Optimized photocatalytic degradation of Alcian Blue 8 GX in the presence of TiO$_2$ suspensions

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Abstract

The photocatalytic degradation of Alcian Blue 8 GX, a cationic copper phthalocyanine dye, has been investigated in aqueous suspensions containing the commercial catalyst TiO$_2$ P-25. The photodegradation of the organic molecule follows approximately a pseudo-first kinetic order, according to the Langmuir–Hinshelwood model. The effect of catalyst concentration, pH of the initial solution and the H$_2$O$_2$ concentration upon the reaction rate was ascertained. It was shown that the photocatalytic degradation reaction can be mathematically described as a function of parameters such as pH, H$_2$O$_2$ concentration and irradiation time, being modeled by the use of the response surface methodology. Optimized values for oxidizing agent, concentration, pH and UV exposure time for the studied system were determined.
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1. Introduction

The release of the colored wastewaters into the ecosystems is a dramatic source of aesthetic pollution and perturbation in the aquatic life, and for this reason, the international environmental standards (ISO 14001, October 1996) concerning the discharge of the colored effluents became more and more stringent. Directive 91/271/CEE foresees values of minimum 70–90% BOD reduction and, minimum 75% COD reduction, respectively, for the discharged municipal treated wastewater. At the same time, in the case of industrial wastewaters that are not evacuated together with the municipal one, are imposed the same treatment conditions as for the latter.

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, this becoming subject of environmental regulations since it is often linked to aquatic toxicity and lower DO (dissolved oxygen) values in receiving streams (US Environmental Protection Agency, 1996).

However, due to the complexity and variety of dyes used for different purposes, as well as their non-biodegradability, it is rather difficult to find a unique treatment method that would result in effective degradation of all types of dyes.

Apart of those dyes used in textile industries, some dyes, called also biological stains, such as Eosin Y, Auramine O, Hematoxylin, Rose Bengal, Alcian Blue, etc. are widely used in biomedical research laboratories and also for diagnostic purposes. Some of these stains are known to be toxic or mutagenic for human and animals [1,2].

Although the volume of the stain solutions used in this kind of laboratories is relatively small, the very high concentration of dyes inside them (i.e. ∼10,000 ppm eosin Y or 5000 ppm rhodamine B in auramine–rhodamine fluorescence solution [3]) results in the formation of wastewaters with high toxicity, low light transparency and high content in organic carbon. According

to our knowledge, the methodology that is mainly used for the removal of these biological stains from their solutions is their sorption either on activated carbon or on a polymeric resin (i.e. Amberlite XAD-16). However the problem is not solved with these methods but is just moved from the liquid to the solid phase. In addition, the recovery efficiency is not the same for all biological stains and, in some cases, a large amount of adsorbent is necessary for their complete removal [1].

The ineffectiveness of the conventional methods for color removal led to the necessity to develop other efficient wastewater treatment processes. Destructive oxidation methods such as heterogeneous photocatalysis (TiO₂/UV-A), ozonation, H₂O₂/UV-B, photo-fenton, sonolysis, etc. are considered very attractive since they transform hazardous pollutants into compounds with a more reduced impact on the environment and are also very effective in destruction of chromophoric structures of the dyes, considering the fact that color removal is an important factor also for water recycling [4–11].

Our present study provides results describing the photocatalytic decolorization and oxidation of Alcian Blue 8 GX, a phthalocyanine dye over semiconducting powders such as TiO_2 under various experimental conditions. Alcian Blue 8 GX is used as counterstain in routine staining of histological tissue sections or as binding assay for the in situ quantification of marine biofilms produced by marine bacteria [12,13]. Its structure is presented below (CAS 33864-99-2):
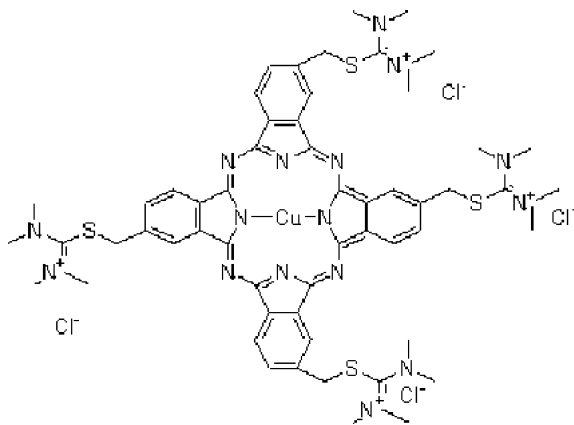
The heterogeneous photocatalytic oxidation process consists in illumination of particles of semiconducting materials, such as titanium dioxide, with light energy higher that their band gap energy resulting in appearance of excited high energy states of electron and holes pairs that can migrate to the surface of the particles and initiate a wide range of redox reactions [14,15]. These reactions could lead to complete destruction of the pollutant. To optimize the kinetic of the process, a series of parameters such as catalyst and oxidizing agent concentrations, as well as pH, were studied.

Additionally, an experimental factorial design of the photocatalytic system was used to find the optimal conditions for enhancing the degradation of the studied dye. With this purpose, the following variables were simultaneously changed: initial pH of solution, concentration of H₂O₂ used as oxidizing agent and irradiation time, while catalyst concentration was maintained constant.

2. Experimental

2.1. Reagents

Alcian Blue 8 GX ($C_{56}H_{68}Cl_4CuN_{16}S_4$, $M_W = 1299$), product of Sigma–Chemie GmbH, was used as received. TiO₂ P-25 Degussa (anatase/rutile = 3.6/1, surface area 56 m² g⁻¹) was used for all the photocatalytic experiments, except were otherwise mentioned in the text. TiO₂-A (100% Anatase, 10 m² g⁻¹) and ZnO (10 m² g⁻¹) were purchased from Merck.

2.2. Procedures and analysis

Experiments were carried-out in a closed Pyrex cell of 500 ml capacity, provided with ports, at the top, for bubbling air necessary for the reaction to take place. The reaction mixture was maintained as suspension by magnetic stirring. Previously to irradiation, the reaction mixture was left 30 min in the dark with the aim at achieving the maximum adsorption of the dye onto the semiconductor catalyst surface. The irradiation was performed with a 9 W central lamp. The spectral response of the irradiation source (Osram Dulux S 9 W/78 UV-A) according to the producer is ranged between 350 and 400 nm with a maximum at 366 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 [16]. The initial light flux, under exactly the same conditions as in the photocatalytic experiments, was evaluated to be 7.16×10^{-4} einstein L⁻¹ min⁻¹.

In all cases, during the experiments, 450 mL of Alcian Blue solution containing the appropriate amount of semiconducting powder was magnetically stirred before and during irradiation. 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 Shimadzu UV-160A.

Since a linear dependence between the initial concentration of the Alcian Blue solution and its optical density at 609 nm was observed, the photodecomposition was monitored spectrophotometrically at this wavelength. For alteration of pH in the acid and alkaline area, solutions of H₂SO₄ 0.1N and NaOH 0.1N, respectively, were used. The pH values of the solution were monitored with a Metrohm pH-meter, while the reaction temperature was kept constant at $25 \pm 0.1\,^{\circ}$C.

3. Results and discussion

3.1. Kinetics of photocatalytic degradation of Alcian Blue 8 GX

At first, experiments concerning the photocatalytic oxidation of Alcian Blue 8 GX were accomplished in the presence of different semiconductor catalysts.
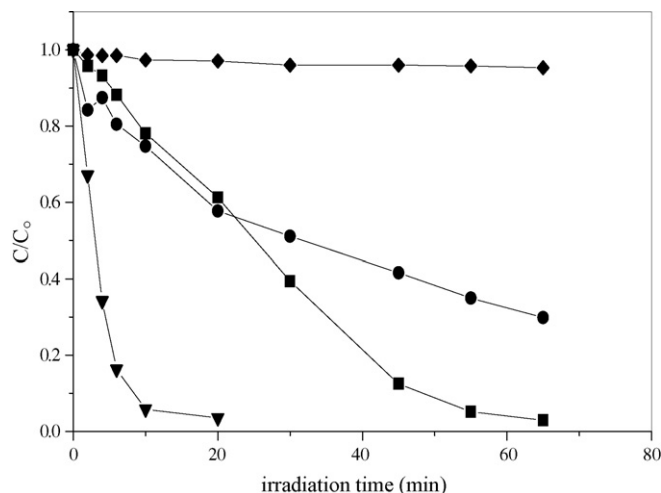
Fig. 1. Photocatalytic degradation of 40 mg L^{-1} Alcian Blue 8 GX as a function of irradiation time in the presence of (■) 0.5 g L^{-1} TiO$_2$ P-25, (●) 0.5 g L^{-1} TiO$_2$-A, (▼) 0.5 g L^{-1} ZnO and (♦) UV-A light, no catalyst.

Results of the photolysis of a 40 mg L^{-1} (0.307 × 10^{-4} M) dye solution containing 0.5 g L^{-1} either TiO$_2$ P-25, TiO$_2$-A or ZnO are depicted in Fig. 1, where the amount of the organic molecule present in the supernatant is plotted as a function of irradiation time. Among these ones, ZnO and TiO$_2$ P-25 exhibited the best results. Under the experimental conditions and in the presence of 0.5 g L^{-1} TiO$_2$ P-25, approximately 96% of the initial concentration of the dye was removed after 65 min, while in the presence of ZnO, the degradation was almost complete after 15 min of irradiation. The degradation in the presence of TiO$_2$-A is a slower process, considering the fact that after 65 min of irradiation, around 35% of the initial concentration remained in solution when this catalyst was used.

On the other hand, direct UV-A light irradiation was insufficient to decolorize the dye solution, a very small decrease in the concentration of the dye being achieved in the absence of any catalyst. This shows that photocatalytic degradation is not in concurrence with direct photolysis.

Although ZnO proved to exhibit the best photocatalytic activity under the given experimental conditions, it is not allowed to be used due to his corrosion/photocorrosion which leads additionally to enhance of the toxicity of the solution [17].

Considering the better performances of the Degussa P-25 toward the anatase catalysts, as well as its stability and resistance to corrosion and photocorrosion in comparison to ZnO, the first was chosen for further experiments.

The effect of varying the quantity of TiO$_2$ P-25 on the observed photodegradation of 40 mg L^{-1} Alcian Blue 8 GX is presented in Fig. 2.

The optimum concentration of TiO$_2$ P-25 required for the decolorization of a 40 mg L^{-1} Alcian Blue 8 GX solution was examined in slurry method by varying the catalyst amount from 0.25 to 4 g L^{-1}. The results revealed that the incident photons were completely absorbed when the TiO$_2$ concentration increased to 0.5 g L^{-1}.

It is obvious that the rate increases with an increase of the amount of catalyst up to a level corresponding to the optimum
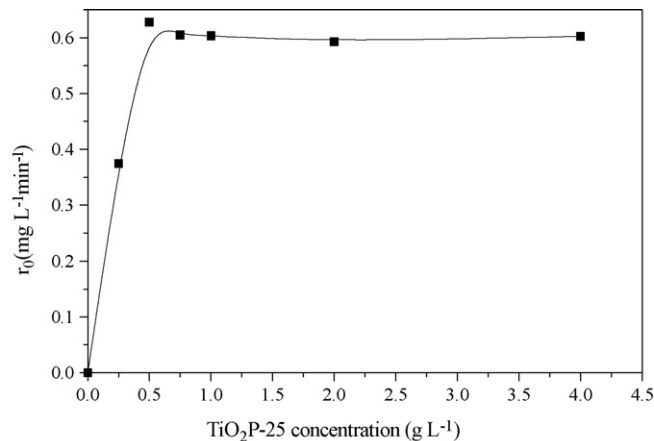

Fig. 2. Dependence of the initial reaction rate (r_0) on the concentration of TiO$_2$ P-25 for constant dye concentration (40 mg L^{-1}).

of light absorption. Above this value the suspended particles of the catalysts block the UV-light passage and increase the light scattering [18–21]. Thus, any further increase of the amount of the catalyst will have no effect on the photodegradation efficiency.

The initial degradation rate of most organic pollutants is described by the Langmuir–Hinshelwood model, developed by Turchi and Ollis [22] and accepted by a great number of researchers. Langmuir–Hinshelwood rate expression has been used with success for determining the relationship between the initial degradation rate and the concentration of the organic substrate in the case of the reactions occurring at the solid–liquid interface within the heterogeneous photocatalytic processes and is expressed by the equation:

$$r_0 = -\frac{dC}{dt} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \tag{1}$$

where r_0 is the initial rate of disappearance of the organic substrate, C_{eq} the equilibrium bulk-solute concentration, K the equilibrium constant for adsorption of the organic molecule onto catalyst and k_r is the reaction rate constant, which reflects the limiting rate of reaction at the maximum coverage under the given experimental conditions. A standard mean of using this equation is to demonstrate linearity of the data when plotted as the inverse initial rate versus the inverse initial concentration:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K} \frac{1}{C_{eq}} \tag{2}$$

Due to the fact that Alcian Blue 8 GX is strongly adsorbed on the TiO$_2$ P-25 surface the equilibrium concentration of the dye (C_{eq}), instead the initial one (C_0), was used in the kinetic study [23].

The effect of altering the equilibrium concentration of the dye on the initial reaction rate (r_0) of the photocatalytic degradation is shown in Fig. 3. The curve is reminiscent of a Langmuir type isotherm, for which the rate value of decomposition increases sharply until it reaches a saturation value. The r_0 values were independently obtained by a linear fit of
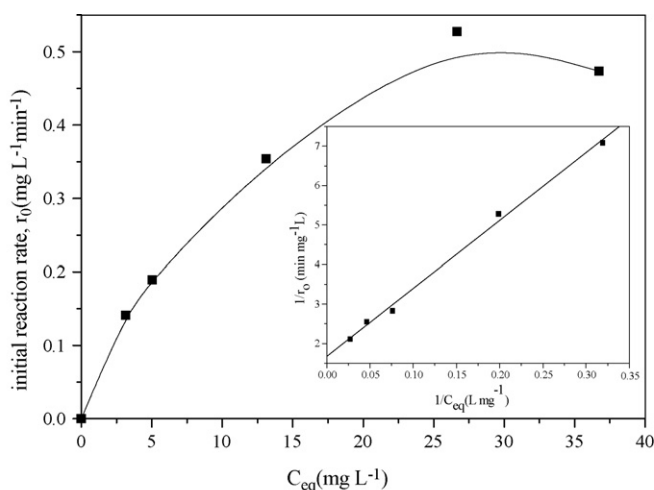
Fig. 3. Plot of r_0 vs. C_{eq} for Alcian Blue 8 GX at different initial concentrations. The inset shows the linear transform of r_0^{-1} vs. C_{eq}^{-1} according to Eq. (2).

the data $C_{eq} - t$ in the range of 5–50 mg L^{-1} initial pollutant concentration.

Only the experimental data obtained during the first 10 min of irradiation were considered in calculus of the initial reaction rate with the aim at minimizing the variations resulted from the competitive effects of intermediates, pH changes etc. It is well known that the intermediate products formed during the photocatalytic degradation furthermore undergo photooxidation, which leads to changes in the initial conditions.

The dependence of $1/r_0$ values on the respective inverse equilibrium concentrations for constant concentration of TiO$_2$ P-25 (0.5 g L^{-1}), is shown in inset of Fig. 3. The k_r and K values calculated according to Eq. (2) from the slope of the straight line ($R^2 = 0.99$) and from the intercept with the $1/r_0$ axis were $k_r = 0.6$ mg L^{-1} min^{-1} (4.6×10^{-6} M min^{-1}) and $K = 0.097$ mg^{-1} L (1.19×10^4 M^{-1}), respectively.

Researches conducted with many types of organic pollutants shown that the dark adsorption equilibrium constants are, generally, different of adsorption constants determined by Langmuir–Hinshelwood kinetic model [24,25]. Moreover, the virtual meanings of parameters k_r and K have not been clarified [26–28]. The different values of adsorption constants in the two cases may owe to the changes appeared in the adsorbing sites onto the catalyst surface under illumination but neither the possibilities of significant photoadsorption and/or occurring of reaction steps in the double layer can be excluded. Studies shown that the adsorption constant K is a function of the light intensity [29,30] and the electronic properties of the TiO$_2$ surface will undergo dramatic changes upon illumination, altering the adsorption sites, as well [31].

In the case of the Alcian Blue 8 GX, the comparison between the results achieved within dark period and those obtained by applying the Langmuir–Hinshelwood model could not have been done since a correct approach of the dark adsorption kinetic was not possible due to extremely fast dye adsorption onto the catalyst surface (above 40% of the dye was adsorbed in 30 s of dark pre-equilibration in most of the cases, even at very low concentrations of catalyst).

3.2. Influence of initial pH on photocatalytic degradation process

The influence of the initial pH of the dye solution on the photodegradation of Alcian Blue 8 GX was studied, considering that pH is one of the most important parameters for the photocatalytic process.

The properties of the solid/electrolyte interface, i.e. the electrical double layer, are modified as the pH of the medium changes and, consequently, the effectiveness of the adsorption/desorption processes and the separation of the photogenerated electron–hole pairs are also substantially affected. The effect of pH on the photocatalytic reaction can be mainly explained by the surface charge of TiO$_2$ (point of zero charge, pzc, of TiO$_2 \sim 5.6$) and its relation to the protonation of the amino groups in Alcian Blue 8 GX. The adsorption of Alcian Blue 8 GX onto the TiO$_2$ surface in the dark is probably the first step and determines the efficiency of the photooxidation. The extent of adsorption of the electron donor onto the surface of TiO$_2$ due to the variation in pH appeared to play a more important role in the resultant photodegradation, than the change in the location of the Fermi level [32,33].

The decolorization of the dye solution was studied only in the pH range 4.2–7.4, due to the fact that in strong acidic and alkaline media ($8 <$ pH ≤ 3) almost 100% color removal of Alcian Blue was observed after a 30 min dark adsorption period. Similar result was reported also for the cationic dye Blue X-GRL [34].

The initial reaction rate values for the photocatalytic degradation of the cationic dye Alcian Blue 8 GX, determined for the first 10 min of UV-A exposure in the studied pH range, are presented in Fig. 4.

When initial pH of the suspension varied from 4.2 to 7.4 the photocatalytic activity reached a maximum at pH 6.3, followed by a decrease of r_0 in the pH region 6.8–7.4. Taking into account that Alcian Blue is a cationic dye it is obviously that its adsorption on the photocatalyst surface is not positively influenced in acidic media due to repulsive forces between positively charged
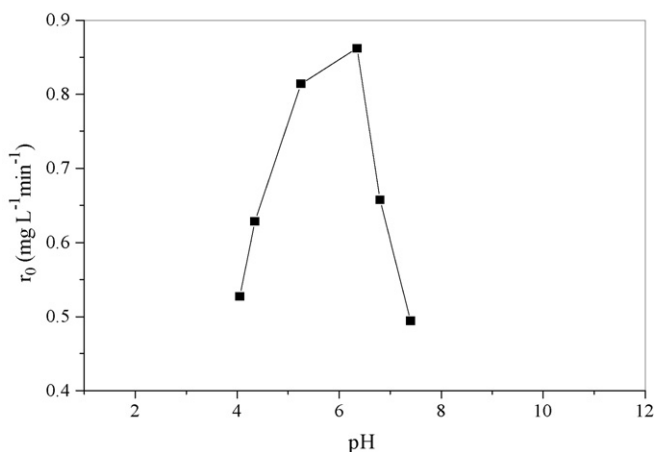

Fig. 4. Effect of pH on the initial reaction rate of the photocatalytic degradation of 40 mg L^{-1} Alcian Blue 8 GX at constant concentration of catalyst (0.5 g L^{-1} TiO$_2$ P-25).

surface and adsorbed group. Adsorption became strongly during decrease of acidity of the medium until the value of pH around that of zero charge point, where the maximum reaction rate was obtained. In the region pH 6.8–7.4, decrease of the degradation rate may due to very strong adsorption of the dye on the catalyst surface, which leads to the dramatic decrease in the active centers on the catalyst surface (decrease in UV-A absorption light by this one). In alkaline media, at pH > 8, the color removal was achieved only by strong adsorption of the cationic dye as a result of strong electrostatic attraction onto TiO^-.

3.3. Influence of H_2O_2 addition on photocatalytic process

The addition of strong powerful oxidizing agents, such as hydrogen peroxide, to TiO_2 suspensions leads in many cases to an increase in the photooxidation rate through generation of more radicals in the presence of light. The role of H_2O_2 in the process of photocatalytic degradation is dual. It accepts a photo-generated 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):

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \tag{3}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\bullet + OH^- + O_2 \tag{4}$$

A possible reaction of H_2O_2 with the photogenerated intermediates also cannot be excluded. When H_2O_2 is in excess, it may act as hole or $OH^\bullet$ scavenger or react with TiO_2 and form peroxo compounds that are detrimental to the photocatalytic action. This explains the need for an optimal concentration of hydrogen peroxide for the maximum effect.

The effect of the amount of H_2O_2 on the initial reaction rates, calculated for the first 10 min of reaction, is shown in Fig. 5. The photocatalytic activity increases with increasing amount of hydrogen peroxide until it reaches a maximum at the concentration of 100 mg L^{-1} oxidant. Under the studied conditions, the addition of hydrogen peroxide accelerates the degradation only
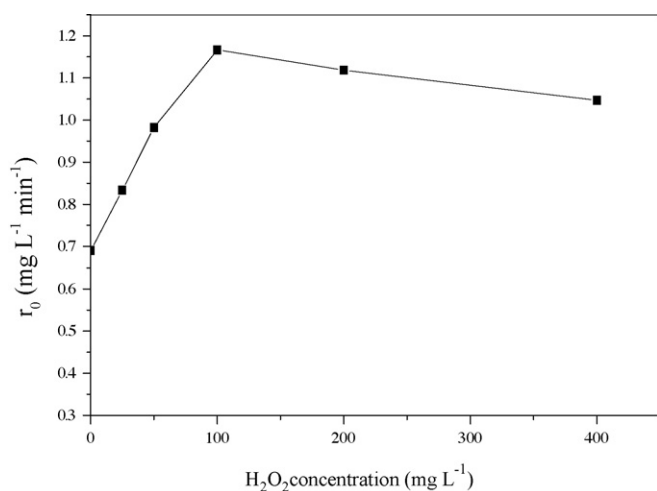
Fig. 5. Effect of H_2O_2 concentration on the photocatalytic degradation rate of 40 mg L^{-1} Alcian Blue in the presence of 0.5 g L^{-1} TiO$_2$.
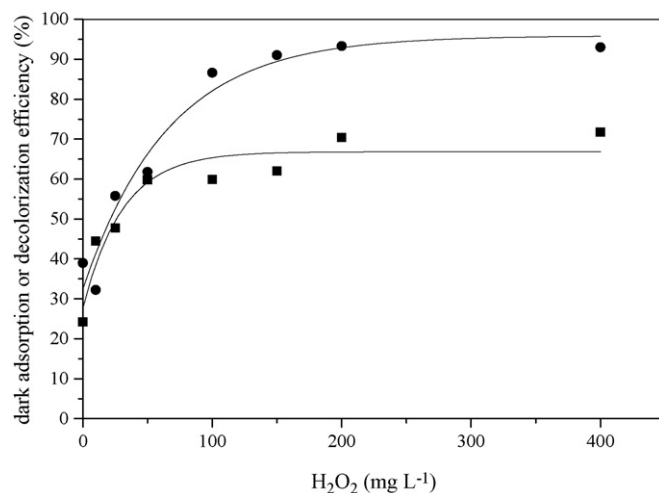
Fig. 6. Influence of H_2O_2 concentration upon dark adsorption (■) and photocatalytic degradation efficiency (●) of 40 mg L^{-1} Alcian Blue 8 GX (0.5 mg L^{-1} TiO$_2$ P-25).

by a factor of 1.85, a relative small positive effect, which has been observed also in other cases [35,36].

The influence of the amount of H_2O_2 addition on dark adsorption and photocatalytic process efficiencies calculated for 20 min of UV exposure, when data concerning removal of color were available for all the used oxidant concentrations ranged between 10 and 400 mg L^{-1} is depicted in Fig. 6.

The dark adsorption and the photocatalytic degradation efficiencies were calculated by expressions:

$$\eta_{ads} = \left[\frac{C_{a0} - C_{at}}{C_{a0}} \right] \times 100 \tag{5}$$

$$\eta_{ph} = \left[\frac{C_{ph0} - C_{pht}}{C_{ph0}} \right] \times 100 \tag{6}$$

where C_{a0} is the concentration of the solution before the catalyst was added, C_{at} the concentration after t minutes of dark adsorption (15 min), C_{ph0} the concentration of dye solution before UV irradiation and C_{pht} is the concentration of solution after t minutes of UV exposure.

As can be seen from Fig. 6, while at natural pH of the solution, in the absence of H_2O_2, the dark adsorption efficiency was around 24%, the presence of oxidizing agent leads to an increase of the adsorption efficiency of the dye onto the catalyst surface. Higher dark adsorption values may be the result of decrease of acidity of the medium by H_2O_2 adding, which have a favorable influence on adsorption of cationic dye onto the catalyst surface, as it was shown when influence of pH was described. pH measurements had shown an increase from 4.35 unit, in the absence of H_2O_2, to 5.7 unit in the presence of 400 mg L^{-1} oxidant.

Additionally, analysis of the H_2O_2 concentration during the photocatalytic reaction shown a total consumption of hydrogen peroxide below its 100 mg L^{-1} concentration, while at higher concentrations an unconsumed amount remains always in the solution, this increasing with increase of the initial H_2O_2 concentration (e.g. 74% for 400 mg L^{-1} H_2O_2). This finding is in

accordance to the results presented in Fig. 6 where it can be seen that above $100 \, \text{mg L}^{-1}$ initial concentration of H_2O_2 the photocatalytic efficiency is almost constant, as well as in accordance to Fig. 5, which shown that the best H_2O_2 initial concentration value is situated in the region of $100 \, \text{mg L}^{-1}$.

3.4. Mathematical modeling and optimization of the photocatalytic process

Conventional and classical methods for studying a process by maintaining other factors involved at an unspecified constant level do not depict properly the combined effect of all factors involved. This methodology is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable. These limitations of a classical method can be eliminated by optimizing all affecting parameters collectively by statistical experimental design such as the "response surface methodology" (RSM). Factorial experiments provide a comprehensive understanding of the impact of operational variables on process performance. The use of the factorial design leads to optimized parameters with a minimum set of experiments and also to the possibility to obtain a polynomial expression that empirically describes the process yield [37–44].

The variables used in this study were: initial pH, concentration of H_2O_2 and irradiation time. The real values of process variables and their variation limits were chosen in accordance with the preliminary tests and coded as shown in Table 1.

Factorial designs are widely used in statistical modeling to obtain empirical models between process response and process factors. In this regard, the 2^3 factorial orthogonal design was employed in this study as it is shown in Table 2, where in the last column, the process yield (removal efficiency), defined as response factor, is given. The calculus of the response factor was done at duration higher than 6 min due to the fact that under this value, desorption of the intermediates occurs in the presence of the oxidant, leading to negative conversions.

The coefficients of the mathematical empirical model (regression equation) were calculated via subsequent equation [45]:

$$\boldsymbol{b} = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{X}^{\mathrm{T}}\boldsymbol{Y} \tag{7}$$

where $\boldsymbol{b}$ is the column matrix of the regression coefficients; $\boldsymbol{X}$ the matrix of coded variables; $\boldsymbol{Y}$ is the column matrix of photodegradation efficiency (experimental values).

Based on the experimental factorial design, the regression equation that sets the correlation between the photodegradation

Table 2
Numerical results of the factorial experimental design of photocatalytic degradation of Alcian Blue 8 GX on TiO$_2$

N	x_1	x_2	x_3	pH	H$_2$O$_2$	t	Y (%)
1	1	1	1	6.15	250	30	95.54
2	−1	−1	−1	4.35	250	30	96.92
3	1	1	1	6.15	50	30	91.17
4	−1	−1	−1	4.35	50	30	88.19
5	1	1	1	6.15	250	10	66.80
6	−1	−1	−1	4.35	250	10	67.60
7	1	1	1	6.15	50	10	47.19
8	−1	−1	−1	4.35	50	10	28.39
9	1.215	0	0	6.3455	150	20	92.98
10	−1.215	0	0	4.1565	150	20	90.84
11	0	1.215	0	5.25	271.5	20	93.63
12	0	−1.215	0	5.25	28.5	20	75.19
13	0	0	1.215	5.25	150	32.15	94.27
14	0	0	−1.215	5.25	150	7.85	49.73
15	0	0	0	5.25	150	20	92.09

efficiency and the process variables was found to be:

$$\hat{Y} = 91.864 + 1.948x_1 + 8.613x_2 + 19.719x_3 - 5.294x_2^2$$
$$- 13.708x_3^2 - 2.996x_1x_2 - 2.051x_1x_3 - 5.714x_2x_3 \tag{8}$$

The polynomial coefficients represent the quantified values of each variable, as well as the interaction between these ones. Within the polynomial expression x_1, x_2 and x_3 are the dimensionless coded values of initial pH, hydrogen peroxide concentrations and irradiation time, respectively.

The Student 't'-test was used to determine the significance of the regression coefficients of the factors. The accordance between the model and experimental data was verified by applying Fischer's test for a confidence level $p = 0.05$ and degrees of freedom $f_1 = 6$ and $f_2 = 1$. For this purpose, the calculated value of the Fischer's test ($F_C = 41.478$) was compared with the tabulated one ($F_T(f_1,f_2) = 233.986$). Since $F_C < F_T$, the mathematical model is truly with a probability of 95%, $i.e.$ the accordance between the model and experimental data is statistically accepted for a confidence level $p = 0.05$. Both calculated and experimental values of the photodegradation efficiency are shown in Fig. 7.

Concordant to empirical model, the 3D diagrams and curves of response surface were plotted (Figs. 8–10). The resulted geometric forms evidence the influence of the factors on process efficiency (yield). Thus, the x_3 variable (time) has a bigger influence than x_2 variable (H$_2$O$_2$ concentration), which, in its turn, has a greater influence than x_1 (pH) factor.

Table 1
Experimental range and levels of independent process variables ($\alpha = 1.215$)

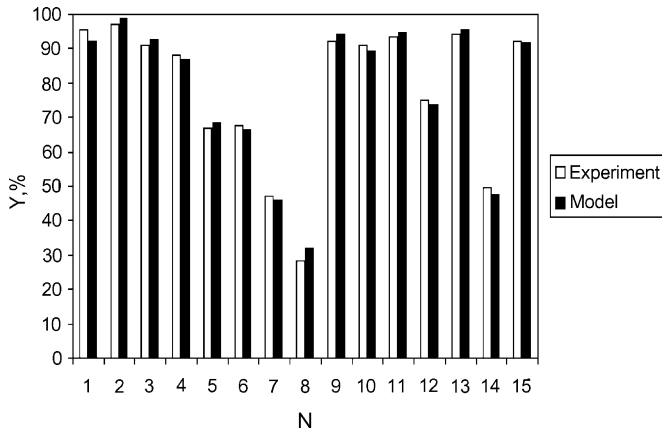| Independent process variables	Code	Real values of coded levels					Step
		$-\alpha$	-1	0	$+1$	$+\alpha$	
Initial pH	x_1	4.1565	4.35	5.25	6.15	6.3455	0.9
Concentration of H$_2$O$_2$ (mg L^{-1})	x_2	28.5	50	150	250	271.5	100
Irradiation time (min)	x_3	7.85	10	20	30	32.15	10

Fig. 7. Correlation between the empirical model and experiments carried-out in given conditions.

This is in accordance with the preliminary experimental results. As it was shown, the photodegradation efficiency after 20 min of irradiation has raised by a factor of 1.95 when pH increased from 4.15 to 6.35 and by a factor of 2.5, respectively,

when H_2O_2 concentration increased in the range 10–100 mg L^{-1} (the best concentration from the point of view of reaction rates calculated for the first 10 min of reaction).

At pH value of 6.35, increasing irradiation time from 6 to 30 min, yielded in two-fold increase of efficiency, while for 100 mg L^{-1} H_2O_2 this was 6 times higher when irradiation time increased in the range 6–20 min (data not shown).

The reaction was optimized to determine the time when 100% yield (efficiency) of the photocatalytic process results in given experimental conditions.

Optimization of objective function (Eq. (8)) was achieved by GRADIENT method. In this regard, the optimal point was searched by means of Eq. (9) [46]:

$$x^{(k+1)} = x^{(k)} + V^{(k)} s^{(k)} \qquad (9)$$

where $x^{(k)} = \{x_1^{(k)}, x_2^{(k)}, x_3^{(k)}\}^T$ denotes the vector of process variables, $V^{(k)} = \{m_1^{(k)}, m_2^{(k)}, m_3^{(k)}\}^T$ the direction of steepest ascent, $s^{(k)}$ the step of searching and k is the stage of searching.
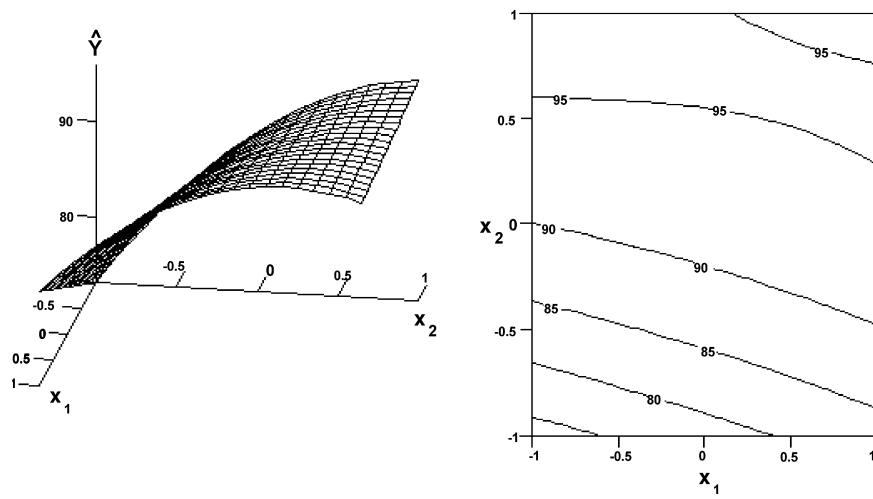

Fig. 8. Response surface and contour curves depending on x_1 and x_2, $x_3 = 0$.
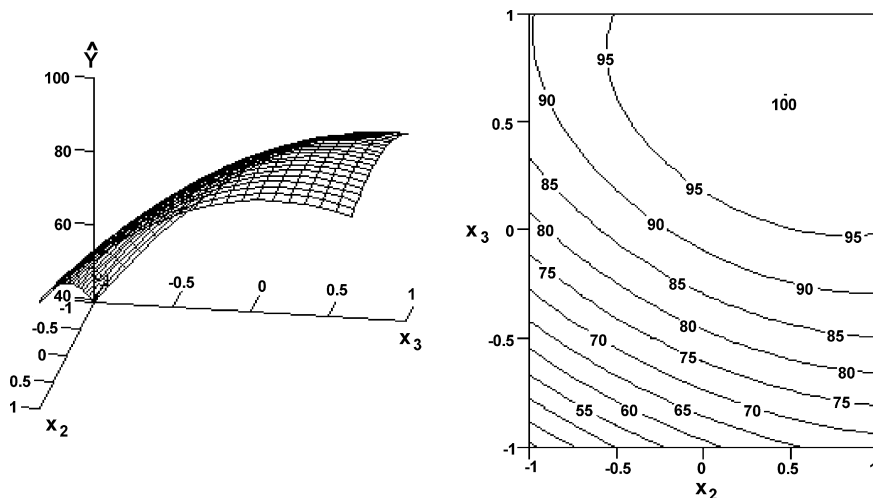

Fig. 9. Response surface and contour curves depending on x_2 and x_3, $x_1 = 0$.
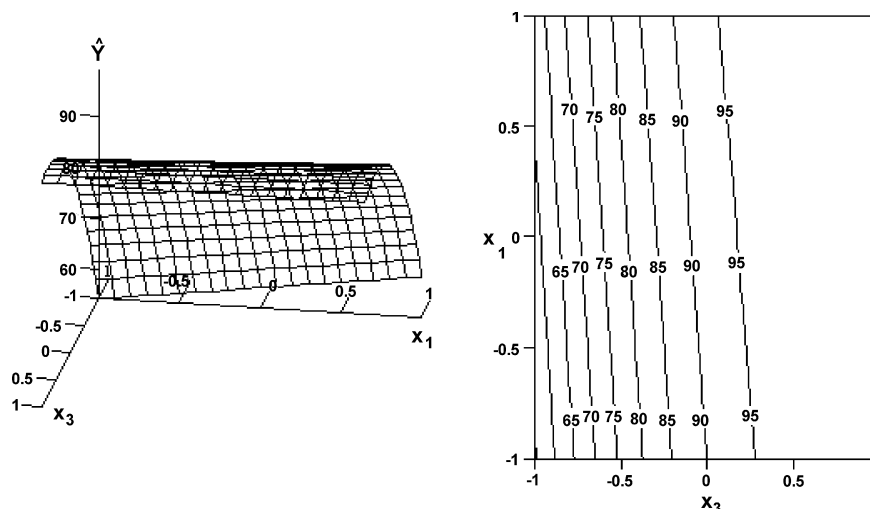
Fig. 10. Response surface and contour curves depending on x_1 and x_3, $x_2 = 0$.

Table 3
Optimization of objective function in accordance with Gradient method

k	pH				H_2O_2				Time (min)				$\hat{Y}(x_1, x_2, x_3)$
	x_1	z_1	m_1	S	x_2	z_2	m_2	s	x_3	z_3	m_3	s	
1	0	5.25	0.09	1	0	150	0.399	1	0	20	0.913	1	91.864
2	0.09	5.33	−0.141	0.1	0.399	189.8	−0.138	0.1	0.913	29.1	−0.98	0.1	98.855
3	0.076	5.32	−0.173	0.1	0.385	188.5	−0.069	0.1	0.815	28.1	−0.983	0.1	99.502
4	0.059	5.30	−0.28	0.1	0.378	187.8	0.144	0.1	0.717	27.2	−0.949	0.1	99.868
5	0.031	5.28	−0.49	0.03	0.392	189.2	0.796	0.03	0.622	26.2	0.354	0.03	99.98
6	**0.016**	**5.26**	–	–	**0.416**	**191.6**	–	–	**0.633**	**26.3**	–	–	**100**

The Eq. (9) written via components becomes:

$$x_i^{(k+1)} = x_i^{(k)} + m_i^{(k)} s_i^{(k)} \tag{10}$$

where

$$m_i^{(k)} = \frac{\pm(\partial \hat{Y}/\partial x_i)_{\bar{x}=\bar{x}^{(k)}}}{\sqrt{\sum_{i=1}^{n}(\partial \hat{Y}/\partial x_i)^2_{\bar{x}=\bar{x}^{(k)}}}} \tag{11}$$

Optimization search by GRADIENT method led to the following optimum point: $pH^* = 5.26$, $[H_2O_2]^* = 191.6$, $t^* = 26.3$ min $\Rightarrow Y = 100\%$ as may be observed from Table 3.

This fits to conclusion resulted from the obtained mathematical empirical model, which suggested that relatively lower pH combined with higher oxidant concentration and irradiation time will improve significantly the removal efficiency.

As one can see in the optimum point the response is $\hat{Y}(x_1, x_2, x_3) = 100\%$ and the process variables do not exceed the valid region. All calculations were performed in high level software environment (MathCAD 12).

4. Conclusions

The photocatalytic degradation of cationic dye Alcian Blue 8 GX in the presence of TiO_2 P-25 was investigated in this study, focusing on the influence of some parameters such as catalyst concentration, initial solution pH and addition of an oxidizing agent as H_2O_2.

According to the mathematic optimization of the process, using the Gradient method, the optimum point when 100% conversion is achieved is given by the following values: pH 5.26, H_2O_2 concentration = 191.6, $t = 26.3$ min of irradiation.

Concordant to the developed empirical model the irradiation time (x_3 variable) has a bigger influence than H_2O_2 concentration (x_2 variable) that, in its turn, has a greater influence than x_1 (pH) factor. This suggests that an insufficient exposure to the radiation results in a decrease of the photodegradation efficiency, no matter which are the values of pH and oxidant concentration. At the same time, the effect of H_2O_2 adding also contains the positive influence of pH considering that the oxidant addition leads to increase of pH value, fact that has a favorable effect on dye adsorption and, consequently, on photodegradation process, as it was shown in preliminary experiments.

From the results of the present work and relevant reports in the literature one could claim that the photocatalytic treatment of waste waters of the biochemical/biomedical laboratories may be employed as a powerful tool for the decolorization and the reduction of the organic content of this liquid waste. The use of an inexpensive and biologically inactive catalyst, such as TiO_2, and the possibility of activating it with harmless UV-A light, combined with the simple technology required for this method, can offer economically reasonable and practical solutions to the processing of this liquid waste.

Acknowledgements

References

[1] G. Lynn, E.B. Sansone, Destruction of Hazardous Chemical in the Laboratory, 2nd ed., Wiley, New York, 1994.

[2] Sax's Dangerous Properties of Industrial Materials, 8th ed., Van-Nostrand-Reinhold, New York, 1992.

[3] F.L. Carson, Histology, A Self-Instructional Text, ASCP Press, Chicago, 1990.

[4] I. Poulios, E. Micropoulou, R. Panou, E. Kostopoulou, Photooxidation of eosin Y in the presence of semiconducting oxides, Appl. Catal. B: Environ. 41 (2003) 345–355.

[5] E. Selli, Synergistic effects of sonolysis combined with photocatalysis in the degradation of an azo dye, Phys. Chem. Chem. Phys. 4 (2002) 6123–6128.

[6] M. Muruganandham, M. Swaminathan, Advanced oxidative decolourisation of Reactive Yellow 14 azo dye by UV/TiO_2, UV/H_2O_2, $UV/H_2O_2/Fe^{2+}$ processes, a comparative study, Sep. Purif. Technol. 48 (2006) 297–303.

[7] M.M. Mitani, A.A. Keller, C.A. Bunton, R.G. Rinker, O.C. Sandall, Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water, J. Hazard. Mater. B 89 (2002) 197–212.

[8] S. Moraes, R.S. Freire, N. Duran, Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes, Chemosphere 40 (2000) 369–373.

[9] N.M. Mahmoodi, M. Arami, N.Y. Limaee, N.S. Tabrizi, Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized TiO_2 photocatalytic reactor, J. Colloid Interf. Sci. 295 (2006) 159–164.

[10] S. Senthilkumaar, K. Porkodi, R. Vidyalakshmi, Photodegradation of a textile dye catalyzed by sol–gel derived nanocrystalline TiO_2 via ultrasonic irradiation, J. Photochem. Photobiol. A: Chem. 170 (2005) 225–232.

[11] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted catalytic degradation of azo dyes in aqueous solutions: kinetic and mechanistic investigations. A review, Appl. Catal. B: Environ. 49 (2004) 1–14.

[12] J.E. Scott, Alcian blue. Now you see it, now you don't, Eur. J. Oral Sci. 104 (1996) 6–9.

[13] C. Bober, Quantification of single-species marine biofilm with Alcian Blue, J. Young Investigators, available on-line at http://www.jyi.org/research/re.php?id=149, 2005.

[14] M.R. Hoffman, S. Martin, W. Choi, D. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[15] E. Pelizzetti, C. Minero, Mechanism of the photooxidative degradation of organic pollutants over TiO_2 particles, Electrochim. Acta 38 (1993) 47–55.

[16] A.M. Braun, M. Maurette, E. Oliveros, Photochemical Technology, Wiley, New York, 1991.

[17] E. Evgenidou, K. Fytianos, I. Poulios, Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalysts, Appl. Catal. B: Environ. 59 (2005) 81–89.

[18] A.B. Prevot, M. Vincenti, A. Bianciotto, E. Pramauro, Appl. Catal. B: Environ. 22 (1999) 149–158.

[19] D. Robert, B. Dongui, J.V. Weber, J. Photochem. Photobiol. A: Chem. 156 (2003) 195–200.

[20] J.M. Herrmann, C. Guillard, CR Acad. Sci. Paris, Serie Iic, Chimie/Chem. 3 (2000) 417–421.

[21] J.P. Percherancier, R. Chapelon, B. Pouyet, J. Photochem. Photobiol. A: Chem. 87 (1995) 261–266.

[22] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanism involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.

[23] J. Cunningham, G. Al-Sayyed, S. Srijaranai, Adsorption of model pollutants onto TiO_2 particles in relation to photoremediation of contaminated water, in: G. Helz, R. Zepp, D. Crosby (Eds.), Aquatic and Surface Photochemistry, CRC Press, Boca Raton, Florida, 1994, pp. 317–348.

[24] S. Parra, J. Olivero, C. Pulgarin, Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO_2 suspension, Appl. Catal. B: Environ. 36 (2002) 75–85.

[25] E. Kusvuran, A. Samil, O.M. Atanur, O. Erbatur, Photocatalytic degradation kinetics of di- and tri-substituted phenolic compounds in aqueous solution by TiO_2/UV, Appl. Catal. B: Environ. 58 (2005) 211–216.

[26] C. Minero, E. Pelizzetti, S. Malato, J. Blanco, Large solar plant photocatalytic water decontamination: effect of operational parameters, Solar Energy 56 (5) (1996) 421–428.

[27] C. Minero, A rigorous kinetic approach to model primary oxidative steps of photocatalytic degradations, Sol. En. Mater. Sol. Cells 38 (1995) 421–430.

[28] J. Cunningham, G. Al-Sayyed, Factors influencing efficiencies of TiO_2-senzitiezed photodegradation. I. Substituted benzoic acids: discrepancies with dark-adsorption parameters, J. Chem. Soc. Faraday Trans. 86 (23) (1990) 3935–3941.

[29] J. Cunningham, J. Sedlak, Kinetic studies of depollution process in TiO_2 slurries: interdependences of adsorption and UV-intensity, Catal. Today 29 (1996) 309–315.

[30] Y. Meng, X. Huang, Y. Wo, X. Wang, Y. Qian, Kinetic study and modeling on photocatalytic degradation of *para*-chlorobenzoate at different light intensities, Environ. Pollut. 117 (2002) 307–313.

[31] Y.M. Xu, C.H. Langford, Variation of Langmuir adsorption constant determined for TiO_2-catalyzed degradation of acetophenone under different light intensity, J. Photochem. Photobiol. A: Chem. 133 (2000) 67–71.

[32] C. Kormann, D.W. Bahnemann, M.R. Hoffman, Photolysis of chloroform and other organic molecules in aqueous suspensions, Environ. Sci. Technol. 25 (1991) 494–500.

[33] A.P. Davis, C.P. Huang, The photocatalytic oxidation of sulfur containing organic compounds using CdS and the effect on CdS photocorrosion, Water Res. 25 (1991) 1273–1278.

[34] C. Hu, Y. Tang, J.C. Yu, P.K. Wong, Photocatalytic degradation of cationic blue X-GRL adsorbed on TiO_2/SiO_2 photocatalyst, Appl. Catal. B: Environ. 40 (2003) 131–140.

[35] I. Poulios, I. Aetopoulou, Photocatalytic degradation of the textile dye Reactive Orange 16 in the presence of TiO_2 suspensions, Environ. Technol. 20 (1999) 479–487.

[36] I. Poulios, G. Kyriacou, Photocatalytic degradation of *p*-coumaric acid over TiO_2 suspensions, Environ. Technol. 23 (2002) 179–187.

[37] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Optimized photodegradation of Reactive Blue 19 on TiO_2 and ZnO suspensions, Catal. Today 76 (2002) 235–246.

[38] U. Bali, Application of Box-Wilson experimental design method for the photodegradation of textile dyestuff with UV/H_2O_2 process, Dyes Pigments 60 (2004) 187–195.

[39] M. Drouiche1, H. Lounici1, N. Mameri1, D.L. Piron, M. Kharroune, Utilization of factorial experiments for the UV/H_2O_2 process in a batch reactor, Water SA 27 (2001) 551–557.

[40] 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.

[41] F. Herrera, A. Lopez, J. Kiwi, Photochemically activated degradation of reactive dyes. Statistical modeling of the reactor performance, J. Photochem. Photobiol. A: Chem. 135 (2000) 45–51.

[42] W.C. Paterlini, R.F.N. Nogueira, Multivariate analysis of photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D, Chemosphere 58 (2005) 1107–1116.

[43] J. Fernandez, J. Kiwi, J. Freer, C. Lizama, H.D. Mansillia, Orange II photocatalysis on immobilised TiO_2. Effect of the pH and H_2O_2, Appl. Catal. B: Environ. 48 (2004) 205–211.

[44] E. Oliveros, O. Legrini, M. Hohl, T. Muller, A.M. Braun, Industrial waste water treatment: large scale development of a light-enhanced Fenton reaction, Chem. Eng. Process. 36 (1997) 397–405.

[45] S.L. Ahnazarova, V.V. Kafarov, Optimizatziya Experimenta v Himii i Himiceskoi Tehnologhii, Vysshaya Shkola, Moskva, 1978.

[46] I. Curievici, Optimizari in Industria Chimica, Editura Didactica & Pedagogica, Bucuresti, 1980.