



Modelling of the simultaneous photodegradation of Acid Red 97, Acid Orange 61 and Acid Brown 425 using factor screening and response surface strategies

Cristina Fernández, M. Soledad Larrechi, M. Pilar Callao*

Department of Analytical and Organic Chemistry, Rovira i Virgili University, Marcel·lí Domingo s/n, Campus Sescelades, E-43007 Tarragona, Spain

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ABSTRACT

In this paper the influence of seven variables that could be relevant in the photodegradation of three textile dyes – Acid Red 97, Acid Orange 61 and Acid Brown 425 – has been studied with the aim of determining the most efficient conditions for this process. The type and concentration of catalyst, the presence and concentration of H_2O_2 , the stirring, the pH and the dye concentration have been studied as variables. In the first stage the more basic variables were analyzed using a screening methodology (saturated fractional factorial design) and it was concluded that the most influential variable was the presence of H_2O_2 . In the second stage, a central composite design was used to establish a response surface for the behavior of the photodegradation. In this stage the concentration of Acid Brown 425 was fixed and the degradation was carried out without catalyst. The most remarkable aspects of the experiment are that brown dye is always the most persistent in the solution and that a catalyst is not needed to degrade the dyes quickly. A second-order equation is needed to model this process. The response surface obtained could be useful for reducing the time and money needed to treat effluent wastewater.

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1. Introduction

The presence of dyes in wastewater is an important environmental problem and many processes have been proposed for eliminating them such as physicochemical treatments involving adsorption onto activated carbon [1], adsorption onto waste materials that are used as low cost adsorbents [2], electrochemical oxidation [3] and biodegradation [4]. In recent years technologies based on advanced oxidation processes have been shown to be efficient procedures. In these processes, highly reactive species (mainly hydroxyl radicals) are used as primary oxidants and no secondary pollution is generated [5]. Some examples of these processes are the photo-Fenton process, in which hydroxyl radicals are generated using iron catalysers and oxygen peroxide [6,7], photolysis, in which the radicals are formed when an oxidant, normally H_2O_2 , is irradiated with UV radiation [8–12] photocatalysis, in which a semiconductor adsorbs UV radiation and generates redox reactions that eliminate the contaminants [13,14], ozonation processes, in which ozone is used as an oxidant [15] and even a combination of electrochemical and photocatalytic processes [16].

There has been much research into determining the most efficient conditions for these processes and in recent years exper-

imental designs have been used because it is known that the ability to systematically remove dyes will vary depending on the synergistic or antagonistic action between different variables. Most studies apply this methodology to the degradation of one dye [5,11,13,15,17–19]. Experimental designs have been used also to study the degradation of dye mixtures using the maximum absorbance of the dyes at different wavelengths [20–22] or the concentration values of the different dyes over time using multivariate methodologies [14,23].

In a previous study [14], our research group developed a rapid methodology that applied the multivariate curve resolution with alternating least squares method (MCR-ALS) to the set of spectra obtained in the UV–Vis during the catalytic photodegradation process of three dyes (Acid Red 97, Acid Orange 61 and Acid Brown 425) using TiO_2 as catalyst. The aim of MCR-ALS method is to decompose a data matrix composed by m rows (spectra recorded at different times) and n columns (absorbance at different wavelengths) in a product of two matrices, one corresponding to the concentration profiles of each compound along the time and another that contains information about the spectral profiles of these compounds [14,24]. This allows the concentrations of the three dyes to be determined over the time of degradation despite their spectra overlapping. In this study we also concluded that the initial concentration of Acid Red 97 has a critical effect on the simultaneous photodegradation of the three dyes.

The primary aim of the actual study is to extend the scope of the previously developed methodology so as to (a) increase the number

* Corresponding author. Tel.: +34 977558199; fax: +34 977558446.

E-mail addresses: mariapilar.callao@urv.cat, mariapilar.callao@urv.net (M.P. Callao).

of variables in order to determine the effect of multiple variables on the photodegradation process and (b) to apply different experimental methodologies to obtain the maximum information with the minimum experimental cost.

The studied variables and their domain were selected according to a previous knowledge and bibliographic revision. The chosen variables were the type of catalyst, the catalyst concentration, the pH, the oxidant concentration and the presence of stirring. We used ZnO and TiO₂ as catalysts because their efficiency in photodegradation processes has been demonstrated [25]. The oxidant H₂O₂ was employed to determine its influence on the process [18,26]. The pH range was chosen on the basis of Kansas et al.'s findings [25]. The catalyst concentration was selected from a previous study [14]. The presence of stirring was evaluated because could be relevant in the simplicity of the process.

To achieve this, first, we employed a screening factor methodology (a saturated fractional factorial, 2⁵⁻²) because this kind of design allows to obtain the main effects of the variables and new experiences could be added, using the experimentation carried out, if more information is required. Secondly, we used the information obtained in the screening process to reduce the number of variables and to find a suitable approximating function in order to predict the behavior of the degradation. For this, we have used a central composite design, that allows to obtain the main effects of the variables, the quadratic effects and the interactions. With this design a second-order response surface could be established.

To our knowledge, no study has investigated screening as an initial step for creating a response surface for dye degradation processes. We are also unaware of any paper that has modelled the effect of various experimental variables on the behavior of various dyes, despite the fact that many residual waters contain several dyes simultaneously.

2. Experimental

2.1. Chemicals

We used analytical grade chemicals in all the analyses. These were NaOH and H₂SO₄ from PROLABO and purified water from a Milli-Q water system from MILLIPORE, USA. We used H₂O₂ (30%) from Scharlau as an oxidant. In the screening process, we used TiO₂ in the anatase form (99.8%) and ZnO powder <1 μm (99.9%) as photocatalysts without further treatment and these were obtained from Sigma-Aldrich.

Dyes were obtained from Trumpler Española, S.A. (Barberà del Vallès, Barcelona, Spain). Solutions of dyes were prepared in Ultra-pure Milli-Q water.

2.2. Instrumental and software

Photodegradation studies were carried out in the cylindrical annular batch reactor illustrated in Fig. 1. The data were acquired and monitored with a Hewlett-Packard 8452A spectrophotometer using HP89531A software. The spectra were recorded from 244 to 720 nm in 2 nm steps.

A Crison pH meter was used to measure the pH of the samples. The pH meter was calibrated each day.

Multivariate curve resolution with alternating least squares (MCR-ALS) was performed using software written in the laboratory with a MATLAB 6.5 computer environment [27]. This software can be found in Ref. [28]. Calculations for the experimental design were made using STATGRAPHICS Plus 5.0 [29] and The Unscrambler 9.0 [30].

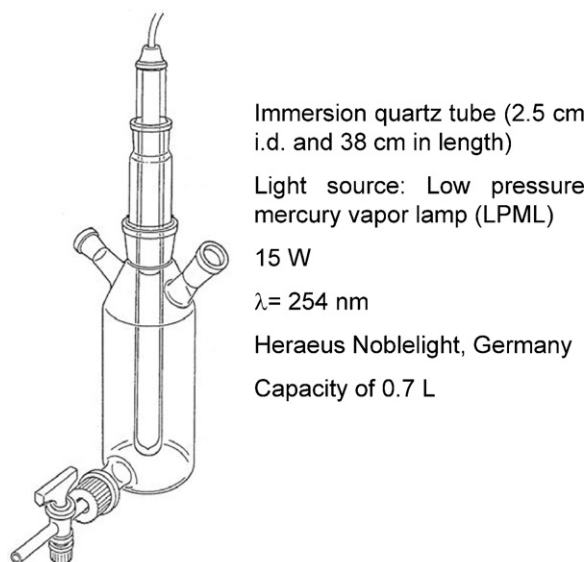


Fig. 1. Photoreactor scheme.

2.3. Photodegradation procedure

Degradation samples were prepared diluting different amounts of each dye according to the values indicated by the experimental designs in the corresponding experience. The pH was adjusted using H₂SO₄ and NaOH solutions and the final sample volume was 500 mL. Degradations were carried out in a cylindrical reactor and different samples of 6 mL of the degradation solution were taken from the reactor during the degradation time. After photodegradation, all the samples were stored in dark conditions and samples containing catalyst were centrifuged in order to separate the catalyst and register the spectra. More details of the experiment can be found in Ref. [14].

2.4. Experimental design

In this paper the photodegradation of the dyes is studied using experimental designs. The different experiments are designed, firstly, according a saturated factorial fractional design and, secondly, according a response surface design. The variables are codified with low and high levels. Each experiment was evaluated by analyzing the response that was related to the reaction rate. Each experience provides a matrix with the spectra obtained throughout the degradation time. In order to improve the results we constructed a new matrix that is the experimental matrix augmented with the pure dye spectra. The spectrum of H₂O₂ was added to the augmented matrix in the resolutions of the experiments in which this oxidant was used. The augmented matrixes were treated with MCR-ALS. This methodology allowed us to quantify each dye at each moment of the degradation, despite the overlap of their spectra, to construct the degradation curves and to determine either the half-life time of each dye or the remaining concentration at a particular time. As an example in Fig. 2 is represented the degradation spectra and the concentration profiles recovered by MCR-ALS of one experience carried out.

2.4.1. Screening step

In the screening designs, the relation between the information obtained about the influence of the variables and the number of experiments is high. For this reason, these designs are employed when there are many controllable variables that may influence the experiment [31]. These designs allow us to determine the main

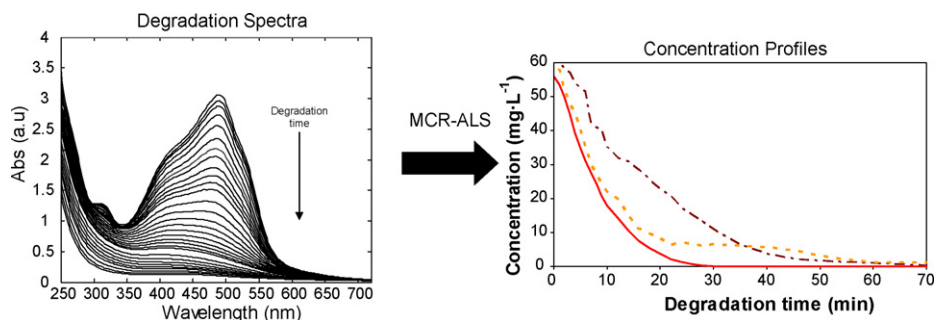


Fig. 2. Degradation spectra and concentration profiles of each dye recovered by MCR-ALS. (–) Corresponds to Acid Red 97 (···) to Acid Orange 61 and (---) to Acid Brown 425. Experimental conditions: concentration of each dye = 60 mg L⁻¹, H₂O₂ concentration = 0.005 M, pH = 2, without catalyst and with stirring.

effects of the variables without taking into account the possible effect of interactions between variables that could influence in the response. In this paper we used a saturated fractional factorial experimental design, which had the advantage that, if necessary, more experiments could be added to build a full factorial and thus determine the effects of the interactions [32,33].

2.4.2. Surface response establishment

With the selected variables in the previous stage, we constructed a 2³ full factorial design in order to determine the effect of the main variables, all the interactions between variables and the suitability of the experimental domain pre-established for the different variables.

When the full factorial design is studied in the suitable domain we can obtain the coefficients to establish the following first-order response surface:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (1)$$

where b_i are the estimation of the effects and x_i are the codified values from -1 to +1 (-1 corresponds to the value of the low level of the variable and +1 corresponds to the value of the high level).

In order to validate this model design, we evaluated the pure quadratic curvature sum of squares ($SS_{\text{pure quadratic}}$) using Eq. (2) [32]:

$$SS_{\text{pure quadratic}} = \frac{n_F n_C (\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \quad (2)$$

where \bar{y}_F is the average of the results obtained in the runs at the factorial points of the design, \bar{y}_C is the average of the response at the central point, and n_F and n_C are the number of runs, in our case n_F is 8 because we employed a 2³ factorial design and n_C is 3 that are the replications in the central point.

An *F*-test is used to compare the $SS_{\text{pure quadratic}}$ and SS_{residual} obtained with the three replications of the central point. If both values are comparable, there is no quadratic curvature. On the other hand if they are not comparable, this means that a quadratic curvature is present and the model has to be represented by a second-order equation [32].

The central composite design (CCD) is the most popular class of design for fitting second-order models; CCD is often practically deployed through sequential experimentation; that is, a 2^k full factorial design is used to fit a first-order model and then axial runs are added to allow the curvature to be estimated [32].

In all of the experimental designs employed, an ANOVA test was carried out by making an additional triplicate central point in order to evaluate the significance of the effects [34].

3. Results and discussion

3.1. Screening process

Three of the five variables studied were qualitative. These were the type of catalyst (high level TiO₂ (+) or low level ZnO (-)); the presence (+) or not (-) of oxidant H₂O₂; and the presence (+) or not (-) of stirring. The other two variables were quantitative. These were pH 9 (+) or 2 (-) and catalyst concentration 1 g/L (+) or 0.05 g/L (-). We used ZnO and TiO₂ as catalysts because their efficiency in photodegradation processes has been demonstrated [25]. The oxidant H₂O₂ was used to determine its influence on the process [18,26]. The pH range was chosen on the basis of Kansas et al.'s findings [25] regarding the effects of the catalysts on pH. The catalyst concentration of the previous study [14] was increased in order to determine its possible influence on the present study. Dye concentration was fixed at 180 ppm (60 ppm of each dye) because the concentration effect of the different dyes has already been evaluated in previous studies [14]. The responses studied were the half-life time of each dye.

Table 1 describes the experimental conditions of the 8 experiments performed. The results are represented in Fig. 3a. In this figure in the center of each square, the half-life time for each dye at each pH level has been represented to analyze the effect of the variables. The figure does not include the levels of stirring or the catalyst concentration for dimensionality reasons and because these are the least influential variables.

Fig. 3a clearly shows two remarkable results: the first is that brown dye is always the most persistent in the solution and the second is that the presence of hydroxide peroxide (experiments 3, 4, 7 and 8) notably reduces the half-life time of the degradation of the three dyes. Other less marked tendencies are that the pH effect in the domain does not significantly alter the degradation rate of the three dyes and that better results are obtained when ZnO is employed instead of TiO₂ (experiments 3 and 4 vs. 7 and 8). However, it should be pointed out here that other variability variables are involved in this comparison (pH and stirring).

It is known that the presence of an oxidant in a heterogeneous catalyst increases the rate of the degradation by enhancing the

Table 1
Screening experimental plan.

Exp.	Catalyst	H ₂ O ₂ (mol L ⁻¹)	pH	[Catalyst] (g L ⁻¹)	Stirring
1	ZnO	0	4	1	Yes
2	TiO ₂	0	4	0.05	No
3	ZnO	0.02	4	0.05	Yes
4	TiO ₂	0.02	4	1	No
5	ZnO	0	9	1	No
6	TiO ₂	0	9	0.05	Yes
7	ZnO	0.02	9	0.05	No
8	TiO ₂	0.02	9	1	Yes

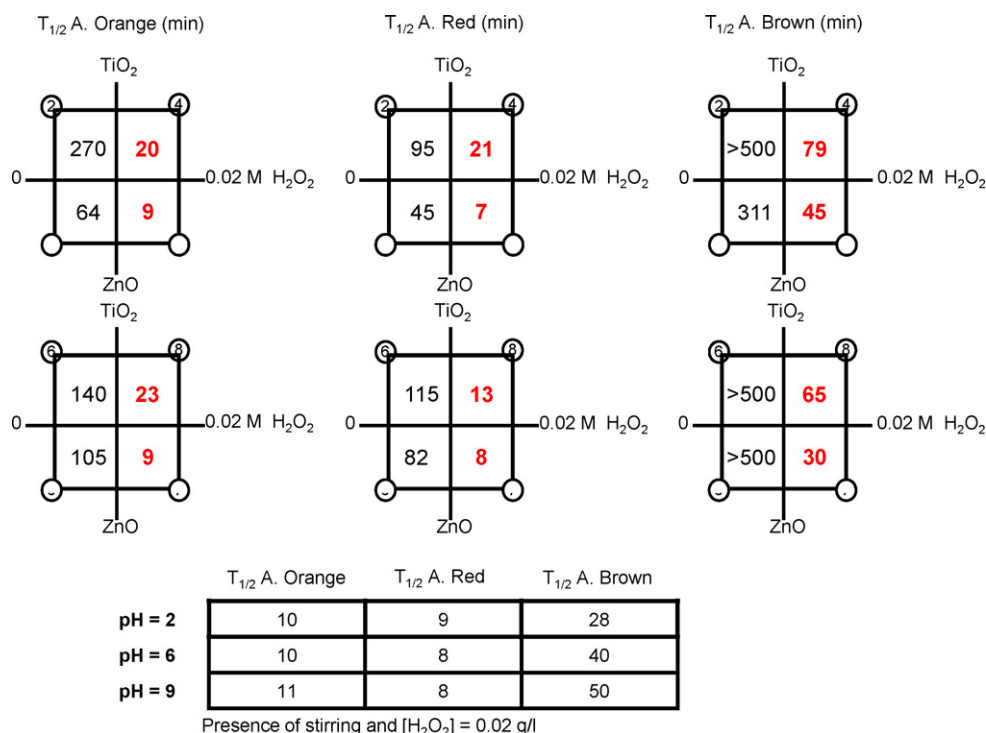


Fig. 3. Screening results.

quantum yield of hydroxyl radicals. However, because of the great magnitude of H_2O_2 effect, we evaluated the degradation rate in a homogeneous medium without a catalyst because this notably simplified the process. We thus carried out three experiments using H_2O_2 but without catalyst. Fig. 3b shows the experimental conditions and the responses obtained.

From the results we deduced that red and orange dyes degrade at the same rate independently of the pH. If the results obtained at pH 9 are compared with the results of the screening experiments 7 and 8 (Fig. 3a), it could be concluded that the degradation is faster without the catalyst TiO_2 than when this catalyst is used, and that when ZnO is employed as catalyst with red and orange dyes the results are similar to those obtained when it is not used. Degradation only improves when ZnO is used for brown dye, although the best values for this dye (which is the most persistent) were obtained at pH 2 and without a catalyst. It is at first sight surprising that the photodegradation results are better without catalyst when an oxidant such H_2O_2 is employed in the reaction. One possible explanation of this fact is that at high dosage, H_2O_2 is a powerful OH^\bullet scavenger [35] and furthermore that high concentrations of this oxidant could cause the dye and the H_2O_2 to compete when adsorbing onto the catalyst, depending on the adsorption behavior of the dyes [36].

3.2. Response surface establishment

3.2.1. Preliminary studies

In this first stage, prior to establishing the response surface, three variables were selected and a full factorial 2^3 was designed in order to analyze whether the experimental domain was suitable for the parameters that could influence the photodegradation process. Given the results of the previous experiments, we decided to work without a catalyst because this way the degradation was just as effective, more economic and left no catalyst residues. The degradation took place with stirring and at a constant pH of 2.

The variables studied were the concentration of H_2O_2 (A): 0.02–0.1 mol/L; the initial concentration of Acid Red 97 (B): 0–60 $mg\ L^{-1}$; and the initial concentration of Acid Orange 61 (C): 0–60 $mg\ L^{-1}$. As can be seen, the H_2O_2 concentration was increased with respect to the screening step in order to more accurately study the effect of the most influential variable. The chosen response was the concentration of brown dye at 20 min of degradation because this dye is the most persistent in the solution (see Fig. 3a) and low concentrations of this dye at this time mean that the other two dyes are almost eliminated. The concentration of brown dye was fixed at 60 $mg\ L^{-1}$. The first 8 rows of Table 2 detail the experimental plan and the results expressed as a percentage of Acid Brown 425 in the medium at 20 min of photodegradation.

The coefficients of the principal effects and interactions were calculated and are shown in the Pareto chart in Fig. 4a. The significance of the effects was evaluated by analysis of variance (ANOVA) and the vertical line in Fig. 4a corresponds to the value above which the effects are significant for a level of significance $\alpha = 0.05$. The analysis of the effects shows that all of the variables are influential and their effects are positive, which means that the concentration of brown dye at 20 min of degradation is higher if the variable values are higher. The effects of the interactions are not relevant. The positive effect of the initial concentration of red dye and orange dye was expected. On the other hand, the positive effect of H_2O_2 means that at high values of oxidant the degradation is less efficient. This fact does not agree with the results obtained in the previous step which demonstrate that hydrogen peroxide favored the degradation process. An initially surprising explanation of this result is that excess H_2O_2 can generate secondary reactions which interfere in the degradation process [8–10]. This indicates that there is an optimum concentration that maximizes the photooxidation rate of this oxidant when it is used to remove the dyes and that we have been working in a domain outside this optimum zone.

At this point of the study, we decided to extend the experimental domain toward lower values of H_2O_2 , where the H_2O_2 concentration is A: 0.005–0.1 mol L^{-1} . For this purpose a full factorial design

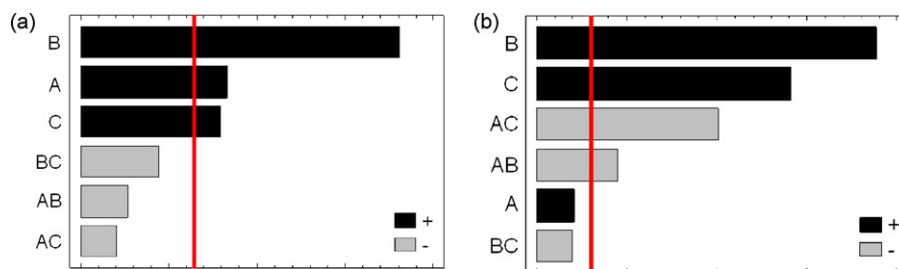


Fig. 4. Pareto charts from the 2^3 experimental designs using the % of Acid Brown 425 at 20 min of degradation as the response. (a) Corresponds to the first design and (b) to the second design. The variables are: A (H_2O_2 concentration), B (Acid Red 97 concentration) and C (Acid Orange 61 concentration).

2^3 was completed for the experiments marked with (a) in Table 2 and for the new experiments represented in the rows 9–12 of the same table.

Fig. 4b shows a Pareto chart containing the values of the variable effects for this second 2^3 design. As in the previous figure, the vertical line shows the value above which the effects are relevant for a significance level of $\alpha=0.05$. In this case the influential variables were the concentrations of red dye and orange dye, and these were as positive as could be expected. The effect of the H_2O_2 concentration was not significant but the interaction of this variable with the other two variables is relevant and negative. This indicates that the concentration of hydrogen peroxide affects the response in different ways depending on the level of the other variables.

3.2.2. Establishment and validation of response surface

The results obtained in the last stage were used to establish a first-order response surface. Once the coefficients of this model had been determined, the curvature test explained in Section 2.4.2 was calculated. The F_{cal} value was 137.42 and the value of $F_{\text{tab}(1,2,0.05,2 \text{ tails})}$ was 38.5, therefore $SS_{\text{pure quadratic}}$ calculated with Eq. (2) and SS_{residual} were not comparable and this means that the response surface was not validated because a quadratic curvature

Table 2

Full factorial and central composite experimental plan.

Exp.	Factors			Response % A. Brown
	H_2O_2	A. Red	A. Orange	
1	0.02	0	0	4.26
2 ^a	0.1	0	0	14.34
3	0.02	60	0	25.73
4 ^a	0.1	60	0	34.93
5	0.02	0	60	15.68
6 ^a	0.1	0	60	26.04
7	0.02	60	60	32.92
8 ^a	0.1	60	60	34.22
CP ^b 1	0.06	30	30	10
CP ^b 2	0.06	30	30	11.5
CP ^b 3	0.06	30	30	12
9	0.005	0	0	3.06
10	0.005	60	0	23.45
11	0.005	0	60	24.96
12	0.005	60	60	50.25
CP ^b 4	0.0525	30	30	19.5
CP ^b 5	0.0525	30	30	18.24
CP ^b 6	0.0525	30	30	17.67
13 ^c	0.005	30	30	29.68
14 ^c	0.1	30	30	23.37
15 ^c	0.0525	0	30	12.89
16 ^c	0.0525	60	30	27.78
17 ^c	0.0525	30	0	13.86
18 ^c	0.0525	30	60	29.37

^a Experiences employed in the second experimental design.

^b CP means central point.

^c Axial points to complete the central composite design.

is present and the model had to be represented by a second-order equation.

In order to fit a second-order model we used a face-centered central composite design in which $\alpha=1$. This design locates the axial points on the centers of the faces of the cube formed in the full factorial design. Table 2 (experiments 13–18) shows the experimental conditions of the axial points added to the full factorial design to complete the central composite.

The response surface obtained is described in the following equation:

$$y = 19.6 + 0.2A + 8.9B + 7.5C + 6.0A^2 - 2.1AB - 4.7AC - 0.2B^2 - 0.9BC + 1.1C^2$$

in which y is the concentration of brown dye at 20 min of degradation and A , B , C correspond to, in codified variables (from -1 to $+1$), the concentration values of H_2O_2 , red dye and orange dye respectively. This equation shows that H_2O_2 presents important coefficients in the quadratic term and in the interactions.

Finally, the model was validated with the experimental points that were used to create the model along with 8 other selected points within the experimental domain in order to cover the whole range of responses. Fig. 5 compares the experimental results with the predicted results for the second-order response surface; (●) corresponds to the points used to elaborate the model and (▲) corresponds to the selected external points. We then applied a joint test of slope 1 and a regression intercept of 0 to the regression between the experimental and predicted responses. The curve obtained ($y=1.004x-0.1599$) was statistically comparable with the ideal curve ($y=x$) and had significance of 5%. This fact proved that the second-order model fits the process studied.

Fig. 6a and b shows the concentration of H_2O_2 , red dye and orange dye on the response surface (i.e. the concentration of brown dye at 20 min of degradation). In Fig. 6a, the concentration of the

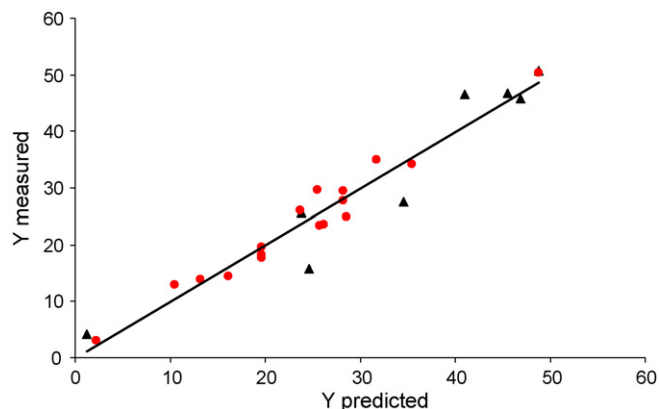


Fig. 5. Comparison of measured results vs. predicted results calculated using the second-order response surface.

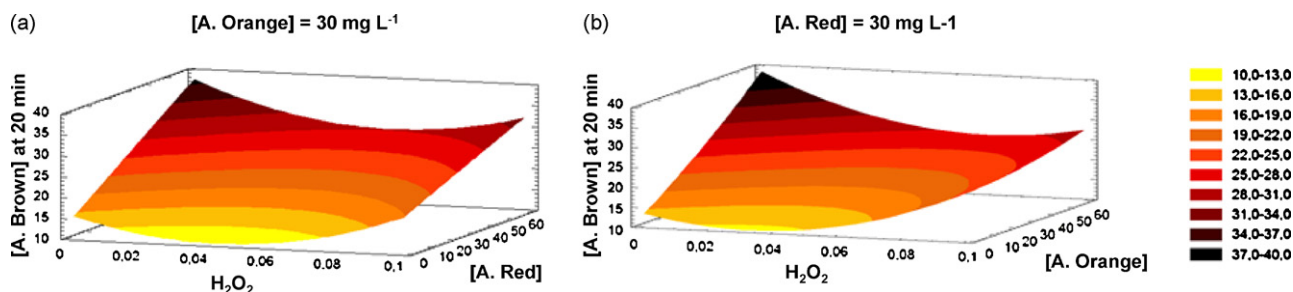


Fig. 6. Second-order response surfaces.

orange dye is fixed at 30 mg L^{-1} whereas in Fig. 6b, the concentration of the red dye is fixed at 30 mg L^{-1} . The model shows that at low values of red or orange dye concentration, it is better to work with low concentrations of H_2O_2 because the concentration of the brown dye increases when there is an excess of this oxidant. It can be also seen that red dye needs a lower concentration of oxidant for degradation than orange dye. These models could be useful for the tanning industry because it is possible to determine the optimum concentration of H_2O_2 for the degradation of a fixed concentration of dyes. This methodology could reduce the time and money needed for the water treatment.

4. Conclusions

Acid Brown 425 is the most persistent dye in all the photodegradation processes. For this reason, its concentration could be related to the degradation time of the other dyes given that the remaining dyes are completely eliminated at low values of brown dye concentration.

Screening showed that the presence of an oxidant, specifically H_2O_2 , has the most important effect on photodegradation. It has been demonstrated that if this compound is added then no catalyst is needed and that the pH does not affect degradation. Using photolysis instead of photocatalysis could be interesting from a practical, economical and environmental point of view because dyes could be degraded without the use of a catalyst.

In the domain studied the concentration of brown dye at 20 min of degradation follows a second-order equation because H_2O_2 has a quadratic influence in the process.

The quadratic function obtained has been validated by experimenting with different points of the domain. Furthermore, this methodology could be used in the textile industry to reduce the cost and time of degradation because, if the concentrations of dyes in textile effluent are known, the optimum amount of H_2O_2 could be calculated in order to eliminate the dyes in little more than 20 min.

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