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Photochemically activated degradation of reactive dyes Statistical modeling of the reactor performance

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Abstract

This paper, reports on the degradation/decoloration of a model reactive dye Uniblue A carried out in a cylindrical concentric photochemical immersion type reactor. The main chemical parameters affecting the photo-assisted Fenton degradation have been evaluated in a quantitative way. The degradation of the pollutant was studied in the 5–35 TOC (mg C/l) range. A single exponential function was constructed for the treatment of the data seeking the most economical use of chemicals, electrical energy and time to degrade a given concentration of pollutant. The degradation data was used evaluate the coefficients of the exponential expression rendering 2D-contour plots. The abatement of the pollutant up to almost complete disappearance was susceptible to modeling. The standard deviation between the experimental and the values predicted through modeling by the exponential function was seen to be small.

Keywords: Fenton photo-assisted reaction; Exponential modeling; Photocatalysis; Solution parameters; Uniblue A; Reactive dyes

1. Introduction

The treatment of textile dyeing waters by conventional methods such as flocculation, reverse osmosis, activated carbon adsorption, are in common practice but have drawbacks due to the increasing number of refractory materials found in wastewater effluents and the difficulties in the complete removal of color [1]. The cost of ozonization which is widely used still needs to be reduced for competitiveness.

This study addresses the photoreactor optimization of the destruction of the reactive dye Uniblue A and Remazol Brilliant Blue R (RB 19) developed by Hoechst [2]. Textile-dyes in general are non-biodegradable in aerobic atmosphere [3].

Reactive dyes link through chemical bonding to fibers. Also during the dyeing process less losses are seen than with other textile dyes. These dyes are resistant to light irradiation, the action of atmospheric agents, and some acids and bases. The same properties that make these dyes suitable dyestuffs, make them difficult to degrade/decolorize once they escape into water bodies.

Scheme 1 shows the structure and hydrolysis of RB 19 and the way it is subsequently linked to the fibers like cellulose. Scheme 1 shows how RB 19 reacts and partly hydrolises forming a covalent bond to cellulose. The anchor group is vinyl-sulfonate. The process involves the addition of a nucleophilic–OH group of the fiber to viny l-sulfonate involving a Michael-type 1,4-nucleophilic mechanism. The fixation rate between the reactive dye and the fiber can reach as high as 90% [4].

Only very few studies have been recently directed towards the removal and abatement of reactive dyes like Uniblue A [5,6] and Remazol Brilliant Blue R [7]. Our laboratory has recently used photoreactors to abate a variety of pollutants like non-biodegradable *p*-nitrotoluene sulfonates [8,9], naphthalene disulfonates [10] and azo-dyes [11,12]. The conditions used for their degradation require low energy sources and mild reaction conditions which makes this approach environmentally attractive.

2. Experimental

2.1. Materials

The H_2O_2, $Fe(ClO_4)_3{\cdot}9H_2O$, $HClO_4$, acetonitril, H_2SO_4 and ammonium acetate (NH_4OAc) were Fluka p.a. and were used as received without further purification. The pH values

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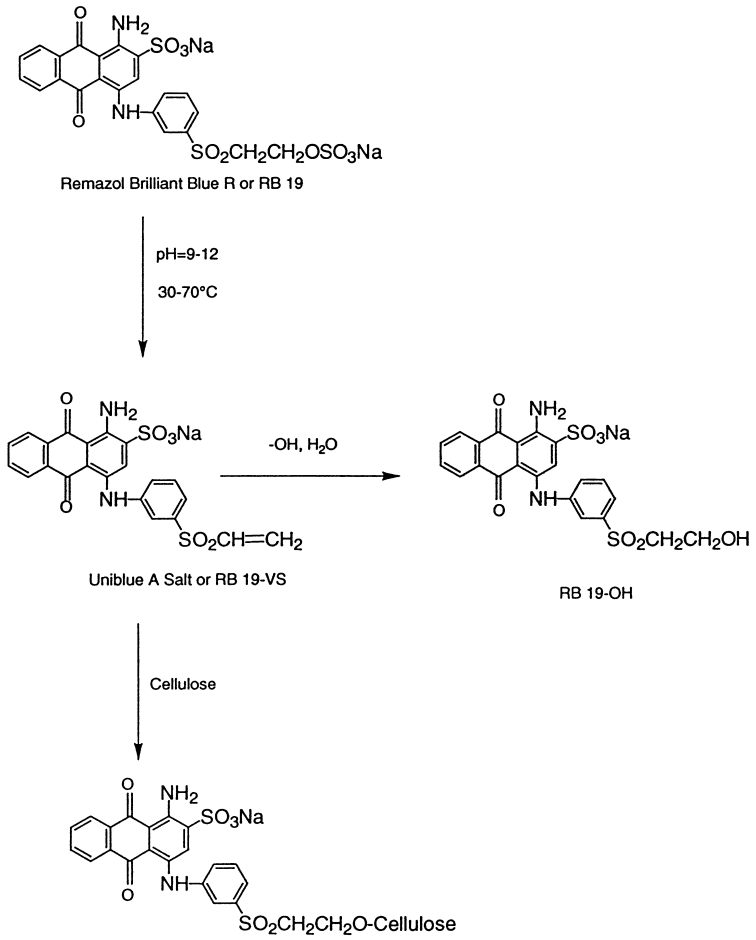

Scheme 1.

of aqueous solutions were adjusted to the desired values with $HClO_4$.

Uniblue A sodium salt (UB) was from Aldrich 29,640-9, p.a. grade, MW=506.49, λ_{max}=594 nm with $\varepsilon_{594\,nm}$=5570/M cm puriss. 98%, CAS number 14541-90-3.

2.2. High pressure liquid chromatogram (HPLC) analysis of Uniblue A

The equipment used was a Varian star work-station provided with solvent delivery system Varian 9020Q, an automatic injection 9300 and a Varian pro-star diode array detector (DAD). Modules were piloted by way of a Varian star 5.3® software for liquid chromatography. Supelco ABZ-plus reverse-phase and interaction ORH 801 columns were used for the analysis at 40 or 60°C and the analysis time was 30 min. The ABZ-plus column was used with a gradient mobile phase composed of aqueous ammonium acetate:acetonitril in percentages of 100:0 at 0 min, 70:30 at 17 min, 70:30 at 23 min and 100:0 at 30 min, flow rate 1.0 ml/min. The interaction column used an isocratic mobile phase H_2SO_4 (0.01 N) at a flow rate of 0.8 ml/min.

2.3. Total organic carbon (TOC) determination

A Shimadzu TOC-5000 analyzer was used for TOC determination of the C-content in solution. Stripping was not necessary because the pH range where the experiments were carried out (<pH 3.0) low enough to keep the solutions free of CO_2 coming from the atmosphere.

2.4. Photoreactor

A Phillips 36 W (1.20 m long and 26 mm diameter, TLD 36 W/08) black actinic light source was employed, in such a way that its center passed through the focal axis of the reactor. This is shown in Fig. 1. The lamp radiation was centered at λ=366 nm with a wavelength distribution between 330 and 390 nm. The reactor was used in batch mode operation. Two peristaltic pumps were used during normal operation as shown in Fig. 1. The first pump added H_2O_2 into the mixer at determined time intervals (Fig. 3) and the second pump recirculated the solution in the photo-reactor. The total reactor volume was 1.2 l. Samples for analyses were taken from the mixer.

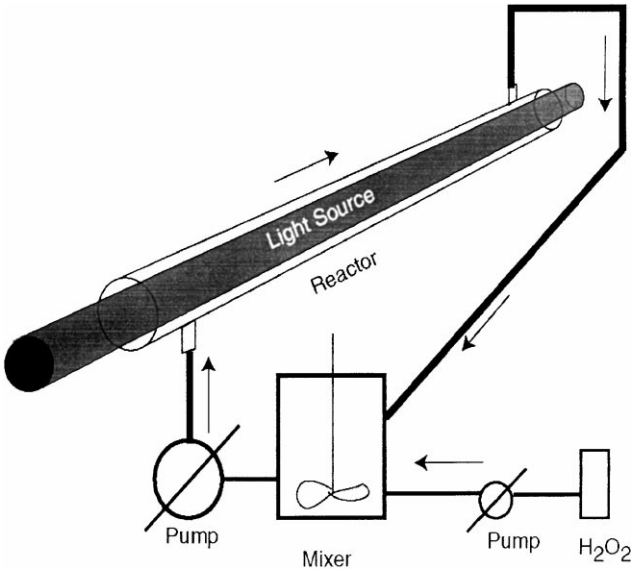

Fig. 1. Photo-reactor used the degradation of Uniblue A. For other details see text.

2.5. Modeling of the polynomial (exponential function)

The numerical work was done using Matlab 5.3 for Macintosh. Contour plots were obtained in a power Macintosh 8200/120. The routines for the modeling were written during the course of this study.

3. Results and discussion

3.1. HPLC studies during Uniblue A degradation

HPLC analysis of the dye Uniblue A photo-degradation is shown in Fig. 2. In Fig. 2, it is seen that the abatement of Uniblue A occurs in ~50 min. The chromatograms peaks are plotted at 0, 10, 20 min time intervals. It is interesting to note that even if Uniblue A disappears [7] from the solution, the solution remains colored. This is due to the formation of aromatic intermediates which absorb at wavelengths in the visible range. Separation of intermediates in solution was attempted at different times of degradation by way of the column mentioned in the experimental section. A Multi compound analysis facility provided with Varian software was used to test the purity of the peaks observed. Nevertheless, the identification of the intermediates against the external standards using available standard reference products from Fluka, Aldrich, Sigma and Across Chemical Co. was not successful.

3.2. Results for Uniblue A degradation following TOC

TOC analysis of the Uniblue A photo-degradation in photo-assisted Fenton reaction was followed focusing on different experimental parameters. The results shown in Figs. 3–5 indicate that full mineralization is attained for Uniblue A within 80 min reactor during batch operation. The approximate reaction stoichiometry can be estimated from the oxidant to pollutant ratio.

$$C_{22}H_{16}N_2O_7S_2 + 40H_2O_2 + 8O_2 \rightarrow 22CO_2 + 45H_2O + 2HNO_3 + 2H_2SO_4 \quad (1)$$

In Eq. (1), 40 moles of H_2O_2 were added for each mole of Uniblue A. For the stoichiometric balance it is necessary to add 8 moles of O_2 from the air atmosphere. The three main parameters investigated during reactor operation were: the variation of H_2O_2 and Fe^{3+} concentrations and the recirculation time (or residence time). The results are indicated in Figs. 4–6. These experimental data will be used later for the statistical modeling of the solution parameters affecting the reaction performance.

Fig. 3 shows that the most efficient degradation takes place with the lowest concentration of H_2O_2 (0.0246 M) as seen in trace 3. The concentration of H_2O_2 was followed by way of the Merckoquant® peroxide test a known organic indicator specific for peroxides based on the redox reaction of *o*-toluidine. At the end of the experiment a concentration of 5 mg/l of H_2O_2 was still observed in solution. This is equivalent to 1.4×10^{-4} M H_2O_2 (or 0.57% of the initial 2.46×10^{-2} M H_2O_2 used). Fig. 3 shows that the lowest concentration of H_2O_2 (2.46×10^{-2} M) is the one that removes more efficiently the TOC of Uniblue A. The scavenging of H_2O_2 in the presence of the OH radical decreases the degradative performance at high concentrations of H_2O_2 [13]

$$^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}HO_2 + H_2O \quad (2)$$

decreasing the $^{\bullet}OH$ radical available for the hydroxylation of the aromatic ring.

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad (3)$$

In Fig. 4, a low concentration for the Fe^{3+} ion is used in the upper trace. In the middle trace, a concentration 10 times higher is used with concomitant increase in the degradation rate. The lower trace shows the results for a five-fold concentration respect to the concentration in the middle trace. As observed from these traces a higher concentration of Fe ion accelerates the degradation which was observed to be too slow and ineffective in the presence of very low Fe concentrations. Recently our laboratory reported that Uniblue A forms complexes in aqueous solution with Fe^{3+} ion [7]. These complexes were shown to absorb light and photosensitize the dye increasing the degradation rate.

Fig. 5 shows that when the recirculating rate is decreased the degradation becomes more efficient. A slower recirculation increases the contact time of Uniblue A and Fe^{3+}/H_2O_2 with the light source. This in turn leads to the formation of a higher amount of $^{\bullet}OH$ radicals favoring a higher degradation rate.

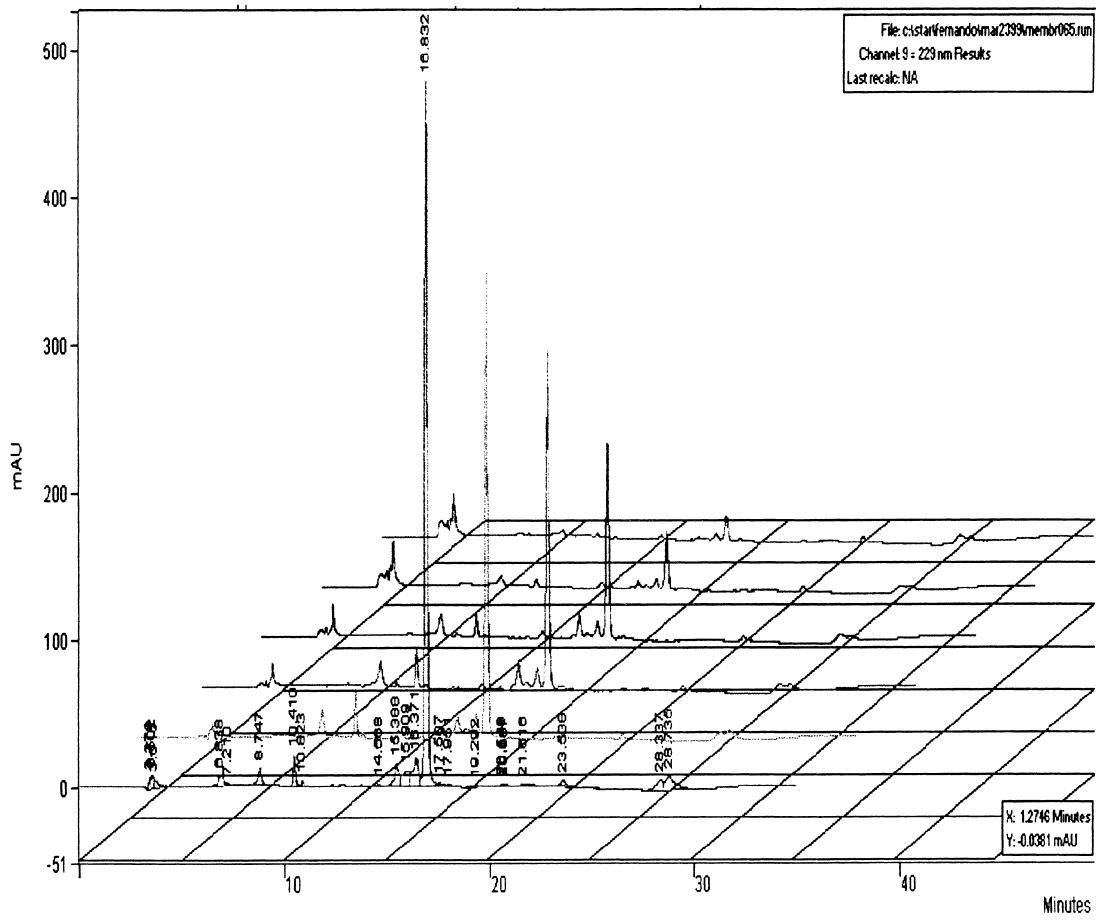

Fig. 2. HPLC chromatogram showing the abatement of Uniblue A in the photo-reactor by way of Fenton photo-assisted oxidations in ~50 min. For further experimental details see text.

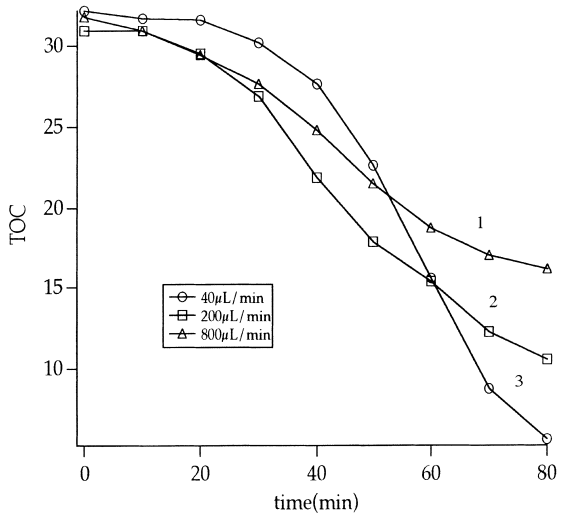

Fig. 3. Degradation of Uniblue A as function of H_2O_2 concentration. The experimental conditions were: Fe^{3+} (0.1695 mM), recirculation (416 ml/min) and concentration of Uniblue A (100 mg/l). The equivalent concentrations of H_2O_2 are: 0.492 M (trace 1), 0.123 M (trace 2) and 0.0246 M (trace 3).

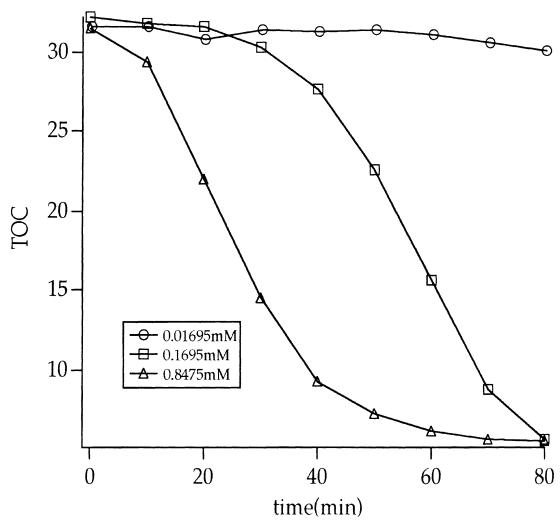

Fig. 4. Degradation of Uniblue A as a function of the Fe^{3+} ion concentration as noted in the caption. Addition of H_2O_2 (40 μl/min) was carried out on the mixer, reactor recirculation of the solution at (416 ml/min) and the concentration of Uniblue A (100 mg/l).

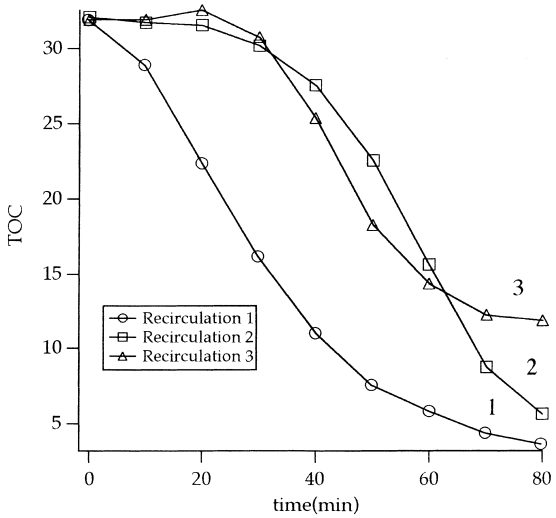

Fig. 5. Degradation of Uniblue A as function of recirculation rate in the photo-reactor. The recirculation rates were: (1) 208 ml/min; (2) 416 ml/min and (3) 624 ml/min as shown in the caption. Other experimental conditions used were: Fe^{3+} (0.1695 mM), H_2O_2 (0.0246 M) and Uniblue A (100 mg/l).

3.3. Surface response methodology: an option for complex systems

The surface response methodology [14,15] has recently provided a method of designing a statistical significant model for a reaction by performing the minimum number of well chosen experiments. This approach has shown to be very useful when a given variable depends on the setting of another one (interaction effects). These techniques are very useful for the empirical study of response functions such as: reaction yield, solution absorption and a number of input variables (factors) like temperature, pressure and concentration. In this study, the TOC evolution was the response function. The input variables (factors) taken were: the concentration of H_2O_2 used, the concentration of the catalyst and the recirculation rate of the solution in the photo-reactor. The intensity of the the light source (as shown in the Fig. 1 experimental section) was a fixed value (36 W). The solution pH=3 was used, since, it has been reported to be optimal for photo-Fenton processes (8–13). Both were not considered as input values in the modeling. The TOC dependency on the concentration of the Uniblue A was not modeled since Uniblue A had a solubility of 200 g/l providing the maximum possible optical density (0.5) for the pathlength available at the immersion reactor (d=1 cm)

It is not necessary in the modeling procedure to know the reaction mechanism since the mathematical model is empirical. The modeling allows drawing contour plots or curves of constant response value (as shown in the Section 3.4). Once this operation has been carried out it is possible to predict the values of the response(s) at any point of the experimental region in Figs. 3–5. This methodology has been applied to study the dependence of the TOC response function on the input variables (factors) such as H_2O_2, Fe^{3+} ion and recirculation rate in Figs. 3–5, respectively.

The magnitude of the interaction between the variables is reflected in the value of the coefficients of the single polynomial expression to fit the experimental data. The method for calculating the coefficients b_i and b_{ij}. After identifying the most important variables it is possible to construct Z-functions (Z=TOC the C-content of the solution in ppm of C) of a pair of experimental variables (X_i, X_j), via contour plots representing curves of constant response Z for the values (X_i, X_j) within the experimental region). In this way, it is possible to predict the optimum values of X_i, X_j that yield a minimum value of Z(TOC), i.e. the optimum numerical values for the parameters leading to the best degradation in terms of materials, time and energy. Contour plots giving the minima of the TOC achieved during photo-degradation are determined through Eq. (4) the modeling of the data function through an exponential

$$Y(\mathrm{TOC}) = b_0 \exp\left[s\left(\sum b_i X_i + \sum b_{ii} X_i^2 + \sum\sum b_{ij} X_i X_j\right)\right] \quad (4)$$

Each value of TOC can be calculated in Eq. (4) by way of the coefficients b_0, b_i, b_{ii} and b_{ij} with s as the scaling factor. Since different input variables had different dimensional units, their effect can only be compared, if they are coded [9,14]. The use of coded variables in the place of the input variables facilitates the construction of the experimental design.

3.4. Surface response methodology: exponential modeling of the Uniblue A degradation

Fig. 6 shows the contour plots obtained from the exponential model for the decrease of TOC(Y) during photo-degradation taking the pair of variables Fe^{3+}–H_2O_2. These plots were obtained by calculating the coefficients of Eq. (5) and drawing subsequently the contour for the

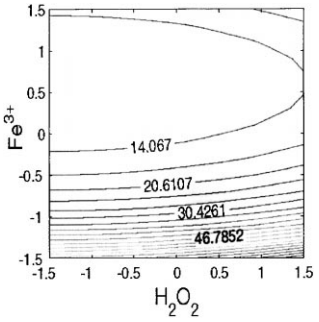

Fig. 6. Two dimensional contour plot obtained from the experimental data reported in Fig. 3 for the pair of variables Fe^{3+}–H_2O_2. The surface response modeling (SRM) followed a single exponential function.

Fe^{3+}–H_2O_2 pair of variables. The central region for the contour plots in Fig. 6 indicate the minimum value of the function TOC(Y).

Some chemical reactions and in particular photochemical reactions follow exponential or close to exponential behavior. An exponential expression to fit the experimental data reported in Figs. 3–5 renders an a function with an error much lower than when a single polynomial expression was used to fit the Uniblue A degradation data.

The exponential expression (4) can be linearized attaining the form

$$\ln(\text{TOC}) \text{ or } \ln Y = \ln b_0 + b_1X_1 + b_2X_2 + b_{11}X_{11}^2 + b_{22}X_{22}^2 + b_{12}X_1X_2 \quad (5)$$

Least-square regression analysis is applied and the exponential expression obtained for the pair H_2O_2–Fe^{3+} (from the data in Fig. 6) is

$$\ln Y = 2.58 + 0.86X_1 - 0.48X_2 + 0.029X_{11}^2 + 0.39X_{22}^2 \quad (6)$$

A maximal error of 1.19 was found. This error is the maximum deviation between the real data and the model and in relative terms is seen to be low.

Fig. 7 shows the contour plots obtained from the exponential model for the decrease of TOC(Y) during photodegradation taking the pair of variables recirculation H_2O_2. The TOC values (mg C/l) decrease from 28.1 to 4.9. Applying the treatment as above for the data in Fig. 6 but this time for the pair of variables shown in Fig. 7 the exponential expression for the pair recirculation H_2O_2 is

$$\ln Y = 3.04 + 0.49X_1 - 0.086X_2 - 0.41X_{11}^2 + 0.023X_{22}^2 \quad (7)$$

with a maximal error of 1.39.

Fig. 8 shows the same as in the preceding two paragraphs treatment for the Fe^{3+} recirculation pair. The TOC values

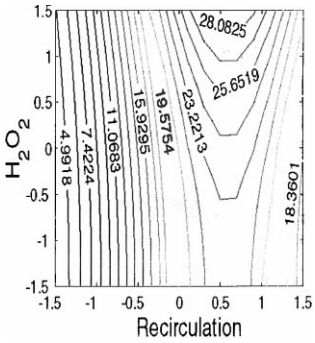

Fig. 7. Two dimensional contour plot obtained from the experimental data reported in Fig. 4 for the pair of variables recirculation H_2O_2. The surface response modeling (SRM) followed a single exponential function.

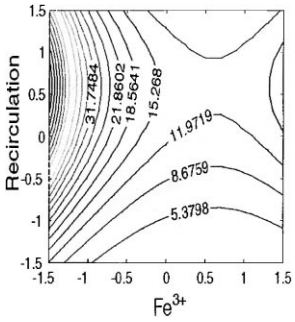

Fig. 8. Two dimensional contour plot obtained from the experimental data reported in Fig. 5 for the pair of variables recirculation Fe^{3+}. The surface response modeling (SRM) followed a single exponential function.

(mg of C/l) decrease from 31.74 to 5.38. The exponential expression for this pair is

$$\ln Y = 2.53 - 0.48X_1 + 0.48X_2 + 0.39X_{11}^2 - 0.41X_{22}^2 \quad (8)$$

with a maximal error of 1.38.

Fig. 9 indicates, the minimum value of Y(TOC)=5.38 (mg C/l) obtained from the equal value response curves common to the contour plots shown in Figs. 5–7. Fig. 9 is plotted from the intersection of the contour plots seeking the minima values in coded variables. This operation has been carried out with the experimental data related to the H_2O_2, recirculation and Fe^{3+} ion concentration. In this way it is possible to obtain the most suitable concentration range of H_2O_2, recirculation and Fe^{3+} ion concentration to attain the lowest TOC value within the 80 min reaction time.

Fig. 10 shows the plot of Fig. 9 but where the coded variables have been back transformed into the usual solution parameters with their respective dimensions. The back transformation of coded variables is carried out as outlined in Section 3.3. The modeling allows to predict the optimal range for the degradation of Uniblue A up to 5.38 mg C/l or ~15% of its initial value.

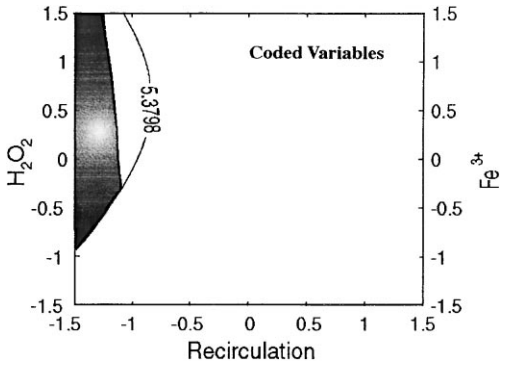

Fig. 9. Intersection of contour plots (exponential model) showing the region where the lowest TOC is attained as a function of the Fe^{3+} concentration, H_2O_2 concentration and reactor recirculation rate in coded dimensionless variables as used during the modeling.

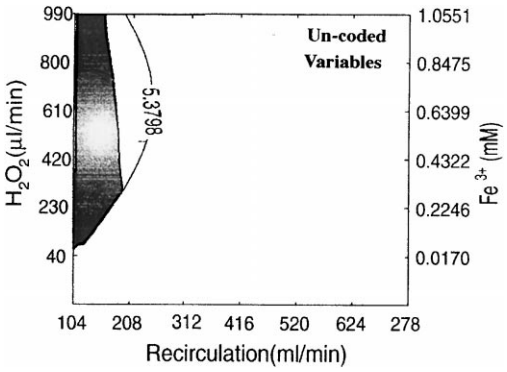

Fig. 10. Intersection of contour plots (exponential model) showing the region where the lowest TOC is attained as a function of the Fe^{3+} concentration, H_2O_2 concentration and reactor recirculation rate in un-coded variables.

4. Conclusions

A systematic study of the main variables affecting the decoloration/degradation of the reactive dye Uniblue A in a photo-reactor through Fenton photo-assisted reactions has been carried out. The experimental data for the TOC values as a function of time (for the three input variables) could be fit by single exponential expression. Statistical modeling enabled the construction of this single exponential with very low deviation from the experimental data. The model permits the minimization of the reaction time, amount of oxidant and electrical energy during reactor operation. The optimization of the two last parameters is of particular importance. They refer to chemicals and UV-photons used only for the shortest time during cost-effective reactor operation. The design methodology was successful in modeling complex processes occurring during the abatement of Uniblue A without the detailed knowledge of the reaction sequence. This allows to predict the optimal way to attain low *Y*(TOC) values for systems of three variables (this study). But this approach is also valid for a higher number of input variables. [14,15].

Acknowledgements

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