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Response surface optimization of the photocatalytic decolorization of a simulated dyestuff effluent

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Abstract

The experimental design methodology was applied for response surface modeling and optimization of the photocatalytic decolorization of a simulated dyestuff effluent (SDE), containing the azo dye Reactive Black 5 (RB5) as colorant. The variables considered were the initial concentration of TiO_2, Fe^{3+} and H_2O_2. The multivariate experimental design allowed developing a quadratic model as a functional relationship between color removal efficiency and the independent variables. Under the optimum conditions established, the performance of 99.3% for color removal was experimentally reached. It was found that all factors considered have an important effect in the degradation efficiency of the organic matter.

Keywords: Photocatalysis; Simulated dyestuff wastewater; Reactive Black 5; TiO_2; Response surface optimization

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1. Introduction

The textile industry is a worldwide water-pollution source. Considering the volume discharged and effluent composition, the wastewater generated from dyeing and finishing operations is rated as one of the most polluting among all industrial sectors. The industrial effluents arising from textile industry are strongly colored and it was stated that a total of 30% of the world production of dyes is lost during the dyeing process and is released in textile effluents. The releasing of the colored wastewaters in the ecosystems is a dramatic source of aesthetic pollution and perturbation in the aquatic life, and for this reason, the international environmental standards became more and more stringent. In order to be able to discharge the treated colored wastewaters into waters at a level that meets the discharge standards, apart of the degradation of the harmful compounds without causing secondary pollution, the removal of the color is an obligation. However, due to the complexity and variety of dyestuffs used for different purposes it is rather difficult to find out a unique treatment method that resulting effective degradation of all types of dyes [1–3].

During the last years, new and more severe regulations coupled with enforcement against wastewater discharges have been established in most of the industrial-developed countries. In order to meet with these new restrictions and due to ineffectiveness of conventional treatment methods, such as, adsorption, precipitation, chemical coagulation etc. in decolorization and organic content reduction of the textile wastewater, the research interest was directed towards finding alternative low-cost technologies for the on-site wastewater treatment, that are able to destroy the hazardous organic compounds, rather than transferring them to other media. Destructive oxidation methods, the so called Advanced Oxidation Processes (AOPs), such as heterogeneous photocatalysis (TiO_2/UV-A), ozonation, H_2O_2/UV-B, Photo-Fenton, etc. are able to transform hazardous pollutants into compounds with a more reduced impact on the environment, resulting so in a substantial solution of the detoxification of different kind of wastewater, exactly at the site where they are released [4].

Photocatalytic oxidation in the presence of semiconducting materials such as TiO_2, of organic compounds with environ-

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mental concern (e.g. pesticides, dyes, etc.), have been studied extensively during the last 20 years and it has been demonstrated that heterogeneous photocatalysis can be an alternative to conventional methods for the removal of organic pollutants from water and air [5–7]. The illumination of the TiO_2 particles with light energy greater than the bandgap energy of the semiconductor ($h\nu > E_g = 3.2\,eV$) produces excited high energy states of electron and hole pairs (e^-/h^+) that can migrate to the surface of the particle and initiate a wide range of chemical redox reactions. The photogenerated electrons react with the adsorbed molecular O_2 on the Ti(III)-sites, reducing it to superoxide radical anion $O_2{}^{\bullet -}$, while the photogenerated holes can oxidize either the organic molecules directly or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to $OH^\bullet$ radicals [8,9], which act as strong oxidizing agents. These can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading finally to their complete mineralization. The disappearance of these compounds could take place via formation of partially oxidized intermediates that could be even more toxic than the original pollutants. Additionally, an advantage of the photocatalytic process is its mild operating conditions and the fact that it can be powered by sunlight, thus reducing significantly the electric power required and therefore the operating costs [10].

On the other hand, Fenton reagent, a mixture of Fe salts and H_2O_2, is an attractive oxidative system, which produces in a very simple way $OH^\bullet$ radicals (Eq. (1)) for wastewater treatment, due to the fact that iron is a very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. Furthermore it was found that the reaction can be enhanced by UV–vis light (artificial or natural), producing additional $OH^\bullet$ radicals and leading to the regeneration of the catalyst (Eq. (2)) (Photo-Fenton reaction).

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

$$Fe^{3+} + H_2O + h\nu(< 450\,nm) \rightarrow Fe^{2+} + H^+ + OH^\bullet \qquad (2)$$

The photocatalytic degradation of different type of dyes has been studied using TiO_2 or the Photo-Fenton reagent in aqueous solutions under solar and UV-A irradiation [11–15]. The combination of both processes, as has been reported by other authors [16,17] leads to an enhancement of the removal rate of the pollutants, due to the fact that Fe^{3+} ions and H_2O_2 act as scanvengers of the electrons, which are photogenerated in the conduction band of TiO_2, avoiding so the electron–hole recombination, while the produced Fe^{2+} ions can participate again in the Fenton reaction (Eq. (1)).

In order to enhance the dyes degradation performance, an optimization approach such as response surface methodology (RSM) should be employed. Several works have proved that RSM is a powerful statistical tool for optimization of photocatalytic oxidation processes [18–22]. Therefore further investigation in this direction should be carried out in order to find out the optimal settings of reaction parameters useful to design properly the cleanup process at pilot or industrial scale. The RSM deals with multivariant experimental design strategy, statistical modeling and process optimization. According to RSM, the empirical statistical modeling provides the appropriate approximating relationship between the response and the factors to be optimized. Based on the developed model (objective function) the optimization methods are applied to find the optimal values of the process variables, that produce desirable values of the response.

The present paper provides data concerning the photocatalytic decolorization of a simulated dyestuff effluent, containing the azo dye Reactive Black 5 as colorant and a commercial available TiO_2 powder as catalyst. The optimization of the reaction parameters of the Reactive Black 5 (RB5) photodegradation was performed by response surface methodology and experimental design. The color removal efficiency was selected as the response for optimization and the functional relationship between the response and the most significant independent variables (factors) was established by means of experimental design. The most important factors employed into experimental design were TiO_2 dose and the initial concentrations of H_2O_2 and Fe^{3+}. In order to establish the proper ranges of the parameters for the experimental design, there were carried out some preliminary experiments concerning the decolorization of the SDE under various experimental conditions.

2. Experimental

2.1. Materials

TiO_2 P-25 of Degussa (anatase/rutile = 3.6/1, surface area $56\,m^2\,g^{-1}$ nonporous) were used for all heterogeneous photocatalytic experiments. All other reagent-grade chemicals, such as $FeCl_3 \cdot 6H_2O$, H_2O_2 etc., were purchased from Merck and were used without further purification.

The cotton synthetic wastewater (SDE) was made according to a recipe used for the dyeing of cotton fabrics and was of the following composition: $0.1\,g\,L^{-1}$ HCOOH, $0.33\,g\,L^{-1}$ Sequion, $5\,g\,L^{-1}$ Na_2CO_3, $2\,g\,L^{-1}$ NaOH, $70\,g\,L^{-1}$ NaCl and $1.8\,g\,L^{-1}$ Reactive Black 5 (RB5). Reactive Black 5, with the commercial name HBL, is an azo-dye named according to I.U.P.A.C 2-(*p*-amino-phenylsulfonyl) ethanol sulphate ester (H-acid) ($C_{26}H_{21}O_{19}S_6N_5Na_4$). Its molecular structure is presented in Fig. 1.

For the experiments conducted in this paper a diluted solution was used with an initial Reactive Black concentration of $70\,mg\,L^{-1}$ and an initial organic content expressed as COD, of $120\,mg\,L^{-1}$

2.2. Procedures and analysis

Experiments were carried-out in a closed Pyrex cell of 0.6 L capacity. Its lid was provided with ports for bubbling air needed for the reaction to take place. 0.5 L of the simulated SDE wastewater or just RB5 solutions containing the appropriate amount of the semiconductor powder were fed into the reactor. Before irradiation, the reaction mixture was premixed for 15 min under dark conditions in order to achieve the maximum adsorption of the dye onto the catalyst surface. Then the lamp was switched on to initiate the photocatalytic reaction and the stirring was main-

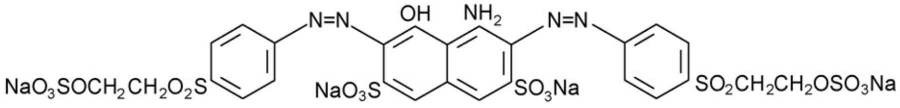

Fig. 1. Molecular structure of Reactive Black 5.

tained during irradiation. The irradiation was performed with a Radium, Ralutec, 9W/78, UV-A Lamp. The spectral response of the irradiation source according to the producer is ranged between 350 and 400, with a maximum at 365 nm and two additional weak lines in the visible region. The photon flow per unit volume of the incident light was determined by chemical actinometry using potassium ferrioxalate [23]. The initial photon flux, under exactly the same conditions as in the photocatalytic experiments, was evaluated to be 1.16×10^{-4} Einstein min^{-1}.

Specific quantities of samples were withdrawn at periodic intervals and filtered through a 0.45 μm filter (Schleicher and Schuell) in order to remove the catalyst particles. With the aim at assessing the extent of color removal, changes in the concentration of the dye were observed from its characteristic absorption band using a UV–vis spectrophotometer (Hitachi U-2000). Since a linear dependence between the initial concentration of the dye solution and his optical density at 585 nm was observed, the photodecomposition was monitored spectrophotometrically at this wavelength. All the photocatalytic experiments were performed at an initial pH value of 3.1. The pH values of the solution were monitored with a Metrohm pH-meter, while the reaction temperature was kept constant at $25 \pm 0.1\,^{\circ}\text{C}$.

2.3. Multivariate experimental design

The central composite experimental design (CCD) was used for the response surface modeling and optimization of the photodegradation process. The experimental factors take into consideration were as follow: the amount of the TiO_2 catalyst and the initial concentrations of the Fe^{3+} ions and H_2O_2. The operating ranges and the levels of the independent variables considered in this study are given in Table 1.

3. Results and discussion

3.1. Photocatalytic degradation of RB5

Results of the photolysis of the simulated dyestuff effluent containing $70\,\text{mg}\,\text{L}^{-1}$ RB5 under various experimental conditions are shown in Fig. 2. The amount of the RB5 in the supernatant, as determined from the spectrophotometric measurements, is plotted as a function of irradiation time. The disappearance of the 585 nm absorption band suggests that the chromophore responsible for the characteristic color of the dye is breaking down. Under these experimental conditions and in the presence of $1\,\text{g}\,\text{L}^{-1}$ TiO_2 P-25, ∼95% of the initial concentration of the dye was removed after 60 min of light exposure, while the addition of H_2O_2 in the suspension leads to an acceleration of the decolorization process. On the other hand, as can be seen in Fig. 2, the presence of H_2O_2 and Fe^{3+} in the TiO_2 suspension results to a superior enhancement of the decolorization rate, leading to a 100% color reduction in less than 5 min. The blank experiments, as can be seen also in Fig. 2, for either the illuminated SDE solution or the SDE suspension containing TiO_2 in the dark, showed that both illumination and the catalyst were necessary for the destruction of the dye. In the presence of the catalyst in the dark a maximum of 15% color reduction is achieved as a result of the adsorption of the dye onto the catalyst surface.

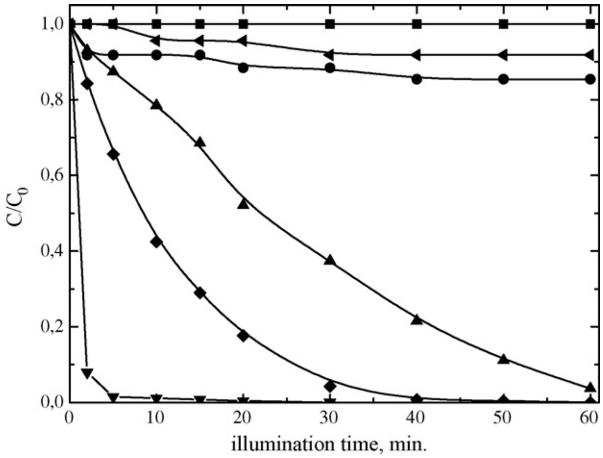

Fig. 2. Photocatalytic decolorization of a SDE solution containing $70\,\text{mg}\,\text{L}^{-1}$ RB5 under different experimental conditions: (■) photolysis without catalyst, (◀) $100\,\text{mg}\,\text{L}^{-1}$ H_2O_2 + UV-A, (●) $1\,\text{g}\,\text{L}^{-1}$ TiO_2, (▲) $1\,\text{g}\,\text{L}^{-1}$ TiO_2 + UV-A, (♦) $1\,\text{g}\,\text{L}^{-1}$ TiO_2 + UV-A + $100\,\text{mg}\,\text{L}^{-1}$ H_2O_2, (▼) $1\,\text{g}\,\text{L}^{-1}$ TiO_2 + UV-A + $56\,\text{mg}\,\text{L}^{-1}$ Fe^{+3} + $200\,\text{mg}\,\text{L}^{-1}$ H_2O_2.

TiO_2 dosage in slurry photocatalytic processes is an important factor that can influence strongly the degradation process.

Table 1
Predictor variables and their coded levels and actual values used for experimental design

Variable	Symbol	Real values of coded levels				
		$-\alpha$	-1	0	+1	$+\alpha$[a]
$[TiO_2]$ ($\text{g}\,\text{L}^{-1}$)	x_1	0.169	0.25	0.625	1	1.081
$[Fe^{+3}]_0$ ($\text{mg}\,\text{L}^{-1}$)	x_2	1.732	7	31.5	56	61.267
$[H_2O_2]_0$ ($\text{mg}\,\text{L}^{-1}$)	x_3	135.5	200	500	800	864.5

[a] $\alpha = 1.215$ (star or axial point for orthogonal CCD in the case of three independent variables).

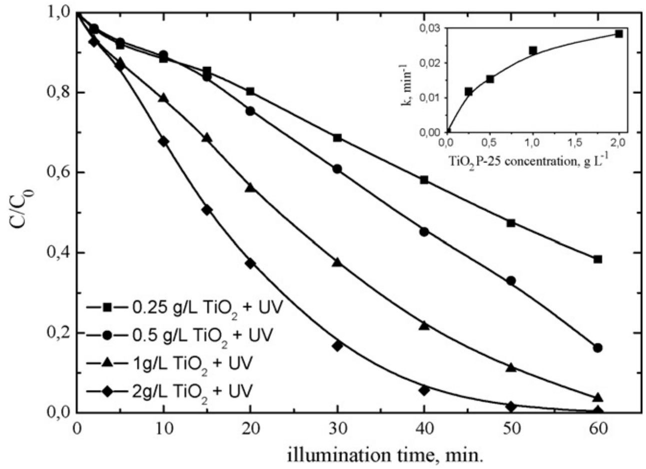

Fig. 3. Photocatalytic decolorization of a SDE solution containing 70 mg L^{-1} RB5 under different concentrations of TiO_2 P-25: (■) 0.25 g L^{-1}, (●) 0.5 g L^{-1}, (▲) 1 g L^{-1}, (◆) 2 g L^{-1}. Inset graph: rate constant (*k*) versus the concentration of TiO_2 P-25 catalyst.

The optimum quantity depends on the nature of the organic compound, as well as the photoreactor's geometry [24]. In our case, as it is presented in Fig. 3, the optimum concentration of the TiO_2 P-25 required for removal of the color of a 70 mg L^{-1} Reactive Black 5 in the SDE solution was examined by varying the catalyst amount from 0.25 to 2 g L^{-1}, while in the inset of Fig. 3 the pseudo first order rate constant of the decolorization, *k*, as a function of the TiO_2 P-25 concentration is presented. As the TiO_2 P-25 concentration increases from 0.25 to 2 g L^{-1} the photocatalytic efficiency of the decolorization increases. The curve is reminiscent of a Langmuir type adsorption isotherm for which the rate of decolorization reaches a saturation value at high TiO_2 concentrations. Increasing further the amount of TiO_2 leads to an aggregation of the catalyst particles causing a decrease in the number of active sites and to an enhancement of the light reflectance and consequently to a decrease in the efficiency of the photodegradation of RB5.

3.2. Influence of H_2O_2 addition on the photocatalytic process

The addition of other powerful oxidizing species such as hydrogen peroxide (H_2O_2) and potassium peroxydisulfate ($K_2S_2O_8$) to TiO_2 suspensions is a well known procedure and in many cases leads to an increase in the rate of photooxidation [25–27].

In our case the photocatalytic degradation of 70 mg L^{-1} RB5 in SDE in the presence of 1 g L^{-1} TiO_2 P-25 has been studied at different H_2O_2 concentrations. The reaction kinetics was similar to those observed without the oxidants.

The role of H_2O_2 in the process of photocatalytic degradation is dual. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation, Eq. (3), and it also forms OH$^\bullet$ radicals via superoxide according Eq. (4), while a possible reaction of H_2O_2 with the photogenerated intermediates cannot be excluded.

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \qquad (3)$$

$$H_2O_2 + O_2{}^- \rightarrow OH^\bullet + OH^- + O_2 \qquad (4)$$

In the presence of excess H_2O_2, it may act as a hole or OH$^\bullet$ scanvenger or react with TiO_2 to form peroxo compounds, which are detrimental to the photocatalytic action. It can also compete with the organic compound for the adsorption sites on the catalyst surface, resulting in a "chromatographic peaking effect" of the pollutant concentration in the solution during the initial stages of the photocatalytic process [28,29]. This explains the need for an optimal concentration of H_2O_2 for the maximum effect.

The effect of the amount of H_2O_2 on the decolorization efficiency of a SDE solution containing 70 mg L^{-1} RB5 is shown in Fig. 4. An increase in the concentration of H_2O_2 from 25 to 200 mg L^{-1} leads to an increase in the photocatalytic activity, while higher concentrations of H_2O_2 result to an inhibition of the decolorization. In inset of Fig. 4 the pseudo first order rate constant, *k*, calculated for the first 10 min of reaction, as function of the H_2O_2 concentration is presented. As can be seen *k* increases with increasing the oxidant concentration until of 200 mg L^{-1}, while above it a slightly decrease of the decolorization takes place. Under the given experimental conditions, the addition of hydrogen peroxide accelerates the decolorization rate by a factor of 4.

3.3. Optimization of the decolorization process

3.3.1. Response surface methodology and experimental design

A 2^3-factorial central composite experimental design, with six axial points ($\alpha = 1.215$) and two replications at the center point ($n_0 = 2$) leading to a total number of 16 experiments (Table 2) was employed for response surface modeling. The

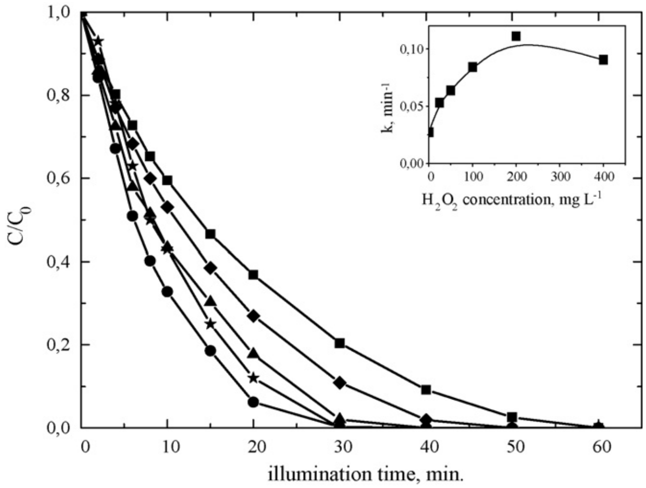

Fig. 4. Effect of H_2O_2 concentration on the photocatalytic decolorization of a SDE solution containing 70 mg L^{-1} RB5 in the presence of 1 g L^{-1} TiO_2: H_2O_2 (■) 25 mg L^{-1}, (◆) 50 mg L^{-1}, (▲) 100 mg L^{-1}, (●) 200 mg L^{-1}, (★) 400 mg L^{-1}. Inset graph: rate constant (*k*) versus the concentration of H_2O_2.

Table 2
Central composite design and experimental results

Run N & type[a]	Input variables	Response						
		[TiO_2], g/L	Level x_1[b]	[Fe^{+3}]$_0$, mg L^{-1}	Level x_2[b]	[H_2O_2]$_0$, mg L^{-1}	Level x_3[b]	Color removal efficiency (Y) % after 4 min
1	O1	1	1	56	1	800	1	98.917
2	O2	0.25	−1	56	1	800	1	97.216
3	O3	1	1	7	−1	800	1	96.255
4	O4	0.25	−1	7	−1	800	1	89.494
5	O5	1	1	56	1	200	−1	98.549
6	O6	0.25	−1	56	1	200	−1	85.620
7	O7	1	1	7	−1	200	−1	91.621
8	O8	0.25	−1	7	−1	200	−1	88.094
9	S1	1.081	α	31.5	0	500	0	98.854
10	S2	0.169	$-\alpha$	31.5	0	500	0	94.574
11	S3	0.625	0	61.267	α	500	0	98.549
12	S4	0.625	0	1.732	$-\alpha$	500	0	64.660
13	S5	0.625	0	31.5	0	864.5	α	99.282
14	S6	0.625	0	31.5	0	135.5	$-\alpha$	94.223
15	C1	0.625	0	31.5	0	500	0	98.176
16	C2	0.625	0	31.5	0	500	0	98.890

[a] O: orthogonal design points, C: center points, S: star or axial points.

[b] −1 = low value, 0 = center value, +1 = high value, +/−α = star point value.

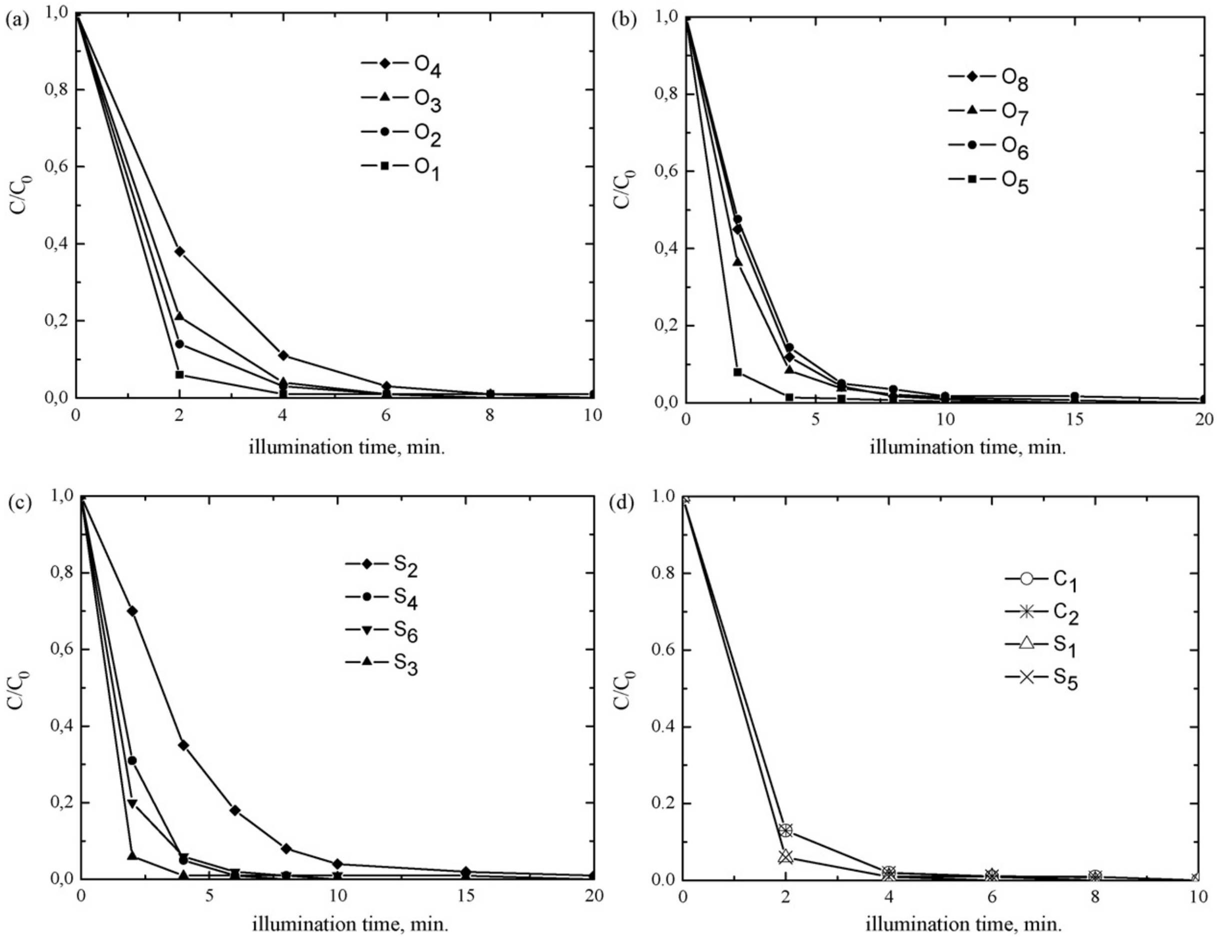

Fig. 5. Photocatalytic decolorizaton of a SDE solution (notations are depicted in Table 2).

operational initial conditions were planned according to experimental design and the kinetic of photocatalytic decolorization of the SDE solution was determined according to planned conditions. The kinetic curves of photocatalytic decolorization are reported in Fig. 5. As response for optimization the color removal efficiency Y (%) was considered being calculated by the following expression:

$$Y = \frac{C_0 - C_t}{C_0} \times 100 \tag{5}$$

where C_0 (mg L^{-1}) is the initial concentration of the dye in the SDE solution and C_t (mg L^{-1}) is the concentration of the dye in the solution after t minutes of UV-A exposure.

The experimental results of color removal efficiency Y (%) have been determined according to planned initial conditions and are reported in the last column of Table 2.

From Fig. 5D, it can be observed a very good concordance between the repeated experiments C1 and C2. Also the values of S1 and S5 experiments are very close. It is observed that the influences of $[TiO_2]$ and $[H_2O_2]_0$ over the objective function are similar. This could be explained tacking into consideration the similar responses obtained for both factors at the same variation level from planned experiments.

By means of Multi Linear Regression method [30,31] a quadratic regression equation was developed based on statistical experimental design. The significance of all regression coefficients was checked by means of Student's t-test. The final regression model in terms of coded factors is presented as follows:

$$\hat{Y} = 93.66 + 2.75x_1 + 5.114x_2 + 2.205x_3 + 3.079x_1^2 - 7.165x_2^2 + 3.105x_3^2 \tag{6}$$

subjected to $-\alpha \le x_j \le +\alpha\ j = 1, 2, 3\ (\alpha = 1.215)$.

In terms of actual factors the color removal efficiency is expressed by following regression equation:

$$\hat{Y} = 84.16 - 20.036[TiO_2] + 0.961[Fe^{3+}]_0 - 0.027[H_2O_2]_0 + 21.895[TiO_2]^2 - 0.012[Fe^{3+}]_0^2 + 3.45 \times 10^{-5}[H_2O_2]_0^2 \tag{7}$$

subjected to $0.169 \le [TiO_2] \le 1.081$ [mg L^{-1}]; $1.732 \le [Fe^{3+}]_0 \le 61.267$ [mg L^{-1}] and $135.5 \le [H_2O_2]_0 \le 864.5$ [mg L^{-1}];

The goodness-of-fit of the regression model can be ascertained by applying the Fischer F-test, i.e. by computing F_{Calc} as the ratio between the residual variance SS_{Res} and replication variance SS_{Rep} [30]:

$$F_{\mathrm{Calc}} = \frac{SS_{\mathrm{Res}}}{SS_{\mathrm{Rep}}} \tag{8}$$

Thus, it was obtained $F_{\mathrm{Calc}} = 194.3$ and for a significance level $p = 0.05$ and degrees of freedom $f_1 = 8$ and $f_2 = 1$ the tabulated value is $F_{\mathrm{Tab}} = 238.9$. Since $F_{\mathrm{Calc}} < F_{\mathrm{Tab}}$, the regression mathematical model is a good fit to experimental data. The parity plot showed a satisfactory correlation between the values of experimental data and predictive values (Fig. 6).

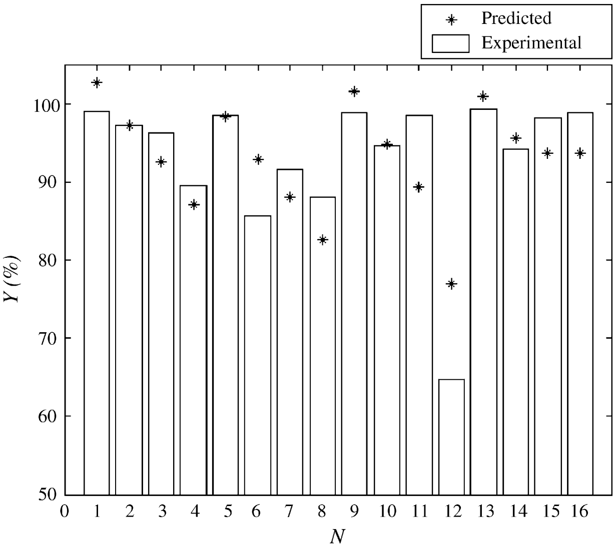

Fig. 6. Comparison between experimental and predicted values of the color removal efficiency.

Figs. 7–9 represent the isoresponse contour and surface plots of the response variable as a function of independent variables. The effects of $[Fe^{3+}]_0$ upon the color removal efficiency are shown in Figs. 7 and 8. As can be seen an increase of $[Fe^{3+}]_0$ up to the value of about 40 mg L^{-1} led to increasing of color removal efficiency and for a further increase of $[Fe^{3+}]_0$ the trend is reversed. The effects of the $[TiO_2]$ and $[H_2O_2]_0$ (Figs. 7–9) indicate that the increasing of color removal efficiency became relevant and gradual for $[TiO_2] > 0.45$ g L^{-1} and $[H_2O_2]_0 > 500$ mg L^{-1}.

3.3.2. *Canonical analysis of the response surface*

The canonical analysis is used to examine the estimated regression model in order to determine the coordinates of stationary point and the nature of this. For this reason the response surface model should be reduced to its canonical form [30,31]:

$$\hat{Y} - \hat{Y}_S = \lambda_1\omega_1^2 + \lambda_2\omega_2^2 + \lambda_3\omega_3^2 \tag{9}$$

where ω_1, ω_2 and ω_3 are a new set of axes called the principal axes or canonical axes with the origin into the stationary point (S-center); $\hat{Y}_S$ is the center of the contours, that is the value of the objective function in stationary point. The canonical coefficients λ_1, λ_2, and λ_3 give the shape of the surface (they are the eigen values of a matrix of second-order coefficients). The stationary point was determined by vanishing first derivatives of the objective function. It was ascertained the following stationary point in coded variables $\bar{x}_S = \{-0.447 \quad 0.357 \quad -0.355\}^T$ being located inside of the valid region and the value of the objective function in this point is $\hat{Y}_S = 93.567$. The canonical form of the response surface model in our case become as follows:

$$\hat{Y} - 93.567 = 3.079\omega_1^2 - 7.165\omega_2^2 + 3.105\omega_3^2 \tag{10}$$

Since the canonical coefficients have unlike signs the response surface is a hyperbolic paraboloid and there is a saddle-

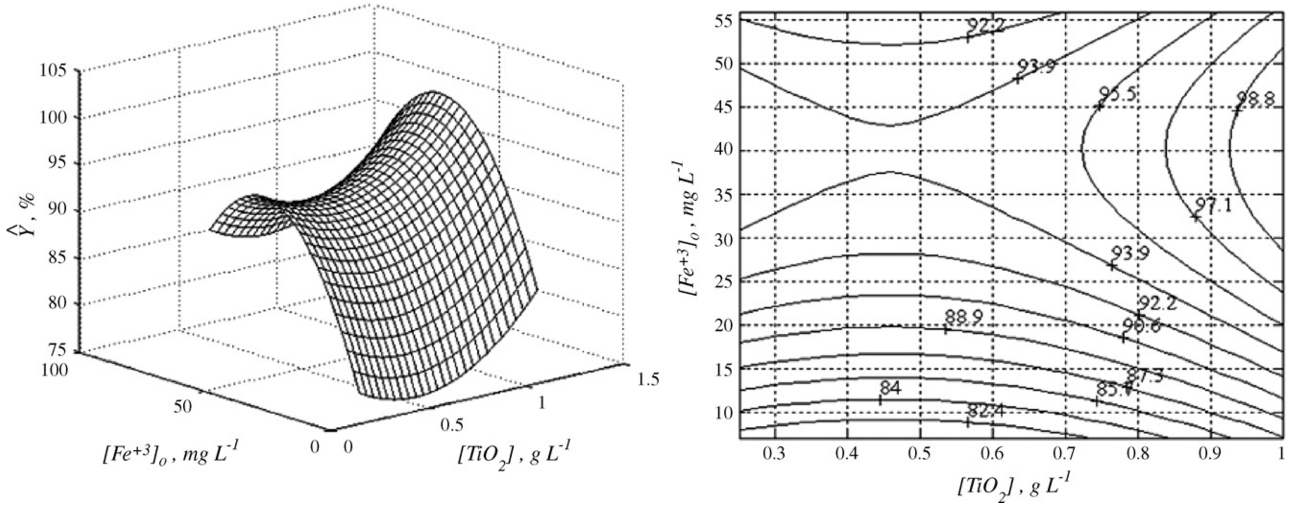

Fig. 7. The response surface plot and contour-line plots of the predicted reaction rate as the function of initial concentrations of $[Fe^{3+}]_0$ and $[TiO_2]$ for $[H_2O_2]_0 = 500\,mg\,L^{-1}$ and $[RB5]_0 = 70\,mg\,L^{-1}$.

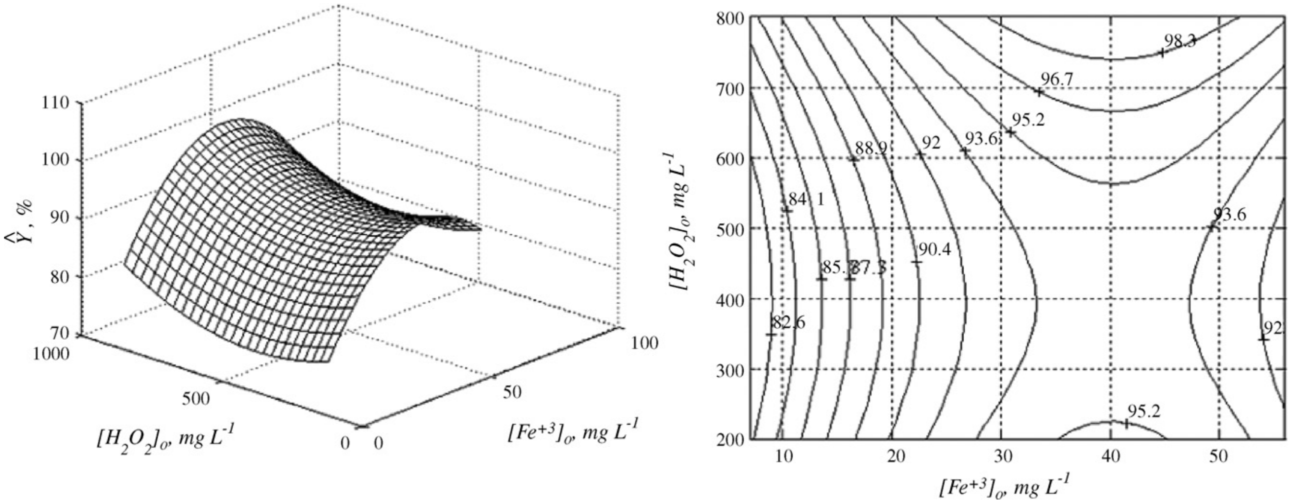

Fig. 8. The response surface plot and contour-line plots of predicted reaction rate as the function of initial concentrations of $[Fe^{3+}]_0$ and $[H_2O_2]_0$ for $[TiO_2] = 0.625\,g\,L^{-1}$ and $[RB5]_0 = 70\,mg\,L^{-1}$.

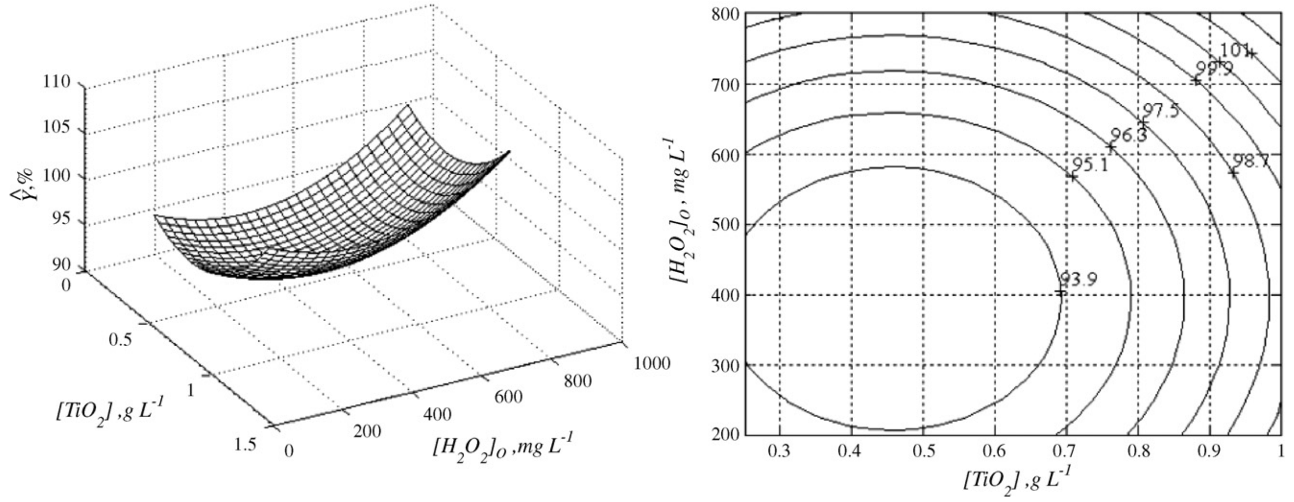

Fig. 9. The response surface plot and contour-line plots of predicted reaction rate as the function of initial concentrations of $[TiO_2]$ and $[H_2O_2]_0$ for $[Fe^{3+}]_0 = 31.5\,mg\,L^{-1}$ and $[RB5]_0 = 70\,mg\,L^{-1}$.

Table 3
The optimal conditions for color removal efficiency

x_1*	$[TiO_2]$* $(g\,L^{-1})$	x_2*	$[Fe^{3+}]_0$* $(mg\,L^{-1})$	x_3*	$[H_2O_2]_0$*, $(mg\,L^{-1})$	Y* (%) Experiment	Y* (%) Predicted
−0.447	0.458	0.357	40.243	1.0843	825.3	99.301	100

* Parameter value under optimal conditions.

point at the stationary point. The saddle-point is also known in RSM literature as "minimax" point [30].

In order to ascertain the feasible optimal point, the response surface was explored in canonical coordinates in the region of the stationary point by moving upon axis direction of maximum positive canonical coefficient. The displacement from the S-center upon the direction of ω_3 axis led to improving of the objective function. Thus, to find the maximum degree of color removal the minimax point should be leave by moving along the canonical axis ω_3 giving the following conditions: $\hat{Y} > \hat{Y}_S$ and $\omega_1 = 0$, $\omega_2 = 0$, in this situation the standard equation becomes:

$$\omega_3 = \sqrt{\frac{\hat{Y} - \hat{Y}_S}{\lambda_3}}, \quad \omega_1 = 0, \quad \omega_2 = 0 \tag{11}$$

The Eq. (11) was solved for $\hat{Y} = 100$ and checking the condition $-\alpha \le x_i \le \alpha$ $(i = 1, 2, 3)$ to be satisfied.

3.3.3. *Experimental validation of the optimum solution*

The feasible optimum solution found by canonical analysis is shown in Table 3 in coded and actual variables. The optimal point is located into the region of experimentation. A confirmation run was carried out and the process performance obtained under these optimal conditions represents the best experimental photodegradation efficiency (>99.3%).

4. Conclusions

In this study the photocatalytic decolorization of a simulated dyestuff effluent, containing RB5 as colorant, was investigated, focusing on the influence of some parameters such as, TiO_2, Fe^{3+} and H_2O_2 concentration. The multivariate experimental design allowed developing a quadratic model as a functional relationship between color removal efficiency and the independent variables. The Response Surface Methodology is a suitable approach to determine easily the factor effects with considerably less experimental effort, as well as to facilitate process modeling and to find the optimum. In the present study the RSM together with CCD were used to find the significance of factors at different levels. A satisfactory goodness-of-fit was observed between the predicted and experimental results, that reflected the applicability of RSM to optimize the process for the simulated dyestuff effluent decolorization.

The optimal conditions of photocatalytic decolorization are the following: $[TiO_2] = 0.458\,g\,L^{-1}$, $[H_2O_2]_0 = 825{,}3\,mg\,L^{-1}$, and $[Fe^{3+}] = 40.243\,mg\,L^{-1}$. Under these conditions the color removal efficiency was of 99.30% being the best experimental point determined into the region of experimentation. Also it was noted that the most significant factor that influence the color removal efficiency is the initial concentration of Fe^{3+} ions. The increasing of this factor leads to increasing of the response till the above mentioned optimal value of $40.243\,mg\,L^{-1}$ is reached. Further increasing of this factor leads to decreasing of efficiency of decolorization. The influence of the TiO_2 and H_2O_2 concentration on the response is comparable between them, but lesser than the influence of the Fe^{3+}. The optimal solution obtained using RSM was experimentally validated.

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