factors took into consideration in photo-Fenton experiments were the initial concentrations of Fe^{2+} and H_2O_2 (independent variables), while decolorization percentage was considered as the response (dependent variable). It should be mentioned that Response Surface Methodologies (RSM) were performed to assess the relationship between decolorization percentage and reagent dose for each dye. Experimental data were analyzed using Design-Expert 8.0.1 software (Stat-Ease, Inc., USA) and fitted to a second-order equation [37]. The best working conditions established to decolorize 97% each azo dye were listed in Table 2. The total reagent concentration ($C^{T}_{H_2O_2}$ and $C^{T}_{Fe^{2+}}$) required to decolorize each model mixture (C^{T}_{mix}) was calculated as the sum of the individual reagent requirements by using Eqs. (8)–(10). In the above mentioned equations R represent reagent to dye mass ratio (see Table 2) required to assure 97% decolorization of each dye.

$$C^{T}_{mix} = C^{AR151} + C^{AO7} + C^{AB113} \tag{8}$$

$$C^{T}_{H_2O_2} = C^{AR151}R^{AR151}_{H_2O_2} + C^{AO7}R^{AO7}_{H_2O_2} + C^{AB113}R^{AB113}_{H_2O_2} \tag{9}$$

$$C^{T}_{Fe^{2+}} = C^{AR151}R^{AR151}_{Fe^{2+}} + C^{AO7}R^{AO7}_{Fe^{2+}} + C^{AB113}R^{AB113}_{Fe^{2+}} \tag{10}$$

2.5.3. Fenton experiments

The Fenton process was applied to a model mixture of 150 mg/L consisted of 50 mg/L each dye. All the experiments were carried out in the dark at room temperature (24 °C) in 250 mL Erlenmeyer flasks at acidic conditions (pH: 2.8 ± 0.2) and constant magnetic stirring (400 rpm). The duration of each experiment was 3 h and 2 mL aliquots were withdrawn over regular intervals of time and subjected for further analyses. The reagent doses used in Fenton experiments were the same as used in the photo-Fenton assays (Table 2). All the experimental runs were repeated at least three times an average were reported.

Table 2
Reagent requirements in Fenton and photo-Fenton experiments.

Reagent	R mass-ratio, mg reagent/mg dye			Mixture concentration C^{T}_{mix}, mg/L		
	AR151[a]	AO7[a]	AB113[a]		150	600
Fe^{2+}	0.08	0.06	0.05	$C^{T}_{Fe^{2+}}$	9.5	38
H_2O_2	1.22	0.97	1.95	$C^{T}_{H_2O_2}$	207	828

[a] Dye concentration: 100 mg/L, irradiation time 1 h (250 ± 15 kJ/L).

3. Results and discussion

The selection of the best alternative to carry out the pre-treatment of the azo dye mixture had the main objective to generate a highly biodegradable effluent and to assure low operative costs, through the reagent reduction. The pre-treatment system should ensure a high color removal, despite the fluctuations in the influent's characteristics.

3.1. Pre-treatment of dye mixture with TiO_2-anatase

The statistical analysis carried out in Design Expert allowed to obtain a semi-empirical quadratic model in terms of coded variables (x_1: TiO_2 and x_2: pH) to represent the decolorization (D) of the dye mixture (Eq. (11)) after 4 h of photo-treatment. The calculated model (*F*-value = 110) indicated there is only a 0.01% chance that a, *Model F-Value*, this large could occur due to noise. Also, the Prob > *F* (0.0001) values indicate model is significant for the determination of decolorization percentage. Furthermore, due to the fact that *r-squared* (r^2: 0.988) and *adjusted-*r^2 (adj-r^2: 0.979) are in a reasonable agreement, it is possible to indicate that the quadratic model (Eq. (11)) could describe the process behavior satisfactorily within the proposed experimental range. The last fact can be evidenced by means Fig. 3a where the predicted and actual values are plotted.

$$D = 75.7 + 3.0x_1 + 4x_2 + 2.3x_1x_2 + 1.9x_1^2 - 3.0x_2^2 \tag{11}$$

It was observed an increase in the TiO_2 concentration (from 0.25 up to 1 g/L, at pH 5) increases the decolorization efficiency (from 74 to 82%), confirming the influence of the increased number of the active sites (Fig. 3b).

It has been reported that as the concentration of the TiO_2 increases above the optimum value, the degradation rate and decolorization efficiencies are reduced because of the interception of the light by the slurry (scattering effect) [13,15–18]. Nevertheless, the above fact was not observed in this work and it is presumably related to the lower catalyst load used (Fig. 3b). As shown in Fig. 3b, pH is an important factor that can influence the decolorization efficiency of the model mixture taking into account the amphoteric behavior of catalyst [13,15,18]. In other words, under acidic or alkaline conditions the catalyst surface can be protonated or deprotonated, respectively as shown in the following reactions (Eqs. (12) and (13)).

$$TiOH + H^{+} \rightarrow TiOH_2{}^{+} \tag{12}$$

$$TiOH + OH^{-} \rightarrow TiO^{-} + H_2O \tag{13}$$

When the pH was increased from 3 to 5, the color removal increased from 68 to 75%, respectively. Further increases of the pH (up to 7) slightly reduce the final decolorization percentage (Fig. 3b). The low decolorization efficiency at acidic conditions (pH 3) may be explained by the aggregation of the TiO_2 particles that reduce the surface area available to dye adsorption and photon absorption as reported by [18,38].

The selection of the best operative conditions in TiO_2-anatase process was realized in the optimization module of Design Expert 8.01. The module searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors [39]. In this work, maximization of the decolorization was selected as the optimization goal while TiO_2 and pH were chosen as constraints. As indicated in Fig. 3b, it is desirable to run the photo-treatment at neutral pH (7) and a high TiO_2 concentration (1 g/L). However, under the selected conditions, it was feasible to decolorize up to 84% de model mixture in 4 h (accumulated energy: 992 ± 10 kJ/L).

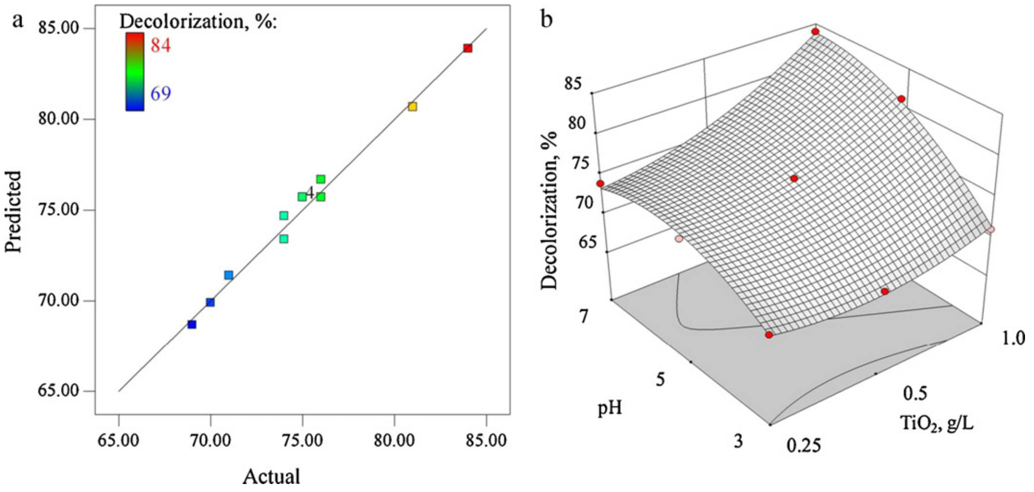

Fig. 3. Heterogeneous phase dye decolorization process. (a) Actual and predicted decolorization percentages and (b) response surface and contour diagram for pH and TiO_2 concentration.

In order to increase the decolorization percentage, hydrogen peroxide was added to the mixture of azo dyes in two concentrations levels (290 and 580 mg/L). After 4 h of photo-treatment the decolorization percentages were 89 and 100%, respectively (Fig. 4a). It should be noted that addition of hydrogen peroxide increased the decolorization rates because its electron acceptor nature that can react with electrons to produce additional $HO^{\bullet}$ radicals (Eq. (14)).

$$H_2O_2 + e^- \rightarrow HO^{\bullet} + OH^- \qquad (14)$$

3.2. Pre-treatment with Fenton and photo-Fenton

It is important to note that the reagent doses applied for the pre-treatment of the mixture of azo dyes (150 mg/L) were calculated considering the reactants required to decolorize separately each azo compound by a photo-Fenton process. As shown in Fig. 5a, the decolorization obtained by the Fenton process was 86% and for the photo-Fenton process was 97%. The DOC removal and the aromatic removal at 254 and 310 nm were, 27, 25 and 43% for Fenton process and 54, 64 and 75% for the photo-Fenton process, respectively. This condition was reached in 60 min of irradiation for the photo-Fenton process (accumulated energy: 250 ± 10 kJ/L).

As the Fenton reaction is carried out in the dark, low-molecular-weight acids can be accumulate allowing the formation highly stable iron complexes which stops the Fenton reaction as shown in Fig. 5b and hence reducing the degradation or transformation of the original compounds [7,8]. The sudden decolorization is related entirely to Fenton chemistry, as indicated by [7] due to Fe^{2+} and H_2O_2 reacts very quickly (53 $M^{-1}\,s^{-1}$) to generate large amounts of $HO^{\bullet}$ radicals (Eq. (1) which are used to decolorize the dye mixture. The accumulation of Fe^{3+} becomes the rate-limiting step owing to catalyst regeneration rate (Eq. (15)) is slower than the observed for the reaction (1). As can be noted the foregoing will generate a two-stage kinetic as mentioned by [7].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet}{}_2 + H^+ \quad k = 0.01\text{–}0.02\,M^{-1}\,s^{-1} \qquad (15)$$

That fact had two important consequences: the presence of residual peroxide (almost 5% of the initial dose) and the accumulation of less-oxidized by-products (mainly aromatic compounds). Residual peroxide may cause bacterial inhibition, whereas aromatic moieties, represented as absorbance at 254 and 310 nm in Fig. 5b, are considered less biodegradable under aerobic conditions [25,27].

It is interesting to note that complete exhaustion of peroxide was reached after 15 min of photo-Fenton treatment (accumulated energy: 55 kJ/L). The last fact indicated that the additional degradation is related to photo-chemical processes. The solar radiation induce the photo-decarboxylation of iron complexes as indicated in Eq. (3) and the production of additional $HO^{\bullet}$ radicals through photo-reduction reactions (Eq. (2)), improving the efficiency of the degradation process.

In the absence of Fenton's reagent, it was found that the dye photolysis represents less than 2% decolorization after 60 min photo-treatment. In general, dyes are scarcely degraded by UV and solar radiation due to dyes are synthesized to resist abrasion, solar

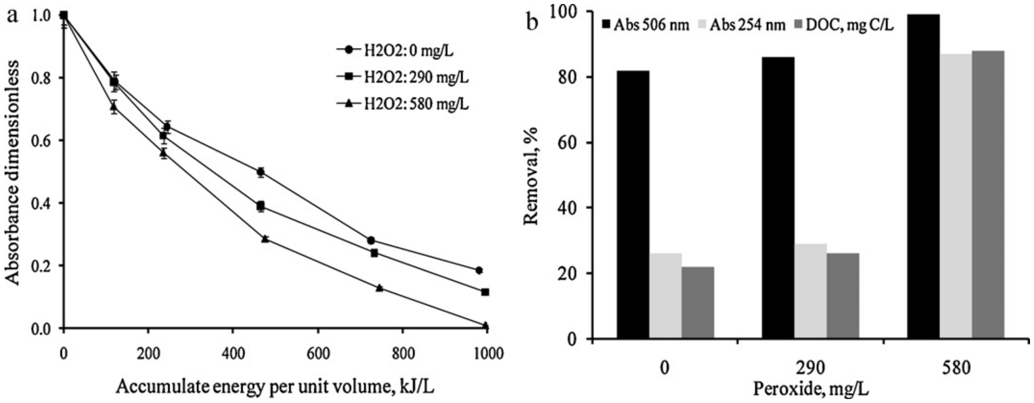

Fig. 4. Effect of initial peroxide concentration into the general performance of TiO_2-anatase process. (a) Decolorization profiles, (b) absorbance and DOC removal. Conditions: TiO_2: 1 g/L, 4 h residence time (accumulated energy: 992 ± 10 kJ/L).

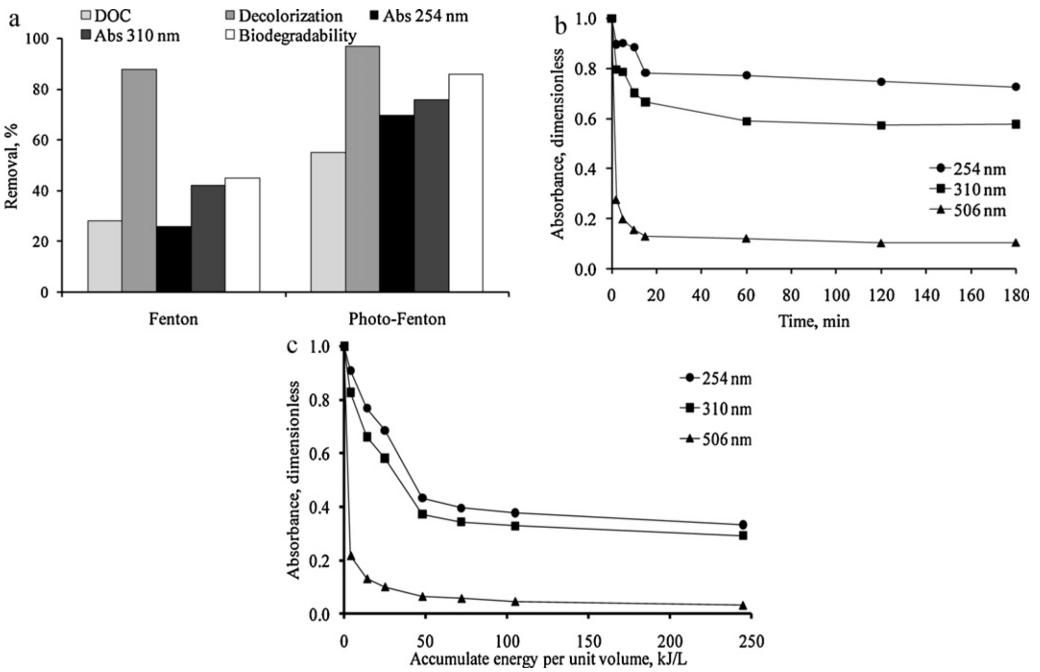

Fig. 5. Pre-treatment of an azo dye mixture by Fenton and photo Fenton processes. (a) General performance of the pre-treatment processes, (b) Fenton process and (c) photo-Fenton process.

radiation, chemical and bacterial attack, which makes them remain unaltered for long periods in the environment [3,11,40].

3.3. Selection of the pre-treatment stage

As indicated in Fig. 4 the TiO_2 process allowed dye decolorization in absence of peroxide. Long residence time and the partial decolorization of the dyes appear to be as the major drawbacks for this alternative. The partial removal of dyes may lead to an inefficient performance of a biological post-treatment stage because of color is quite complex to degrade in an aerobic process [1–3,6]. The experimental results obtained in a pilot plant by Muñoz et al. [41] indicated that the main environmental impact of the heterogeneous phase processes was related to a larger solar collector area, originated by mass-transfer limitations. Although, peroxide injection can overcome the low decolorization percentages reached by TiO_2 process (Fig. 5a), the photo Fenton processes was able to decolorize up to 98% the model mixture in less than an hour.

It is important to note that in Fenton and photo-Fenton processes the oxidant consumption was lowered by 40% with regard to the TiO_2-process. In the Fenton process the presence of residual peroxide and less oxidized by-products is the major concern [42]. The biodegradability of the effluent of the Fenton process was 45%, implying that residual peroxide and by-products formed were less biodegradable than the by-products obtained by photo-Fenton process where the effluent biodegradability was up to 86% (Fig. 5a). The absorbance reduction in visible region reflected the breakdown of the azo bond, while the absorbance diminution at 254 and 310 nm was related to the cleavage of the benzene and naphthalene rings, respectively [43,44].

The GC/MS analyses showed that the $HO^{\bullet}$ addition to the azo bond drives to poli-substituted phenols (benzoquinone, hydroquinone, benzoic acid) and naphthol rings. These compounds are produced simultaneously in photo assisted reactions by desulfonation and hydroxylation of the aromatic rings [43–46]. On this regard, the by-products generated in the photo Fenton treatment, after 5–10 min, included mainly poli-substituted phenols, phthalic anhydride and succinic and maleic acids as shown GC/MS and HPLC analyses, respectively. The phthalic anhydride is considered an intermediate generated from the oxidation of naphthol rings in AOPs [7,45,46]. Anhydride starts to disappear (from 15 to 20 min) leading to the production of short chain acids (formic, acetic and oxalic). Benzoquinone, hydroquinone and benzoic acid rings derived to the formation of additional short chain acids like maleic, formic and oxalic acids, which are simultaneously photo-decarboxylated as indicated by Eq. (3). Under the applied conditions in the biodegradation assays, it would be feasible to degrade the photo-treated effluent in a conventional aerobic process [35,42] due to highly oxidized compounds that appears to be the most abundant by-products.

3.3.1. Robustness of pre-treatment stage

Table 3 reveals the suitability of photo-Fenton process to degrade sulphonated dyes. The above results suggested that

Table 3
Effect of concentration into the process performance.

Concentration, mg/L	Pre-treatment photo-Fenton		Pos-treatment biological assays	
	DOC removal, %	Abs 254 nm, removal, %	Decolorization, %	Biodegradability, %
150[a]	57 ± 2.0	75 ± 1.3	98 ± 0.5	86 ± 3
600[b]	56 ± 2.2	64 ± 1.9	96 ± 0.8	76 ± 3

Note: The preliminary assays indicated that photolysis of the dye (at 150 and 600 mg/L) accounted less than 1.5 and 2%, respectively, after 60 min of photo-treatment (250 ± 15 kJ/L).

[a] Initial DOC 63 mg C/L.

[b] Initial DOC 252 mg C/L.

photo-Fenton process was enough robust to deal with dye mixtures as well as concentration changes. As the dye concentration increase, the DOC and decolorization percentages were slightly affected (less than 2%); conversely, absorbance at 254 nm and biodegradability were reduced up to 10%. Due to the low reagents ratios used (Fe^{2+}/H_2O_2: 0.046 and dye/H_2O_2: 0.72), the radical scavenging reactions were significantly reduced. This do not affected the residual aromatic content when the highest concentration of the dye mixture (600 mg/L) was used, since it was only reduced in 10%, while the concentration was increased 4 times in respect to the low condition.

4. Conclusions

The use of advanced oxidation process in a pre-treatment stage successfully enhanced the decolorization of the selected azo dye model mixture. TiO_2-anatase treatment presented a color removal percentage from 68 to 75% and up to 84% when hydrogen peroxide and 4-h of residence time were applied. These conditions were considered a drawback to combine heterogeneous phase process with an aerobic pos-treatment.

Fenton process was a simple and efficient pre-treatment to decolorize the dye mixture (86% removal). However, residual peroxide and the presence of less transformed by-products showed to be the parameters with higher impact into decolorization and biodegradability performance.

Photo-Fenton process was considered the best alternative to carried out the pre-treatment because the high color removal achieved (up to 96%) and the high biodegradation percentage (86%) observed in less than one hour. Concentration changes slightly affected the biodegradability of the photo-Fenton effluent. An increment on the dye concentration from 150 to 600 mg/L, only decrease the effluent's biodegradability in 10%. This work demonstrated the feasibility to obtain an effective decolorization, by using a photochemical process, and the production of a suitable effluent to be degraded through an aerobic process.

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