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Study of the influential factors in the simultaneous photocatalytic degradation process of three textile dyes

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ABSTRACT

The influence of several factors in the simultaneous photocatalytic degradation of three textile dyes – Acid Red 97, Acid Orange 61 and Acid Brown 425 – has been studied using a fractional factorial design 2^{5-1}. The considered factors were: the initial concentration of each dye, the catalyst concentration (TiO_2) and pH.

First, we developed a rapid analytical methodology based on recording UV–visible spectra during the degradation process and a data treatment using multivariate curve resolution with alternating least squares (MCR-ALS), which enabled the three dyes to be quantified simultaneously despite the overlap of their spectra.

The kinetic constant of degradation for each dye in all the experiments was evaluated. In all cases the degradation followed a first order kinetics. For a significance level of 5%, the most important factor in the photodegradation of each dye is the concentration of Acid Red 97, the degradation is more effective at higher pHs and, in the studied range, the concentration of the catalyst is not important.

1. Introduction

Dyes are organic compounds that can be dangerous to the environment. The tanning industry uses a wide spectrum of dyes to impart colour to the leather matrix. About 10–15% of these dyes are released in effluents during dyeing processes [1]. The discharge of coloured waste is highly problematic, firstly due to the toxic nature of some dyes or of their biodegradation products and secondly due to their visual impact because dyes are visible even at low concentrations.

Dyes in wastewater can be treated by many different processes: coagulation [2], foam flotation [3], electrochemical oxidation [4], Fenton or photo-Fenton oxidation [5,6], adsorption in waste materials [7], membranes [8], adsorption using activated carbon [9], combined coagulation/carbon adsorption [10], etc. Most of these methods are non-destructive but they generate secondary pollution, because the dyes are transferred to another phase and this phase has to be regenerated. One way to eliminate dyes without generating secondary toxic waste is photodegradation [11–15]. In this process the dyes decompose mainly to CO_2, H_2O, and some intermediates, commonly low molecular weight acids.

In this paper we study the photocatalytic degradation process of three dyes, widely used in textile industries: Acid Red 97, Acid Orange 61 and Acid Brown 425.

In dye photodegradation studies, the dyes are usually quantified with univariate calibration, which records absorbance at one wavelength of the UV–visible spectra [11–13], or with the total carbon content determination (TOC) [14,15] during the degradation. This information only gives information about the behaviour of one species and if there is more than one dye or an interferent in the reaction medium, or if a byproduct is generated during the photodegradation, there is a risk of obtaining erroneous results.

We propose here to make a simultaneous catalytic degradation study of these dyes and evaluate the kinetic order and the corresponding degradation constants for each dye.

We first established a rapid analytical methodology, which recorded UV–visible spectra during the photodegradation process, and a data treatment using multivariate curve resolution-alternating least squares method (MCR-ALS) which allows quantification of analytes in the presence of interfering [16]. These methodologies have been applied successfully by our research group to the resolution of mixtures from data obtained using other instrumental configurations [17,18].

Subsequently, because the optimization of experimental conditions is a subject of interest in photocatalytic processes, we aimed to determine the effect of several factors on the degradation rate so that we could propose the most convenient experimental conditions for carrying out the degradation.

The effect of each variable on the reaction kinetics may not be independent, but research articles that have been published in the field of catalysis usually analyse the influent factors by varying one factor at time [13,14]. This methodology often gives limited

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information about the process. In the last years, can be found some papers [19–21] where the effect of some factor in the photocatalytic degradation of some dye using the response surfaces methodology is analyzed, but in all situations only one dye is considered.

In our case, in order to understand how several factors affected the response we used a fractional factorial design $2^{5\text{-}1}$. The factors considered are: the initial concentration of each dye, the amount of catalyst (TiO_2) and the pH. A simultaneous and exhaustive analysis of all factors (as the background matrix, temperature, etc.) that could affect the feasibility of a photodegradation process of several dyes would be an excessively extensive work. The consideration of initial concentrations of each dye as a factor makes it possible to determine whether there is any competition between dyes during the photodegradation process and if the priority of degradation is conserved in any of the conditions studied. Different dyes do not have the same visual impact, which should be taken into account when fixing the optimal conditions for their degradation from a practical point of view. The present work is focussed in show a useful strategy to analyze quickly the effect of several influential factors in a complex problem as the photodegradation of several dyes.

The responses studied are the half-life time of each dye. The significance of the effects was corroborated using an ANOVA test.

2. Experimental

2.1. Chemicals

In all analyses, we used analytical grade chemicals. These were NaOH and H_2SO_4 from PROLABO and purified water from a Milli-Q water system from MILLIPORE, USA. The anatase form of TiO_2 (99.8%) (Sigma–Aldrich) was used as the photocatalyst without further treatment.

Acid Red 97, Acid Brown 425 and Acid Orange 61 dyes were obtained from Trumpler Española, S.A. (Barberà del Vallès, Barcelona, España). These compounds have acid–base characteristics, acid species and basic species have different UV–visible spectra. The acidic and basic spectra are strongly overlapped [17]. Table 1 shows same physicochemical proprieties of these dyes.

Standard buffer solutions of pH 4 and 7 (Hamilton) were used to calibrate the pH meter.

2.2. Instrumental and software

The photodegradation studies were carried out in a cylindrical annular batch reactor. The reactor consists of an immersion quartz tube (2.5 cm i.d., and 38 cm long) which holds a low pressure mercury vapour lamp (LPML) of 15 W (Heraeus Noblelight, Germany) The light source emitted by the LPML is predominantly at 254 nm and the incident photon flux of the UV reactor is 0.1 W cm^{-1}. The quartz tube was placed in a Pyrex glass outer reactor (0.7 L capacity) in dark conditions.

The data were acquired and monitored by a Hewlett-Packard 8452A spectrophotometer using the 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.

Calculations for multivariate curve resolution with alternating least squares (MCR-ALS) were performed with laboratory-written software under a MATLAB 7.0 computer environment [22]. This software is available in Ref. [23]. Calculations for experimental design were performed with STATGRAPHICS Plus 5.0 [24].

2.3. Standards

Individual standards of 100 mg L^{-1} for Acid Orange 61 and Acid Brown 425 and of 50 mg L^{-1} for Acid Red 97 at pH 6 in ultrapure Milli-Q water were prepared. The reference spectrum for each dye was recorded with their standard.

Using the referenced standards a total of 13 samples (see Table 2), were prepared in aqueous solution, in order to evaluate the ability of the model MCR-ALS to resolve and quantify these analytes.

2.4. Photocatalytic experiments

A total of 16 photodegradation experiments were carried out. The experimental conditions of each experiment were designing according to a $2^{5\text{-}1}$ fractional factorial experimental design. The first six columns in Table 3 show the experimental plan. The chosen factors and their high and low levels were: 20–60 mg L^{-1} for the initial concentration of Acid Red 97, Acid Orange 61 and Acid Brown 425 (code-named A, B, C, respectively), 8–24 mg/500 ml for the amount of catalyst (TiO_2) (code-name, D) and 2–6 for the pH (code-name E). In addition, in order to evaluate the experimental error, there was

Table 1

Structure, name, chemical index and colour $pK_{a,\,max}$ and molecular weight of the dyes.

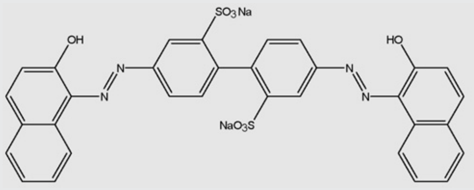
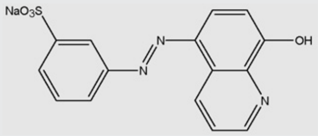
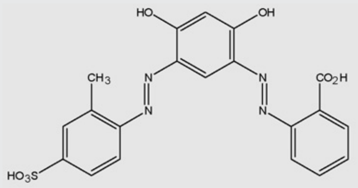
Structure	Name	Colour	pK_a	λ_{max}	MW
	Acid Red 97	Bright yellowish red	11–12	498	698
	Acid Orange 61	Orange	2–3	446	351
	Acid Brown 425	Dull reddish brown	10–11	445	456

Table 2
Concentration of the calibration standards ($mg L^{-1}$).

Standard number	Dye		
	A. Red 97	A. Orange 61	A. Brown 425
1	5	5	10
2	10	10	5
3	15	20	15
4	30	15	20
5	20	25	25
6	25	30	30
7	5	5	20
8	15	5	5
9	5	20	5
10	30	30	30
11	25	35	25
12	25	40	25
13	20	45	20

prepared a triplicate sample in the experimental conditions corresponding to the central point of the experimental domain of each factor (the three last rows in the Table 3). The responses evaluated were the degradation constants of each dye and the experimental half-life time of each dye.

The degradations were carried out in a cylindrical reactor, such as the one described in Section 2.2. The total volume of the solution was 500 ml. The pH was adjusted using H_2SO_4 and NaOH solutions. The reactions were carried out at room temperature with continuous stirring, until the solution lost its colour. Six-millilitre samples were taken through the reactor using a syringe. In the first 10 min samples were taken every minute, then every 2 min (to 20 min), every 5 min (to 60 min), every 10 min (to 220 min), and every 20 min (to the end of degradation). The total volume of extracted sample varies between 180 and 240 mL, depending on the photodegradation rate in each experience. The samples were stored in dark conditions until they were centrifuged in order to separate the catalyst and record the spectra.

2.5. Establishment of the calibration model

The aim of the multivariate curve resolution method with alternating least squares is to transform the theoretical solution obtained by factor analysis of the experimental data matrix **D** and obtain matrices **C** and $\mathbf{S^T}$ which have real chemical significance [16,25].

With this resolution method, the data matrices are modelled using Eq. (1):

$$\mathbf{D} = \mathbf{C} \cdot \mathbf{S^T} + \mathbf{E} \qquad (1)$$

where **D** is the data matrix of the spectra acquired during the photodegradation process at different times, matrix **C** ($m \times p$) has column vectors corresponding to the concentration profiles of the p pure components that are present in matrix **D**. The row vectors of matrix $\mathbf{S^T}$ ($p \times n$) correspond to the spectra of the p pure components, and **E** is the matrix of the residuals. The times and the wavelengths at which the absorbance is recorded are m and n, respectively.

The resolution was performed using the strategy of augmented matrices [16]. An augmented matrix $\mathbf{D_{aug}}$ was constructed appending in the direction of column wise, a matrix $\mathbf{D_1}$ that contains the spectra of the 13 standards, a matrix $\mathbf{D_2}$ that contains the spectra recorded during the photodegradation process considered and the vectors $\mathbf{v_i}$ corresponding to the spectra of each present species in the solution.

The chemical rank of the $\mathbf{D_{aug}}$ was estimated analysing the value of eigenvalues obtained by singular value decomposition (SVD) [26].

The optimization step of MCR-ALS was initiated using the spectra of the individual components $\mathbf{S^T}$. We applied non-negativity constraints to the data matrices. To determine the efficiency of the model we used the lack of fit (lof) and correlation coefficients (r) between the spectra used as references and those retrieved by MCR-ALS.

After the application of the curve resolution methodology, with the concentration profiles of the standards, a calibration curve of pseudo-zero order was built, as in the univariate calibration approach [27].

$$r_i = b_1 \cdot C_i + b_0 \qquad (2)$$

where r_i is the relative value obtained by estimating the concentration in the resolution process (the quotient between the value of each standard relative to the most concentrated analyte) and c_i is

Table 3
Experimental plan and kinetic constants of the dyes in each experiment.

Experimental plan						Responses					
Exp	A	B	C	D	E	A. Red 97		A. Orange 61		A. Brown 425	
						$k \times 10^{-2}$	r	$k \times 10^{-2}$	r	$k \times 10^{-2}$	r
1	20	20	20	8	6	4.44	0.9976	3.04	0.9934	0.85	0.9426
2	60	20	20	8	2	2.41	0.9918	1.17	0.9549	1.15	0.9661
3	20	60	20	8	2	4.47	0.9938	1.83	0.9629	3.44	0.9790
4	60	60	20	8	6	1.39	0.9921	0.83	0.9804	0.44	0.9723
5	20	20	60	8	2	3.19	0.9989	3.38	0.9643	1.37	0.9817
6	60	20	60	8	6	1.49	0.9954	0.83	0.9529	0.50	0.9979
7	20	60	60	8	6	2.27	0.9950	1.57	0.9855	0.76	0.9811
8	60	60	60	8	2	1.89	0.9994	0.53	0.9277	0.99	0.9910
9	20	20	20	24	2	4.23	0.9964	1.55	0.9551	2.44	0.9811
10	60	20	20	24	6	2.06	0.9932	2.92	0.9461	0.57	0.8970
11	20	60	20	24	6	3.48	0.9984	1.95	0.9872	0.72	0.9545
12	60	60	20	24	2	1.50	0.9983	0.95	0.9356	0.08	0.9709
13	20	20	60	24	6	2.72	0.9966	2.96	0.9429	1.24	0.9493
14	60	20	60	24	2	1.70	0.9979	1.25	0.9367	0.68	0.9280
15	20	60	60	24	2	3.26	0.9982	2.11	0.9887	0.91	0.9776
16	60	60	60	24	6	0.98	0.9952	0.59	0.9901	0.33	0.9637
CP[a] 1	40	40	40	16	4	1.18	0.9951	0.89	0.9898	0.32	0.9459
CP[a] 2	40	40	40	16	4	1.33	0.9972	0.77	0.9441	0.39	0.9362
CP[a] 3	40	40	40	16	4	1.34	0.9977	0.78	0.9855	0.41	0.9761

[a] CP: central point.

Table 4
Figures of merit for the calibrations of the three dyes Acid Red 97, Acid Orange 61 and Acid Brown 425.

	Dye		
	A. Red 97	A. Orange 61	A. Brown 425
b_1	1.0126	1.0112	0.9910
b_0	0.0098	−0.0071	0.0067
r	0.9987	0.9982	0.9969
n	13	13	13
F_{cal}	1.98	0.58	0.91
F_{critic} (0.05, 2, 11)	5.26		

the correspondent relative concentration. The calibration line was validated by comparing the line obtained with the line of identity (regression slope = 1, regression intercept = 0) [26].

With the concentration values obtained during each experiment a first order kinetic model was proposed using the following equation:

$$\ln \frac{C_0}{C_i} = kt \qquad (3)$$

where C_0 and C_i are the concentrations at time zero and time t, respectively.

3. Results

In order to prove the resolution possibilities of the proposed methodology, MCR-ALS was first applied to the augmented matrix $[\mathbf{D_1};\mathbf{v_1};\mathbf{v_2};\mathbf{v_3}]$, where $\mathbf{v_1}$, $\mathbf{v_2}$ and $\mathbf{v_3}$ are the spectra for Acid Orange 61, Acid Red 97 and Acid Brown 425, respectively. After the resolution, two matrices were obtained: a matrix **C**, with the calculated values of the 13 calibration standards, and a matrix **S**, containing the spectra of each standard. The spectral correlation was higher than 0.9990 for the three dyes. Using the values of matrix **C**, a calibration line was established by applying Eq. (2). Table 4 shows the values obtained for the slopes and regression intercepts of the regression lines, the correlation coefficient and the F value calculated in the joint test of slope 1 and regression intercept 0. All the regression lines passed the test, so the methodology was considered valid for quantifying these three dyes simultaneously.

As an example, Fig. 1 shows the graphic to data matrix ($\mathbf{D_2}$) for the first experiment of the design. When SVD was applied to the data matrices augmented for each of the 16 degradation experiments, 4 significant components were obtained in all cases. This may be because of the presence of a degradation compound of these dyes.

Fig. 2 shows for the first experiment, the spectral and concentration profiles for the three dyes and the fourth component obtained by MCR-ALS. To improve the resolution, we have added a vector corresponding to the last degradation time at which this fourth component was predominant over the dyes studied. The figures of merit of this method for the 16 experiments were satisfactory: lof had a mean value of 1.2656, and the similarities between the spectra profiles obtained for each component and the pure spectra of each dye were evaluated by the correlation coefficient and shown to be higher than 0.9990 in all cases. Fig. 3 shows the degradation curves for each dye for the 16th experiment of the experimental design, which was the slowest one.

Assuming that in the experimental conditions the photodegradation reactions fitted to a kinetic of pseudo-first-order, the concentrations values obtained by MCR-ALS were used to calculate, using Eq. (3), a constant k representative of kinetic of each dye in each experiment. These values and the correlation coefficient of the model adjustment for each dye and experiment are shown in the last six columns in Table 3. The correlation coefficients are close to 1 so we can conclude that the photodegradations in all the conditions studied follow a pseudo-first-order kinetic. The values obtained for the degradation constants are of the same order of magnitude as the degradation constants obtained for Methyl Orange and Rhodamine 6G [13] and for a six-dye mixture from a textile effluent [11].

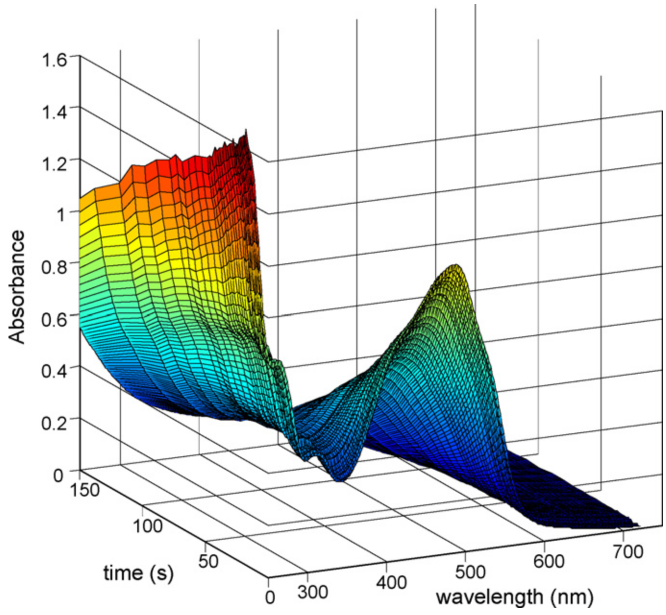


Fig. 1. Spectra recorded during the photodegradation process ($\mathbf{D_2}$) for the first experiment in Table 3.

It was observed that the red dye always degraded faster than the others, and that the orange dye tended to degrade faster than the brown dye, although this was not the case in all the experi-

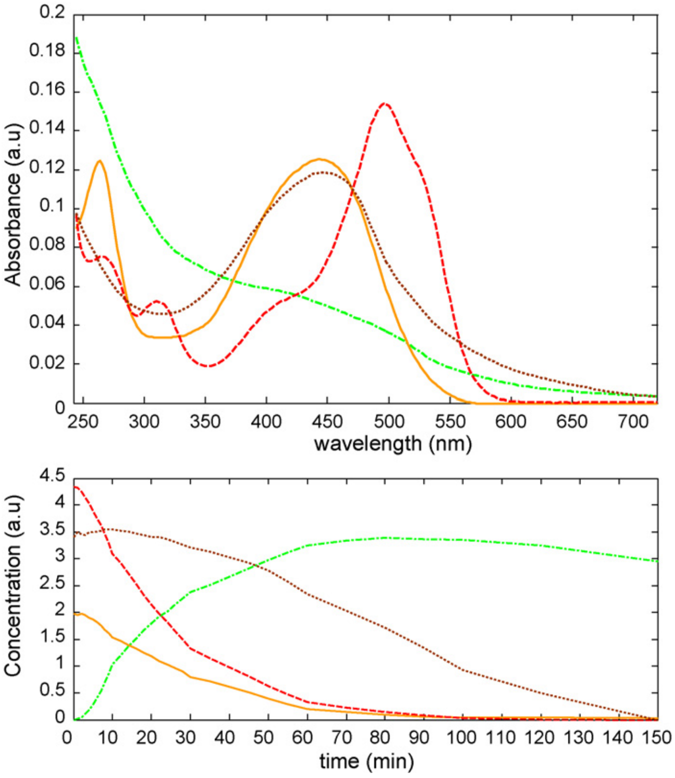


Fig. 2. Spectra and concentration profiles recovered by multivariate curve resolution of the data matrix arising from the first experiment in Table 3. (- - -) corresponds to Acid Red 97, (–) to Acid Orange 61, (···) to Acid Brown 425 and (-·-·-·) to the new compound formed during the photodegradation.

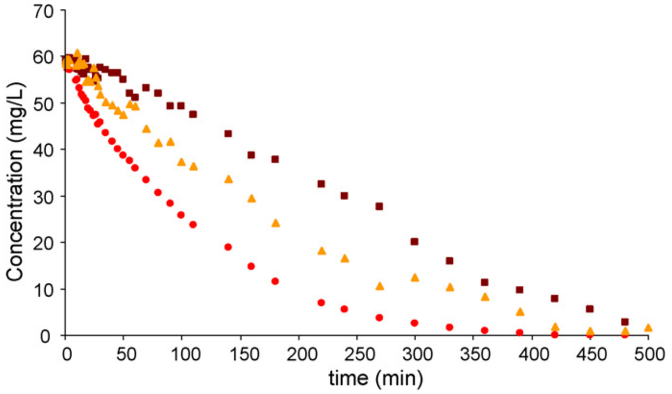


Fig. 3. Kinetic profiles for the 16th experiment in Table 3. (●) Acid Red 97, (▲) Acid Orange 61 and (■) Acid Brown 425.

ments. Some possible explanations for this behaviour are: (a) the degree and the rate of the photocatalytic degradation of each dye would be higher for the dye with higher molar absorption coefficient that is the Acid Red. (b) The catalyst at the working pH is charged positively (pH 2) or neutral (pH 6), so the dye with the greatest tendency to be charged negatively (red dye), has the greatest affinity in the adsorption process. Studies carried out with dyes of similar characteristics [28–30] reinforce this hypothesis. (c) Another aspect to consider in the ease of degradation is the number of azo groups present in the molecule. Azo bonds are the most active bonds in azo-dye molecules and can been oxidized by positive hole or hydroxyl radicals or reduced by electrons in the conduction band [31]. These tendencies have been reported in several studies on azo-dyes [32,33]. The orange dye, then, would be the most favourably degraded, although the results obtained showed that some mechanisms have a competitive influence on the degradation.

In order to evaluate the effect of the factors considered on the degradation kinetics, we decided to study the half-life time obtained experimentally because this response takes into account the induction period of the catalyst (that is, the time during which the catalyst adsorbs the dyes before the degradation process starts.

Table 5
Results of ANOVA test for the relevant factors.

Dye	Effect	d.f.	$\text{SS} \times 10^{+3}$	$\text{MS} \times 10^{+3}$	F_{cal}
A. Red 97	A	1	3.192	3.192	48.861
A. Orange 61	A	1	6.765	6.765	241.609
	B	1	1.660	1.660	59.306
	E	1	4.455	4.455	159.127
	CE	1	2.376	2.376	84.877
A. Brown 425	A	1	13.225	13.225	106.653
	E	1	9.801	9.801	79.040
F_{critic} (1, 2, 0, 05)	38.5				

Fig. 4 shows the Pareto chart obtained for each dye. It can be observed that most of the effects of the factors considered are positive. To evaluate the importance of these effects, we used an ANOVA test [27]. Table 5 shows the values of the relevant factors for the significance level considered.

The commented results can indicate that: (a) the concentration of red dye has an important effect on the behaviour of the three dyes. As has been mentioned above, this dye has a great tendency to be adsorbed on the catalyst, which blocks the surface of the catalyst to a greater or lesser extent (depending on the concentration) thus affecting the behaviour of other species. (b) The concentration of catalyst is not a relevant factor in the degradation of any dye. Since is known that when the catalyst loading increases the adsorption and degradation also increase, one possible interpretation of the obtained results is that our range of catalyst concentrations was too small to detect its influence and as a consequence small changes in its concentration do not affect the degradation process.

The other factors influence the degradation of each dye in a different way. The red dye degradation was not affected by the concentration of the other two dyes. This may be because this dye degrades very easily and because the other two dyes do not compete in the degradation process. Although the ANOVA test shows

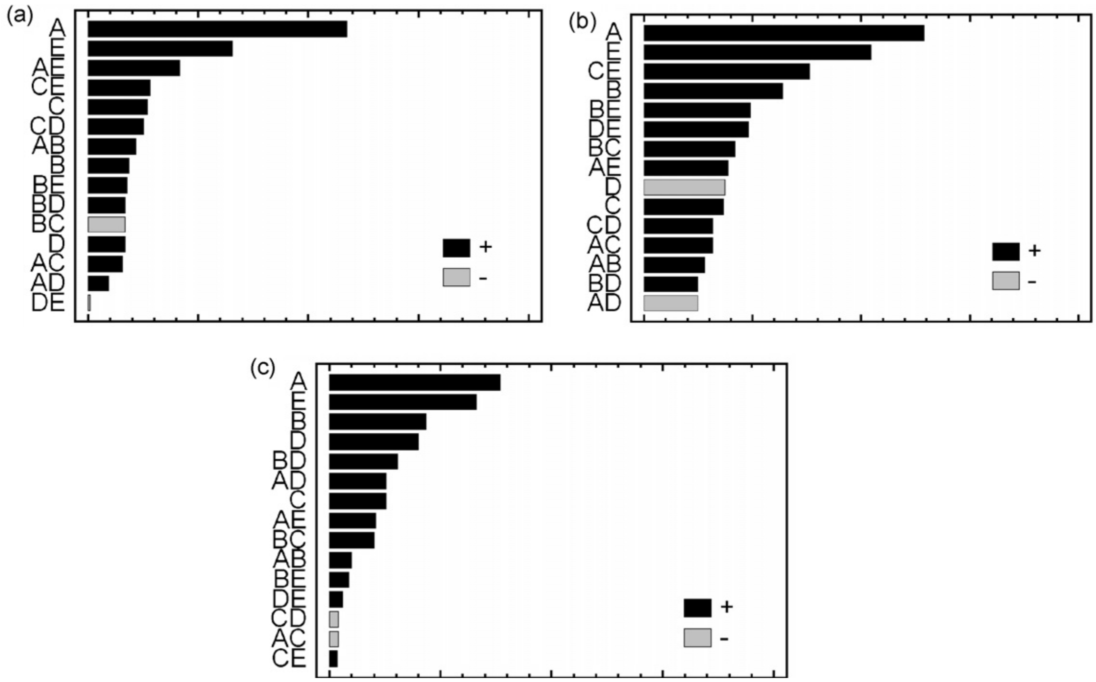


Fig. 4. Pareto charts from the fractional factorial design considering the $t_{1/2}$ of each dye as response. (a) Corresponds to Acid Red 97, (b) to Acid Orange 61 and (c) to Acid Brown 425.

that pH is not an influential factor for the level of significance considered, the Pareto chart for this dye (Fig. 4(a)) shows that the pH and its interaction with the red dye concentration are the following influential factors in the degradation. This result can indicate that a higher pHs higher degradation periods have been obtained, probably because the catalyst reduces their positive charge and this fact difficult the adsorption process of the dye.

As well as the red dye concentration mentioned above, the factors that affect orange dye degradation are the pH, the concentration of orange dye and the interaction between the pH and the brown dye concentration. The reasons why pH has an influence may be the same as those for the red dye. The influence of the initial concentration is as expected. The interaction between the pH and the brown dye concentration is important because the concentration is indirectly influenced by the pH of the solution. This influence is strong at high pH because the two dyes start to compete in the adsorption process on the catalyst.

The brown dye is affected bye the red dye concentration and the pH, which have the same effect as the cases above. The Pareto chart (Fig. 4(c)) shows that the next most influential factors are the catalyst concentration and the orange dye concentration. It should be pointed out that its own concentration does not affect its degradation. To explain this result, which at first sight is surprising, we must take into account that the considered response is the half-life time and that the three dyes compete in a degradation process in which the brown dye is the least favoured. Probably if longer times of degradation are considered, in which the other dyes have had time to disappear from the medium, the concentration of brown dye may be important for its own degradation.

4. Conclusions

Using spectrophotometric measurements in the UV–visible region during the degradation process and the curve resolution method MCR-ALS, a rapid methodology can be established for simultaneously quantifying three dyes – Acid Red 97, Acid Orange 61 and Acid Brown 425 – despite the presence of unknown interferents.

Photodegradation using TiO_2 as catalyst is efficient at removing the three acid dyes from wastewater. The kinetics of these degradations follows a first-order model and a new compound, probably of low molecular weight, appears.

Experimental design methodology allows to determine the influence of the factors considered on the half-life time of the dyes and shows that the most important factor in photodegradation is the initial concentration of Acid Red 97, that the amount of catalyst does not affect the response in the studied region for a significance level of 5%, that photocatalysis is more effective at pH 6 and that the photodegradation process is competitive because the adsorption of the dyes in the catalyst depends on their concentration in the solution.

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