



## Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design

Carmen S.D. Rodrigues<sup>a</sup>, Luis M. Madeira<sup>b</sup>, Rui A.R. Boaventura<sup>a,\*</sup>

<sup>a</sup> LSRE – Laboratory of Separation and Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering at Porto University, R. Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

<sup>b</sup> LEPAE – Laboratory for Process, Environmental and Energy Engineering, Department of Chemical Engineering, Faculty of Engineering at Porto University, R. Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

### ARTICLE INFO

#### Article history:

Received 19 June 2008

Received in revised form 27 August 2008

Accepted 28 August 2008

Available online 10 September 2008

#### Keywords:

Advanced chemical oxidation

Fenton's reagent

Dye

Procion Red H-EXL

Central composite design

### ABSTRACT

Chemical oxidation by Fenton's reagent of a reactive azo dye (Procion Deep Red H-EXL gran) solution has been optimized making use of the experimental design methodology. The variables considered for the oxidative process optimization were the temperature and the initial concentrations of hydrogen peroxide and ferrous ion, for a dye concentration of 100 mg/L at pH 3.5, the latter being fixed after some preliminary runs. Experiments were carried out according to a central composite design approach. The methodology employed allowed to evaluate and identify the effects and interactions of the considered variables with statistical meaning in the process response, i.e., in the total organic carbon (TOC) reduction after 120 min of reaction. A quadratic model with good adherence to the experimental data in the domain analysed was developed, which was used to plot the response surface curves and to perform process optimization. It was concluded that temperature and ferrous ion concentration are the only variables that affect TOC removal, and due to the cross-interactions, the effect of each variable depends on the value of the other one, thus affecting positively or negatively the process response.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

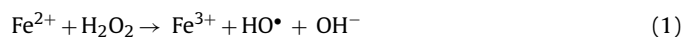
Dyes used in the textile industries can originate colour in the water courses that receive the discharges of their liquid effluents, generating important environmental impacts, among which it must be pointed out the decrease of the solar light penetration (thus reducing the primary productivity). The degradation of the water aesthetic aspect is also of concern, as well as the impacts in all living organisms, because some dyes are often carcinogenic and toxic for most species [1].

Azo dyes, commonly used in dye-houses, contain in their structure at least one azo group (–N=N–) linked to at least one aromatic ring. These dyes are non-biodegradable under aerobic conditions, and therefore the discharge of azo dyes-containing wastewaters can cause several problems to the aquatic life [2].

The conventional treatment techniques applied to textile wastewaters, such as coagulation/flocculation, membrane separation and adsorptive processes (for instance using activated carbon), simply concentrate and transfer the pollutant(s) from one phase to

another, remaining their degradation one problem to be solved. The biological treatment is not a solution to this problematic due to the low biodegradability or toxicity of some dyes. For these reasons, recent efforts have been directed towards the development of destructive treatment technologies, leading to the partial or total elimination of recalcitrant and dangerous pollutants. In this sense, the advanced (chemical) oxidation processes (AOPs), based on the generation of highly reactive hydroxyl radicals, appear as emerging alternatives for the mineralization of organic pollutants [3]. Among them, oxidation with Fenton's reagent has been considered to be a promising and attractive treatment technology for the discolouration and effective degradation of textile dyes [4–7]. In addition, it has been applied to a wide range of organic pollutants, because of its simplicity and ease of implementation, running under mild conditions of temperature and pressure [8].

Oxidation with Fenton's reagent can be described as a catalytic and homogeneous process (although it can also be developed heterogeneously) that is based on the hydrogen peroxide decomposition in acid medium, catalyzed by ferrous ion. The process is rather complex, with numerous parallel and consecutive reactions, but can be shortly represented by the following and dominant one [9]:



\* Corresponding author. Tel.: +351 22 5081683; fax: +351 22 5081449.

E-mail addresses: [carmen.deus@gmail.com](mailto:carmen.deus@gmail.com) (C.S.D. Rodrigues), [mmadeira@fe.up.pt](mailto:mmadeira@fe.up.pt) (L.M. Madeira), [bventura@fe.up.pt](mailto:bventura@fe.up.pt) (R.A.R. Boaventura).

The oxidation efficiency of the Fenton's process depends on several variables, namely the pH of the reaction medium, the temperature, the time of reaction (for a batch system), the hydrogen peroxide concentration and the amount of catalyst used, for a given wastewater or parent compound concentration. In most studies reported in the literature the effect of each variable is studied independently, while keeping the others constant. However, this approach is time-consuming and not efficient because this way interactions between variables and their effects in the process responses are not determined. The design of experiments (DoE) is a statistically based approach that allows overcoming this limitation. Actually, it permits to determine the influence of the independent variables (and of their cross-interactions) in a specific dependent variable (process response) by carrying out a reduced number of experiments [10].

Several studies can be found in the open literature focused on the use of DoE methodologies applied to Fenton's process for wastewater treatment. Among them, one can refer, for instance, the degradation of dyes [5,11] and of phenol and its derivatives [12–14], as well as the treatment of landfill leachates [15] and other industrial effluents [16]. Among other advantages, this methodology allows also process optimization, with a reduced effort on experimentation.

In this work, the Fenton's process has been used to study the oxidation of a reactive azo dye widely used in the Portuguese cotton dyeing industry: Procion Deep Red H-EXL gran. In such industry, huge amounts of reactive dyes are used in the dyeing stage. However, because the dyes are not completely retained by the fibres, they are present in the final effluents. Some studies were found in the literature for Procion dyes degradation; this is the case of the reactive Procion Red H-E7B, by combination of a photo-Fenton process and a biological sequential batch reactor [17], and of Procion Black 5B, by electrochemical processes at pilot scale [18]. It is also worth mentioning the discolouration of Procion Red MX-5B by electrocoagulation, UV/titanium dioxide and ozone [19], of some Procion H-EXL dyes by different AOPs [20] or the degradation of the azo dye Procion MX-5B by photo-catalytic oxidation with TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> [21]. However, and up to our knowledge, no studies have been performed dealing with oxidation of the dye studied in this work. For process optimization, a DoE methodology was employed.

## 2. Experimental design

The main objective of the experimental design (or DoE) is to determine, with a minimum effort (i.e., with a reduced number of experiments), the effects of the different factors and of their interactions in the process response(s), within the range of the studied variables. Besides, the information obtained allows to decide how many and which factors and/or interactions are statistically significant, and if it is or not necessary to consider a more complex model to describe conveniently the phenomenon under study. For that, statistical techniques (e.g. analysis of variance (ANOVA)) need to be used [22].

In the experimental design, the Yates' algorithm was firstly adopted [22]. Basically this provides a table with a standard disposition of the runs to perform in the factorial design. In the 2<sup>3</sup>-type factorial design adopted (two levels, three variables), the obtained set of experiments is shown in Table 1. The negative and positive signs refer to levels -1 and +1, respectively, of the experimental plan at two levels, being -1/+1 the minimum/maximum value for each coded variable in the studied domain. The methodology used requires that experiments outside the cubic domain are performed to allow a better fitting of the response functions in such a range; the conditions of those runs are defined in Table 1 as

**Table 1**

Yates' algorithm, illustrating the experiments to perform and the conditions (in terms of coded variables).

Run no.	Levels		
	$x_1$	$x_2$	$x_3$
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9	0	0	0
10	0	0	0
11	0	0	0
E1	-1.682	0	0
E2	+1.682	0	0
E3	0	-1.682	0
E4	0	+1.682	0
E5	0	0	-1.682
E6	0	0	+1.682

$\pm 1.682$  (extreme levels of the expansion). Finally, central points are denoted as 0. Among the 17 runs to perform (see Table 1), 8 correspond to the factorial design, 6 to the expansions (nos. E1–E6) and 3 were performed in the centre of the cubic domain to check the reproducibility and evaluate the errors (nos. 9–11).

For the statistical calculations, the natural variables (denoted as  $X_i$ ) are converted into dimensionless codified values ( $x_i$ ) to allow comparison of factors of different natures with different units and to decrease the error in the polynomial fit [10]. This is done using the following relationship:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad (2)$$

where  $X_0$  refers to the value of variable  $i$  in the centre of the domain (i.e., it corresponds to  $x_i = 0$ ) and  $\Delta X$  corresponds to the difference of that variable between the maximum level and the centre of the domain (variation of the coded variable equal to +1).

The experimental results obtained for the considered response(s) or objective function(s),  $Y_i$ , are then fitted to a quadratic model (Eq. (3)) that takes into account the linear and the quadratic effects of the  $n$  variables, as well as the interactions among them. Such least-squares fitting was performed using the commercial software JMP 5.0.1.

$$Y_i = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{j>i}^n \sum_{i=1}^n \beta_{ij} x_i x_j \quad (3)$$

In Eq. (3),  $x_i$  refers to the coded variable associated to parameter  $i$  (in this study it varies between 1 and 3, for temperature, hydrogen peroxide concentration and ferrous ion concentration, respectively, as described below);  $\beta_0$  is the interception term and corresponds to the response value when  $x_i$  is null for all variables;  $\beta_i$  determines the influence of parameter  $i$  in the response (linear term);  $\beta_{ii}$  is a parameter that determines the shape of the curve (quadratic effect); and finally  $\beta_{ij}$  refers to the effect of the interaction among variables  $i$  and  $j$ . The least-squares regression analysis provided the estimates of these coefficients in the second-order model.

The statistical analysis proceeds with an ANOVA, which evaluates the adequacy of the model fitting. ANOVA subdivides the total variance in two components: the variance associated with the model and the one associated with the experimental error [23]. If the value associated with the model is large when compared with that of the experimental error, one can conclude that the changes in the responses can be attributed to the model only and are not due

to random errors. Such comparison is given by the *F*-ratio, which is computed using the following equations [23]:

$$F\text{-ratio} = \frac{MS_{\text{model}}}{MS_{\text{error}}} \quad (4)$$

$$MS_{\text{model}} = \frac{SS_{\text{model}}}{df_{\text{model}}} \quad (5)$$

$$MS_{\text{error}} = \frac{SS_{\text{error}}}{df_{\text{error}}} \quad (6)$$

In the above equations,  $df_{\text{model}}$  and  $df_{\text{error}}$  stand for the degrees of freedom of the model and of the experimental error, respectively;  $SS_{\text{model}}$  represents the sum of square residues from the fitting of Eq. (3) to the experimental data, while  $SS_{\text{error}}$  represents the sum of square residues of the error, calculated with the following equation [22]:

$$SS_{\text{error}} = \sum_i (Y_i - Y_{i,\text{mod}})^2 \quad (7)$$

where  $Y_i$  is the response for run  $i$  and  $Y_{i,\text{mod}}$  is the response obtained with the model for run  $i$ .

To evaluate if the variance of the model is higher than that of the experimental error, the *F*-ratio (Eq. (4)) has to be higher than the *F*-value, which depends on the number of degrees of freedom and the confidence level, commonly 95%.

Nevertheless, other statistical criteria were also adopted to evaluate the adequacy of the model fitting. For instance, the *F*-probability ( $P > F$ ) indicates the probability of the results variation be due to random errors [10]. Finally, the  $R^2$  value estimates the proportion of the response variation around the mean that can be attributed to terms in the model rather than to random error.

To determine which of the parameters and/or interactions in Eq. (3) have statistical meaning, the Student's *t*-test was used. Therefore, the corresponding *t*-probability value was compared with the significance level of 0.05. If the *t*-probability is smaller than that value, then the respective parameter or interaction has statistical meaning and should be included in the model [23].

### 3. Experimental

#### 3.1. Materials

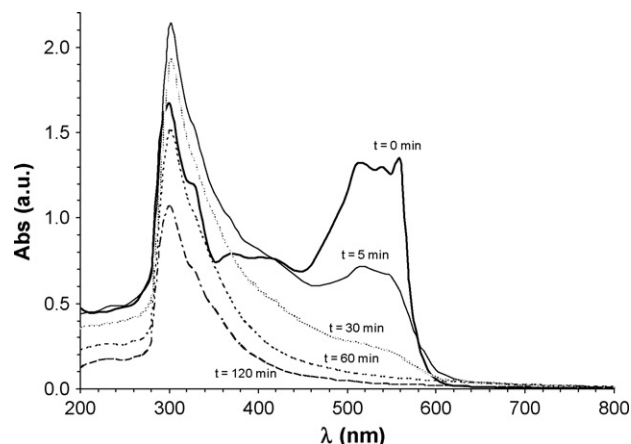
In this study, a commercial reactive azo dye (Procion Deep Red H-EXL gran), from DyStar, was used. The dye solutions used in the experiments (100 mg/L) were prepared by dissolving the required amount of dye in distilled water.

Reagents employed in the oxidation process were  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Panreac) and  $\text{H}_2\text{O}_2$  (30 wt.%, from Riedel-de Haën). The pH in the reaction mixture was adjusted to the desired value using  $\text{H}_2\text{SO}_4$  (95–97%, Fluka) or a 6 M solution of NaOH (prepared with NaOH from Merck). To stop the reaction in samples taken along time, residual  $\text{H}_2\text{O}_2$  reduction by  $\text{Na}_2\text{SO}_3$  (Merck) was performed.

#### 3.2. Analytical methods

To evaluate the dye (colour) removal along the oxidative process, absorbance was measured at the maximum wavelength ( $\lambda_{\text{max}}$ ) in the visible region (coefficient of variation (CV)=0.1%) using a UV–vis spectrophotometer (Thermo Electron Corporation, model Heyios). The dye characteristic wavelength of 560 nm was obtained from the corresponding spectrum (cf. Fig. 1). In the range of dye concentrations used in this study, a linear dependence was obtained when they were plotted against the absorbance at  $\lambda_{\text{max}}$ .

The total organic carbon (TOC) was determined by catalytic oxidation followed by quantification of the  $\text{CO}_2$  formed through



**Fig. 1.** UV–vis spectra of samples taken along time in a typical experiment ( $T = 30^\circ\text{C}$ ,  $C_{\text{H}_2\text{O}_2} = 8.8 \text{ mM}$ ,  $\text{pH} = 2.0$  and  $C_{\text{Fe}^{2+}} = 0.26 \text{ mM}$ ).

infra-red spectrometry, as described in Method No. 5310D of the Standard Methods for the Examination of Water and Wastewater [24]. For that, a Shimadzu 5000A TOC analyser was used. TOC values reported represent the average of at least two measurements; in most cases each sample was injected three times, validation being performed by the apparatus only if CV is smaller than 2%.

#### 3.3. Chemical oxidation experiments

Chemical oxidation, with Fenton's reagent, of the red dye solutions was carried out in a closed jacketed batch reactor (1 L capacity). The reactor is provided with constant stirring, accomplished through a magnetic bar and a Falc magnetic stirrer. The temperature of the reaction mixture was kept constant by coupling the reactor to a Huber thermostatic bath (Polystat CC1).

Before each run, the dye solution (0.5 L) was put in the reactor, and the temperature stabilized. After pH adjustment, the catalyst (iron sulphate) was introduced, this way avoiding iron precipitation. Time zero of the runs coincides with addition of the hydrogen peroxide solution. Samples were taken for TOC analysis along time, as described above. However, large excess of  $\text{Na}_2\text{SO}_3$  was added to each sample to guarantee instantaneous consumption of residual hydrogen peroxide, thus stopping the Fenton's reaction.

In the oxidative process, temperature, pH and absorbance (at  $\lambda = 560 \text{ nm}$ ) were continuously measured, the computer interface being programmed with software Labview 5.0 (from National Instruments) for data monitoring and saving. To measure the solution temperature and pH, a thermocouple and a pH electrode (WTW, Sentix 41 model), connected to a pH-meter from WTW (model inolab pH Level 2), were used, respectively. For on-line absorbance monitoring, a peristaltic pump ensured recirculation of the solution through a flow-trough cell placed inside the UV–vis spectrophotometer, as described elsewhere [11].

## 4. Results and discussion

#### 4.1. Preliminary runs

For oxidation with the Fenton's reagent, four operating variables have to be considered (for a given parent compound concentration), namely the pH, the concentration of hydrogen peroxide, the temperature and the concentration of ferrous ion. A high number of experiments would be required if these four variables are considered in the experimental design (27 instead of the 17 shown in Table 1). For that reason some preliminary runs were carried out, to

find a suitable initial pH value to be kept constant. In addition, and as above-mentioned, in the experimental design it is important to have some previous knowledge regarding the system behaviour to better define the levels for each considered variable (see Table 1). Consequently, some further preliminary runs were then performed, in order to evaluate the responses (in terms of dye and TOC removal) when changing the other process variables. In all runs, a dye concentration of 100 mg/L was employed, to which corresponds an average total organic carbon content of ca. 31.6 mg/L.

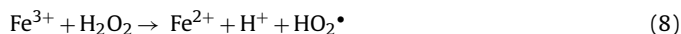
First of all, two blank experiments were carried out, in the presence of either hydrogen peroxide (8.8 mM) or ferrous ions (0.27 mM) alone to evaluate the need of their simultaneous presence. A reaction temperature of 30 °C and an initial pH of 3 were used. In both cases colour reduction was negligible (<1.5%), and the slight reduction in TOC (~10%) is close to the experimental uncertainty, although the hypothesis of some organic matter removal by a coagulation/flocculation process cannot be ruled out (in the run with only iron). Thus, and comparing with the performances shown below in the presence of both reagents, one can conclude that oxidation proceeds through a Fenton-like scheme.

In a typical experiment absorbance decreases along reaction time not only at the dye characteristic wavelength of 560 nm, but also in almost all visible region. This can be seen in Fig. 1, evidencing also that in the UV region (ca. 300 nm) absorbance inclusively increases for short reaction times, possibly due to intermediate organic compounds which aromatic part absorbs in this range. For longer times, this peak decreases due to a mineralization of the organic matter, as shown below with TOC analyses. In the following sections, colour removal data concern only to those registered at  $\lambda_{\max} = 560$  nm.

#### 4.1.1. Effect of the initial pH

Experiments performed at different pH values between 2 and 5 showed that the maximum dye removal rate was reached for a pH of 3.0 (Fig. 2a) while better TOC reduction was reached for a pH of 3.0–3.5 (Fig. 2b). In both cases, differences in the performances reached after 2 h are almost insignificant, whatever is the pH (3.0 or 3.5). Consequently, in the experimental design a pH of 3.5 was considered because in industrial practice this would require less acid in the previous acidification step of textile dyeing wastewaters, which are generally alkaline.

The optimal pH values obtained are within the range commonly found for the Fenton's process, which usually falls in acidic values of pH between 3 and 4 [7,25]. Under more alkaline conditions (pH > 4) the precipitation of iron hydroxide ( $\text{Fe}(\text{OH})_3$ ) occurs, decreasing the concentration of dissolved  $\text{Fe}^{3+}$  and consequently of  $\text{Fe}^{2+}$  species [12]. Besides, in such conditions hydrogen peroxide is less stable, being decomposed into water and oxygen [11]; therefore less hydroxyl radicals are formed, reducing the process efficiency. On the other hand, for pH values below 3 the process efficiency also decreases because the regeneration of  $\text{Fe}^{2+}$  (through reaction between  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ —cf. Eq. (8)) is partly inhibited [26]. This is due to the decrease of the soluble amount of  $\text{Fe}^{3+}$  that is in equilibrium with other iron species ( $\text{Fe}(\text{OH})^{2+}$  and  $\text{Fe}(\text{OH})_2^+$ ) under such conditions [7].



Further tests were performed at pH 3.0 and 3.5 with two main goals in mind: (i) to evaluate the reproducibility of the results and (ii) to extend the reaction time up to 240 min. It was found that the runs are reasonably reproducible: average absolute deviations of 1.3 and 3.4% for colour and TOC removal, respectively, have been obtained (average standard deviations of 0.6 and 2.4%). Besides, slightly better decolorisations were again reached at a pH of 3.0 (~99% vs. 98% at a pH of 3.5) while mineralization is increased

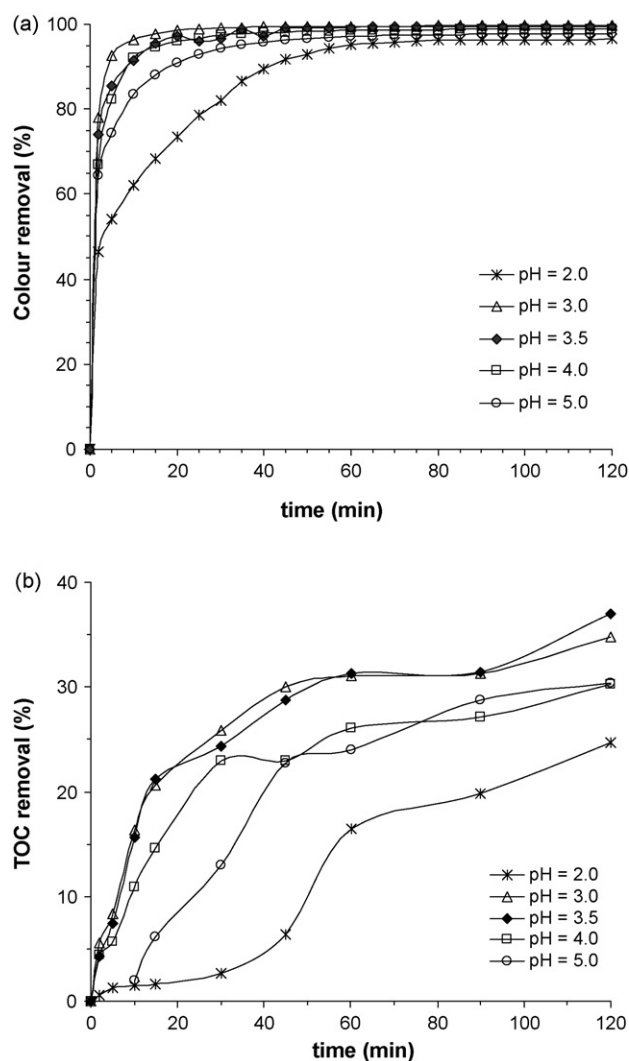


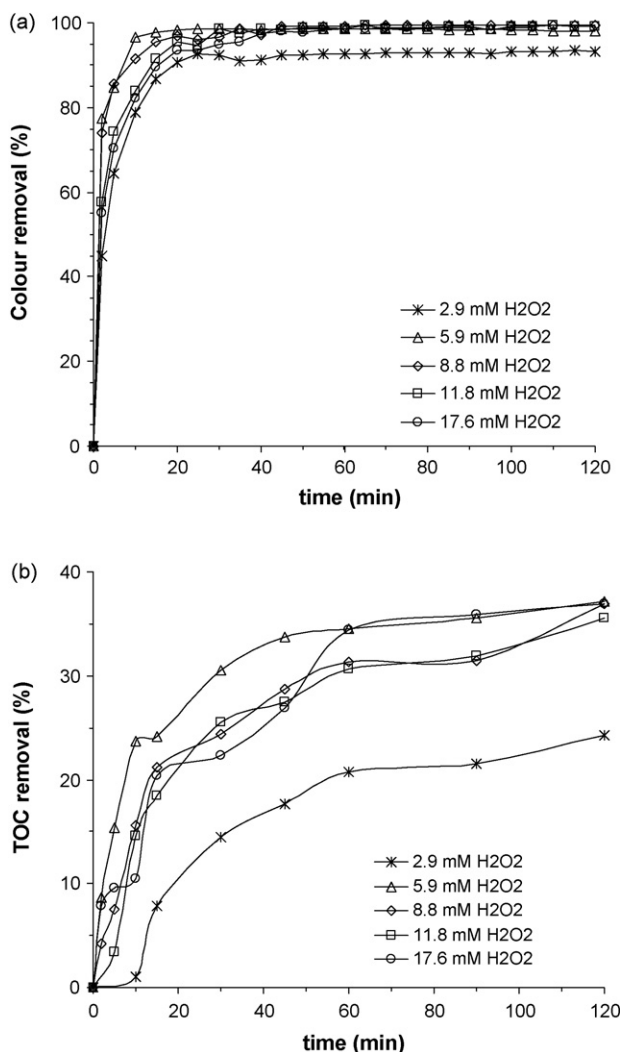
Fig. 2. Evolution of the dye (a) and of the total organic carbon (b) removal along time for different initial pH values ( $T = 30$  °C,  $C_{\text{H}_2\text{O}_2} = 8.8$  mM and  $C_{\text{Fe}^{2+}} = 0.27$  mM).

for a pH of 3.5. Finally, and as expected, it was concluded that colour removal remains unaffected for reaction times between 120 and 240 min; TOC removal in this time interval increases, but only slightly (from 38 to 44%, at pH = 3.5). Consequently, in subsequent runs reaction time was kept at 120 min and initial pH at 3.5. As mentioned above, in the following runs the effects of the other process variables will be analysed, an issue that is quite important before the DoE, particularly for defining the ranges of the variables associated with the Yates' algorithm.

#### 4.1.2. Effect of the $\text{H}_2\text{O}_2$ concentration

In what concerns the influence of the hydrogen peroxide concentration, data shown in Fig. 3 put into evidence that in the tested range the dye and TOC removal efficiencies (and initial rates) increase when the oxidant dosage is raised up to 5.9–8.8 mM. Nevertheless, for higher concentrations oxidation performance remains practically unaffected, or even decreases. This is a common behaviour in the Fenton's process, often attributed to the parallel and undesired reaction between excess hydrogen peroxide and hydroxyl radicals (scavenging effect) [26]:





**Fig. 3.** Evolution of the dye (a) and of the total organic carbon (b) removal along time for different hydrogen peroxide concentrations (pH 3.5,  $T = 30^\circ\text{C}$ , and  $C_{\text{Fe}^{2+}} = 0.27\text{ mM}$ ).

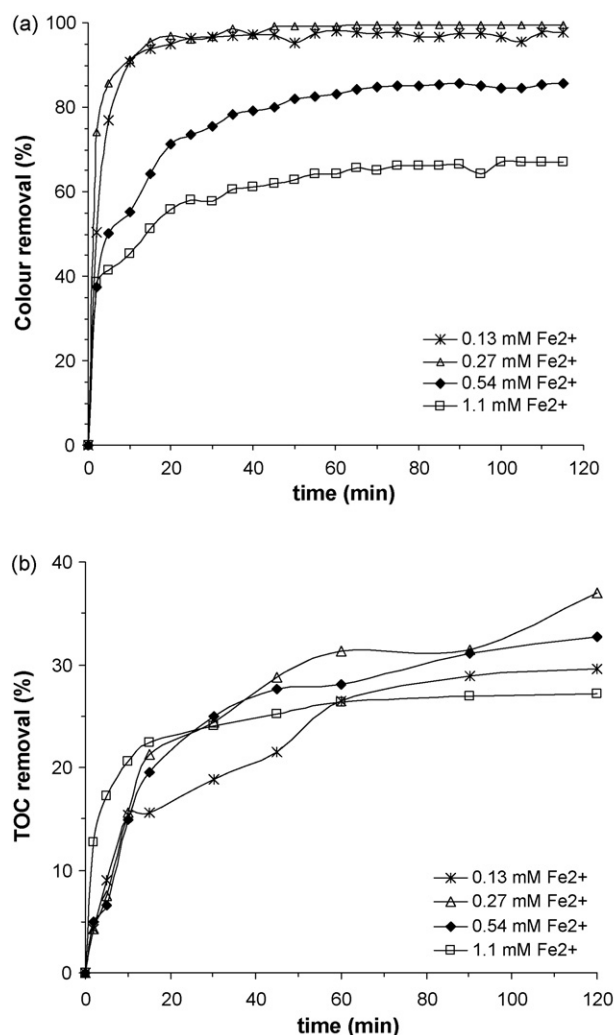
Consequently, the effective amount of these highly reactive species ( $\text{HO}^\bullet$ ) that is available to degrade the dye and/or the intermediate compounds decreases. Although another radical is formed ( $\text{HO}_2^\bullet$ ), it has an oxidation potential significantly smaller than that of the hydroxyl one [8].

#### 4.1.3. Effect of the $\text{Fe}^{2+}$ concentration

To evaluate the effect of the ferrous ion concentration in the oxidative process, further runs were then performed in which this variable was varied separately (Fig. 4). It can be seen that, in general, maximum dye and TOC removal levels are reached for a ferrous ion concentration of 0.27 mM, the performance being worst for higher loads. Such detrimental effect of excessive catalyst dosages can be ascribed to other undesirable and competitive reactions that decrease the amount of radicals available to oxidise the organic matter, by reaction with excess iron ions. For ferrous ions they are represented as follows [26]:



being also of concern similar reactions that involve  $\text{Fe}^{3+}$  species instead of  $\text{Fe}^{2+}$ .



**Fig. 4.** Evolution of the dye (a) and of the total organic carbon (b) removal along time for different ferrous ion concentrations (pH 3.5,  $T = 30^\circ\text{C}$ , and  $C_{\text{H}_2\text{O}_2} = 8.8\text{ mM}$ ).

#### 4.1.4. Effect of the reaction temperature

For the optimal catalyst dose of 0.27 mM, Fig. 5 illustrates that Fenton's process performance increases with temperature, a trend that can be justified by the kinetic constants raise with that variable (Arrhenius law). However, such effect is much more pronounced on the mineralization rate (TOC removal). For simple dye degradation temperatures of  $20^\circ\text{C}$  are enough to provide fast decolourisation.

#### 4.2. Experimental design of the 2<sup>3</sup>-type with expansion (central composite design)

After the exploratory runs, wherein the effects of the process variables (temperature, and concentrations of hydrogen peroxide and ferrous ion) were briefly analysed, the ranges to be used in the experimental design were established (Table 2). It is worth noting that these ranges were defined taking into account that too high iron and peroxide concentrations revealed to be useless ( $>0.54$  and  $\sim 18\text{ mM}$ , respectively). Temperature had a positive effect on TOC removal, up to  $70^\circ\text{C}$ , but it is not physically possible to extend much further this value. The preliminary tests allowed also defining on which of the system responses the study will focus on. Only the organic matter (TOC) removal will be considered, because in

**Table 2**  
Levels of the parameters studied in the expanded  $2^3$  experimental design.

Parameter	Level				
	-1.682	-1	0	+1	+1.682
$T$ ( $^{\circ}\text{C}$ )	6.4	20	40	60	73.6
$C_{\text{H}_2\text{O}_2}$ (mM)	0.4	2.9	6.6	10.3	12.8
$C_{\text{Fe}^{2+}}$ (mM)	0.12	0.18	0.27	0.36	0.42

the above-described runs it was verified that colour removal is in all cases almost complete (usually above 95%) and it occurs in the initial period of the reaction (up to 15 min). Thus, maximizing mineralization after 2 h will result in satisfactory colour leaching, as shown later on.

The experiments performed, as defined by the Yates' algorithm (see Table 1), and the values of the obtained responses are reported in Table 3. As above-mentioned, three of the experiments were performed in the centre of the cubic domain, i.e., under the same conditions. For such replicates (runs no. 9–11), TOC removal lies between 39.8 and 43.9% (standard deviation of 1.9%).

The DoE software allowed determining the coefficients of the second order fitting equation, which was analysed based on the above-mentioned statistical criteria. In particular, the suitability of

**Table 3**  
Responses obtained in the runs performed in the experimental design.

Run No.	$T$ ( $^{\circ}\text{C}$ )	$C_{\text{H}_2\text{O}_2}$ (mM)	$C_{\text{Fe}^{2+}}$ (mM)	TOC removal (%)
1	20	2.9	0.18	27.4
2	60	2.9	0.18	50.4
3	20	2.9	0.36	24.3
4	60	2.9	0.36	51.5
5	20	10.3	0.18	29.7
6	60	10.3	0.18	38.6
7	20	10.3	0.36	31.8
8	60	10.3	0.36	42.3
9	40	6.6	0.27	43.6
10	40	6.6	0.27	39.8
11	40	6.6	0.27	43.9
E1	6.4	6.6	0.27	19.4
E2	73.6	6.6	0.27	47.5
E3	40	0.4	0.27	35.8
E4	40	12.8	0.27	46.9
E5	40	6.6	0.12	33.3
E6	40	6.6	0.42	47.5

**Table 4**  
Analysis of variance regarding the TOC removal quadratic model.

Variation source	df	SS	MS	$F$ -ratio	$P > F$
Model	9	1311.17	145.69		
Error	7	146.95	20.99	6.94	0.009
Total	16	1458.12			

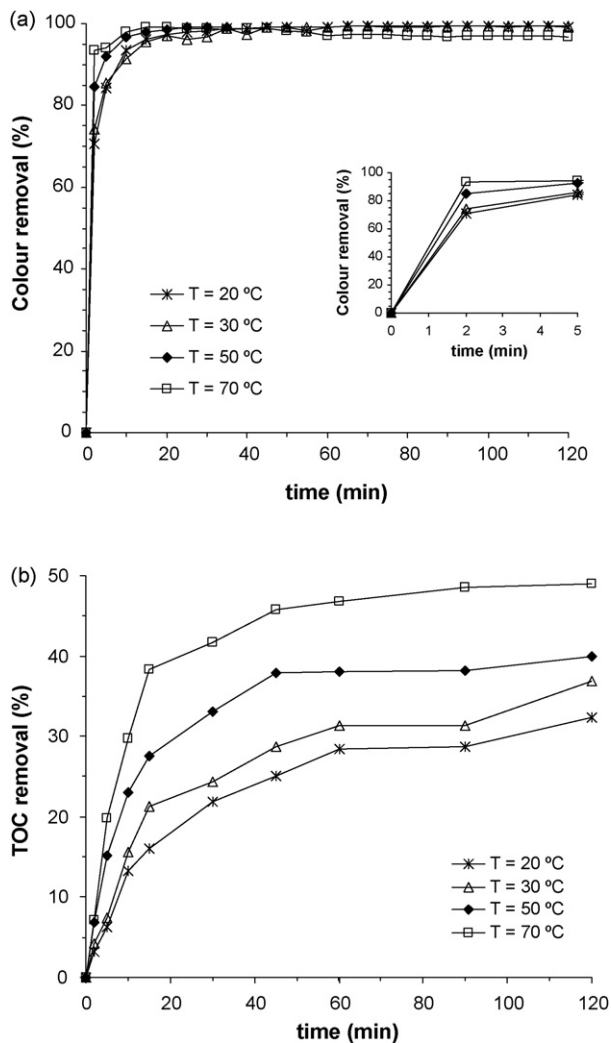
$R^2 = 0.899$ .

the model was tested by the ANOVA test. Table 4 summarizes the obtained results. In the ANOVA test, the  $F$ -ratio value obtained for the percentage of TOC removal is higher than the Fisher's  $F$ -value ( $F_{9,7} = 3.80$ ), and so one can conclude that the variations that occur in the responses are associated to the model, not to random errors. This is confirmed by the  $F$ -probability obtained, once it is smaller than 0.05 (for a 95% confidence level). The value of  $R^2$  indicates that 89.9% of the response variability is explained by the model. It can thus be concluded that the model fits reasonably well the experimental data obtained.

After analysis of the second order model adherence and suitability, the statistically significant variables and/or interactions were identified, using the Student's  $t$ -test. In Table 5 are shown the results obtained. It can be seen that the process variables and interactions that are statistically significant are the temperature ( $x_1$  and  $x_1^2$ ) and its interaction with the ferrous ion concentration ( $x_1x_3$ ), because these parameters present  $P > |t|$  values smaller than 0.05 (for 95% of statistical meaning). This means that hydrogen peroxide effect is negligible as compared to the other variables, a behaviour also found for another azo dye degradation [11]. Consequently, the equation obtained for the model response ( $Y_1$ ), which provides the TOC removal at  $t = 120$  min in the studied range of the parameters, is

**Table 5**  
Estimates of the model regression for TOC removal.

Term	Estimate	Standard error	$t$ -Ratio	$P >  t $
Intercept	42.48	2.64	16.09	<0.0001
$x_1$	8.55	1.24	6.90	0.0002
$x_2$	1.65	1.24	1.33	0.2241
$x_3$	0.94	1.24	0.76	0.4728
$x_1x_2$	0.72	1.62	0.45	0.6696
$x_1x_3$	-3.84	1.62	-2.37	0.0496
$x_2x_3$	0.99	1.62	0.61	0.5609
$x_1^2$	-3.42	1.36	-2.51	0.0405
$x_2^2$	-0.64	1.36	-0.47	0.6547
$x_3^2$	-0.97	1.36	-0.71	0.5010



**Fig. 5.** Evolution of the dye (a) and of the total organic carbon (b) removal along time for different temperatures (pH 3.5,  $C_{\text{H}_2\text{O}_2} = 8.8$  mM and  $C_{\text{Fe}^{2+}} = 0.27$  mM).

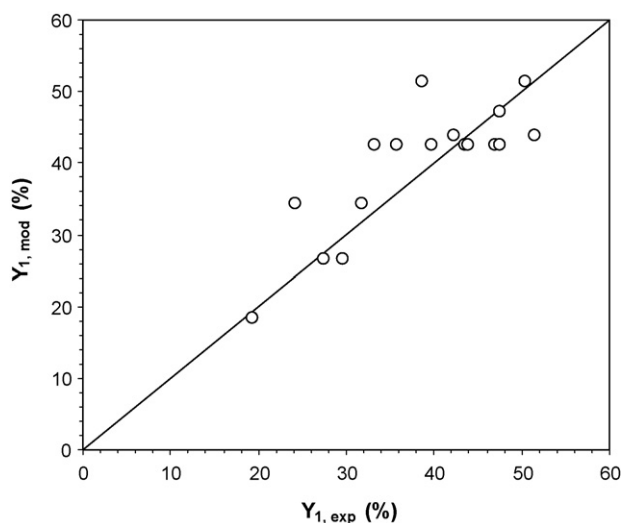


Fig. 6. Parity plot comparing the TOC removal data for  $t = 120$  min (cf. Table 3) with the model predictions by Eq. (12).

given by:

$$Y_1 = 42.48 + 8.55 \left( \frac{T - 40}{20} \right) - 3.42 \left( \frac{T - 40}{20} \right)^2 - 3.84 \left( \left( \frac{C_{\text{Fe}^{2+}} - 0.27}{0.09} \right) \left( \frac{T - 40}{20} \right) \right) \quad (12)$$

The comparisons of the model prediction vs. the experimental responses are given in the parity plot of Fig. 6. Although absolute deviations as high as 12.9% are observed, on average they are only 4.2%.

As predicted from Eq. (12), and due to the existence of the cross-interactions, the effect of each independent variable on the process response depends on the value of the other one, a common behaviour found in DoE studies applied to the Fenton's process [5,11,13,15]. For instance, the ferrous ion concentration increases the TOC removal for temperatures below 40 °C; at higher temperatures the opposite effect is noticed. This can also be seen in the response surface illustrated in Fig. 7, which is a graphical representation of Eq. (12). As regards the effect of temperature, it can be concluded that at low catalyst dosages it affects positively the

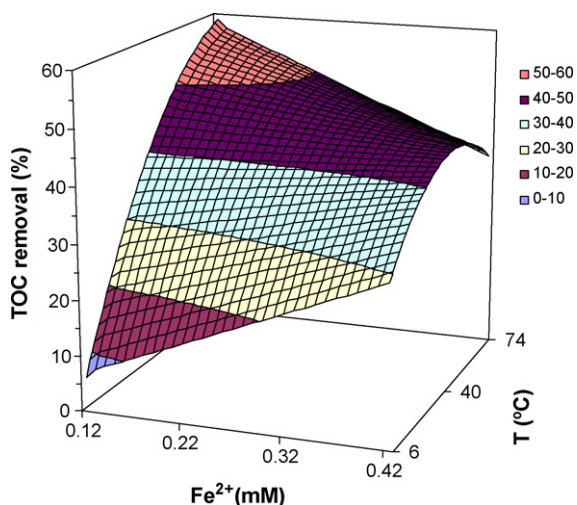


Fig. 7. Variation of the TOC removal (for  $t = 120$  min) with the temperature and with the ferrous ion concentration as predicted by Eq. (12).

mineralization degree, corroborating the preliminary runs. However, when one moves towards higher ferrous ion loads, excessive temperatures have a detrimental effect on TOC removal after 2 h of reaction. Concluding, the response surface curve shown in Fig. 7 illustrates that the process variables only have a detrimental effect on the response when the other variable (ferrous ion concentration or temperature) also exhibits high values (typically above the central point considered in the study). Only in such conditions the existence of several undesirable phenomena becomes evident and has also been reported by Herney-Ramirez et al. [11] during Orange II degradation by a heterogeneous Fenton-like process. The reason for this might be related with the scavenging of radicals that occurs at high iron dosages (Eqs. (10) and (11) and equivalent reactions involving ferric ions) and high temperatures, as a consequence of the moderate activation energies and high rate constants of those reactions [27,28]. Therefore, the reaction rates for such phenomena increase significantly with both parameters, affecting negatively the process performance. Although reactions between iron species and hydrogen peroxide to generate the radicals have similar or even higher activation energies [27,28], at elevated temperatures their rates are strongly affected by the thermal decomposition of hydrogen peroxide into water and oxygen [11,28].

An interesting feature is that the 3D plot of Fig. 7 (or Eq. (12)) allows determining the optimum conditions, i.e., those that maximize the system response. This occurs at the maximum temperature and minimum ferrous ion concentration of the space domain analysed, i.e., 73.6 °C and 0.12 mM, respectively. Under such conditions, Eq. (12) predicts a mineralization degree of 57.9% after 2 h. Nevertheless, Fig. 7 shows that good performances can also be attained at lower temperatures, although requiring slightly higher catalyst dosages. For real applications, one could select the lowest hydrogen peroxide concentration employed in the experimental design because it does not affect the oxidative process; this way, the consumption of such reagent would be minimized and consequently the operation costs.

With these issues in mind, an additional experiment was performed under the conditions that maximize TOC removal. Results obtained are shown in Fig. 8. A dye mineralization degree of 52.3% was reached, which is only 5.6% below the model prediction (a deviation similar to those reported in Fig. 6). Besides, one can also confirm the hypothesis initially advanced of attaining a practically complete colour elimination (99.6% in 2 h), which is also very fast

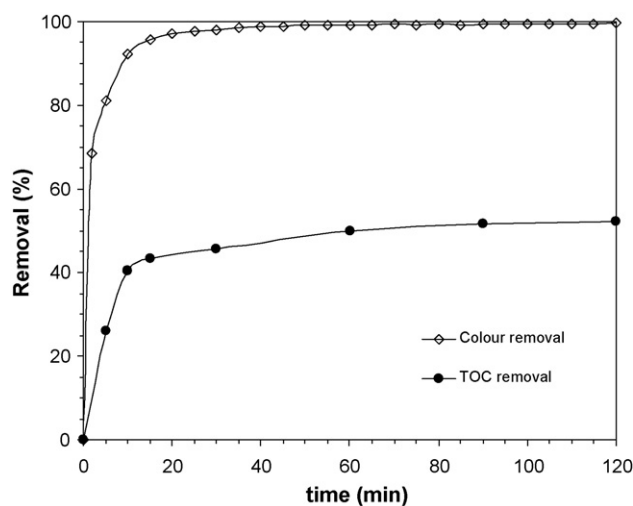


Fig. 8. Evolution of the dye and total organic carbon removal along time under theoretical conditions that maximize TOC elimination ( $\text{pH } 3.5$ ,  $T = 73.6$  °C,  $C_{\text{H}_2\text{O}_2} = 2.9$  mM and  $C_{\text{Fe}^{2+}} = 0.12$  mM).

(95.7% in 15 min), even for very low doses of catalyst and hydrogen peroxide.

## 5. Conclusions

The degradation of the dye Procion Deep Red H-EXL gran by oxidation with Fenton's reagent depends upon several process variables. From some preliminary runs it was concluded that the pH value that maximizes dye removal is 3.0, while for TOC a value of 3.5 was found. Nevertheless, because at pH 3.5 colour removal is high enough and a smaller amount of acid is required to adjust the pH in textile dye-house effluents, this was the value established for subsequent runs.

For the experimental conditions adopted, the reaction time required to achieve colour removals above 95% is around 15 min, indicating that rate constants for simple chromophore breakdown are high. However, mineralization of the organic matter proceeds at a slower rate, and so the time of reaction was fixed in 120 min for the experimental design; this way, optimization of TOC removal ensure almost complete decolourisation of the wastewater.

The experimental design (of the  $2^3$ -type with expansion) allowed to conclude that among the three process variables considered, only temperature and catalyst concentration affect the mineralization degree after 2 h of reaction (TOC removal considered as process response), while the oxidant dosage seems to have no effect on it. The quadratic model developed fits reasonably the experimental data and allowed concluding that the effect of each independent variable on the response depends on the value of the other one, due to the existence of cross-interactions. This way, both ferrous ion dosage and temperature might affect positively or negatively the mineralization degree attained, which has a maximum value of 57.9% (in the space domain investigated).

## Acknowledgement

The authors are grateful to Erfoc - Acabamentos Têxteis S.A (located near Famalicão, in the north of Portugal), that gently provided the dye used in this study.

## References

- [1] B. Lodha, S. Chaudhari, Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions, *J. Hazard. Mater.* 148 (2007) 459–466.
- [2] S. Wang, A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, *Dyes Pigments* 76 (2008) 714–720.
- [3] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, *Catal. Today* 53 (1999) 51–59.
- [4] P.C. Vandevivere, R. Bianchi, W. Verstraete, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, *J. Chem. Technol. Biotechnol.* 72 (1998) 289–302.
- [5] J.H. Ramirez, C.A. Costa, L.M. Madeira, Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent, *Catal. Today* 107–108 (2005) 68–76.
- [6] S.-F. Kang, C.-H. Liao, M.-C. Chen, Pre-oxidation and coagulation of textile wastewater by the Fenton process, *Chemosphere* 46 (2002) 923–928.
- [7] M.S. Lucas, J.A. Peres, Decolorization of the azo dye reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments* 71 (2006) 236–244.
- [8] R.J. Bigda, Consider Fenton's chemistry for wastewater treatment, *Chem. Eng. Prog.* 91 (1995) 62–66.
- [9] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- [10] D.C. Montgomery, *Design and Analysis of Experiments*, fifth ed., John Wiley & Sons, New York, 2001.
- [11] J. Herney-Ramirez, M. Lampinen, M.A. Vicente, C.A. Costa, L.M. Madeira, Experimental design to optimize the oxidation of Orange II dye solution using a clay-based Fenton-like catalyst, *Ind. Eng. Chem. Res.* 47 (2008) 284–294.
- [12] R. Oliveira, M.F. Almeida, L. Santos, L.M. Madeira, Experimental design of 2,4-dichlorophenol oxidation by Fenton's reaction, *Ind. Eng. Chem. Res.* 45 (2006) 1266–1276.
- [13] J.A. Melerio, G. Calleja, F. Martínez, R. Molina, M.I. Pariente, Nanocomposite  $\text{Fe}_2\text{O}_3/\text{SBA}-15$ : an efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions, *Chem. Eng. J.* 131 (2007) 245–256.
- [14] M. Pérez-Moya, M. Graells, L.J. del Valle, E. Centelles, H.D. Mansilla, Fenton and photo-Fenton degradation of 2-chlorophenol: multivariate analysis and toxicity monitoring, *Catal. Today* 124 (2007) 163–171.
- [15] H. Zhang, H.J. Choi, P. Canazo, C.-P. Huang, Multivariate approach to the Fenton process for the treatment of landfill leachate, *J. Hazard. Mater.* 161 (2009) 1306–1312.
- [16] N.S.S. Martínez, J.F. Fernández, X.F. Segura, A.S. Ferrer, Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent, *J. Hazard. Mater.* 101 (2003) 315–322.
- [17] J. García-Montano, F. Torrades, J.A. García-Hortal, X. Domènech, J. Peral, Degradation of Procion Red H-E7B reactive dye by coupling a photo-Fenton system with a sequencing batch reactor, *J. Hazard. Mater.* 134 (2006) 220–229.
- [18] S. Raghu, C.A. Basha, Electrochemical treatment of Procion Black 5B using cylindrical flow reactor—a pilot plant study, *J. Hazard. Mater.* 139 (2007) 381–390.
- [19] C.-H. Wu, C.-L. Chang, C.-Y. Kuo, Decolorization of Procion Red MX-5B in electrocoagulation (EC), UV/TiO<sub>2</sub> and ozone-related systems, *Dyes Pigments* 76 (2008) 187–194.
- [20] A. Riga, K. Soutsas, K. Ntampeliotis, V. Karayannis, G. Papapolymerou, Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of H<sub>2</sub>O<sub>2</sub>/UV, Fenton, UV/Fenton, TiO<sub>2</sub>/UV and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub> processes, *Desalination* 211 (2007) 72–86.
- [21] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation, *Chemosphere* 46 (2002) 905–912.
- [22] T.B. Barker, *Quality by Experimental Design*, second ed., Marcel Dekker, New York, 1994.
- [23] D.C. Montgomery, G.C. Runger, *Applied Statistics and Probability for Engineers*, second ed., John Wiley & Sons, New York, 1999.
- [24] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater*, twentieth ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, 1998.
- [25] M.-C. Lu, C.-J. Lin, C.-H. Liao, W.-P. Ting, R.-Y. Huang, Influence of pH on the dewatering of activated sludge by Fenton's reagent, *Water Sci. Technol.* 44 (2001) 327–332.
- [26] S.H. Lin, C.C. Lo, Fenton process for treatment of desizing wastewater, *Water Res.* 31 (1997) 2050–2056.
- [27] T. Lundström, H. Christensen, K. Sehested, Reactions of the HO<sub>2</sub> radical with OH, H, Fe<sup>2+</sup> and Cu<sup>2+</sup> at elevated temperatures, *Radiat. Phys. Chem.* 69 (2004) 211–216.
- [28] Y. Lee, C. Lee, J. Yoon, High temperature dependence of 2,4-dichlorophenoxyacetic acid degradation by Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> system, *Chemosphere* 51 (2003) 963–971.