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Optimized photodegradation of Reactive Blue 19 on TiO_2 and ZnO suspensions

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Abstract

The photocatalytic discoloration of Reactive Blue 19 (RB-19), a textile anthraquinone dye, were investigated in aqueous suspensions containing TiO_2 or ZnO as catalysts. The reactions can be mathematically described as a function of parameters pH, amount of catalyst and dye concentration being modeled by the use of response surfaces methodology. Optimized values for the concentration of the catalyst and the pH for each reaction systems were determined. ZnO showed greater degradation activity than TiO_2 when the reaction was carried out in a 4 l circulating reactor under optimized conditions. The figure-of-merit electric energy per order (EE/O) allows to determine that the electrical energy cost of reducing the color by one order of magnitude was three times higher for TiO_2. In both reaction systems, the acute toxicity evolved from zero to around 50 toxicity units in the initial stages of irradiation, depleting to minimal values after 30 min of reaction.

Keywords: Factorial design; Photocatalysis; Reactive Blue 19; TiO_2; ZnO

1. Introduction

Many industrial effluents are strongly colored, such as those arising from textile processes, kraft mills, dye manufacturing, tannery, foods, cosmetic, and other liquid wastes. Colored substances in the effluents are principally due to undesired sub-products generated in the industrial process, as in the case of lignin produced in the cellulose industry. In the textile industry, color is directly applied to the fabric in a dyeing step. Around 30% of commercially available synthetic reactive dyes consumed in textile processes is lost and cannot be reused because they are chemically modified during the dyeing step [1].

Although most commercial dyes are not directly toxic, the colored waste waters are subject to rigorous environmental legislation due to their negative impact on photosynthetic activity. The conventional technologies currently used to degrade the color of dye contaminated waters may be primary (flocculation and adsorption) [2], secondary (activated sludge) [3] or advanced tertiary treatments (oxidation and electrolysis) [4]. However, in many cases these classical techniques do not work efficiently due to the high solubility of synthetic dyes. On the other hand, most commercial dyes are designed to resist chemical and biological degradation. In addition, an incomplete chemical oxidation or partial biodegradation can be environmentally detrimental because of generation of toxic aromatic amines and phenols.

In recent years, advanced oxidation technologies have been described as efficient procedures for obtaining high oxidation yields from several kinds of

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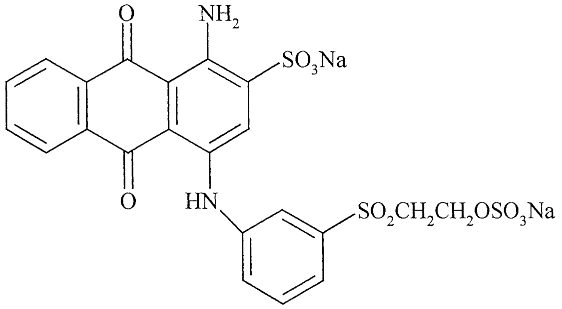

Fig. 1. RB-19 structure.

organic compounds [5–8]. Ozone/UV [9,10], H_2O_2/UV [11,12] and TiO_2 photocatalysis [13–15]. have been used to decolorize natural and synthetic dyes. The oxidative hydroxyl radicals generated by the systems described above promote rapid reactions involving electron transfer, hydrogen abstraction and addition to aromatic rings.

The Reactive Blue 19 (RB-19), also known as Remazol brilliant blue, is very resistant to chemical oxidation due to its aromatic anthraquinone structure highly stabilized by resonance (Fig. 1). In a recent study, in which TiO_2 photocatalysis was used to degrade different reactive dyes, RB-19 was found to be the most recalcitrant to discoloration [16]. In the present study, we compared the photocatalytic activity of TiO_2 and ZnO under optimized conditions. The optimization of the reaction parameters was performed by experimental factorial design using surface response methodology.

2. Experimental

2.1. Materials

Titania P-25 (surface area $50\,m^2\,g^{-1}$) was obtained from Degussa and ZnO (surface area $5\,m^2\,g^{-1}$) from Merck, and were used as received. RB-19 was purchased from Aldrich (dye content ∼50%) and used without further purification. Dye solutions were prepared dissolving the dye in deionized water (Barnstead Nanopure D-4752) at different concentrations in the 30–70 ppm range. The pH of solutions was adjusted in the range 7–10 with NaOH 1 M, after the addition of the catalyst.

2.2. Photochemical reaction

2.2.1. Irradiation without suspension recycling

The reactor configuration without recycling of the slurry is shown in Fig. 2A. It was used in the experiments carried out in order to optimize the discoloration reaction according to the factorial design methodology.

In a typical reaction of dye discoloration in the photo-reactor, 1 l of dye solution, with TiO_2 or ZnO in suspension, was irradiated with a commercial 125 W lamp (Philips HPLN 125 W; $\lambda > 254$ nm). UV photons were determined actinometrically (trisoxalateferrate methodology) in the reactor. A glass filter system to eliminate radiation below 350 nm was used. The total UV output below 350 nm was 2.1×10^{-5} Einstein $l^{-1}\,min^{-1}$ and was maintained constant during all the experiments. The lamp was placed in a quartz jacket immersed in the reaction suspension. Before irradiation, each suspension was stirred in darkness during 30 min to reach the adsorption equilibrium of the dye on the catalyst surface. The aqueous suspension was magnetically stirred and oxygen was bubbled through a sintered glass device placed at the bottom of the reactor, at $300\,ml\,min^{-1}$. The reaction mixture was maintained at room temperature ($25 \pm 2\,^{\circ}C$) by water circulation through the external jacket.

Samples were taken at different times until 30 min of reaction with a 10 ml plastic syringe and then filtered in Millipore disk of 0.45 μm for ZnO and 0.22 μm for TiO_2.

2.2.2. Irradiation with suspension recycling

The scheme of the reactor with recycling of the aqueous suspension is shown in Fig. 2B. This arrangement was used after attaining optimal conditions in the reactor described in Fig. 2A. Reactions performed in the reactor with recycling allow the determination of energy costs, toxicity and TOC.

The reactions were carried out with recycling of 4 l suspensions in a configuration shown in Fig. 2B. The suspension was recycled at $150\,ml\,min^{-1}$ by means of a peristaltic pump. The photochemical reactor (1 l) as well as the external reservoir (3 l) were magnetically stirred during the reactions. Oxygen was bubbled at $300\,ml\,min^{-1}$. Samples (20 ml) were taken each 5 min periods, from the external reservoir by a plastic syringe and filtered as described in Section 2.2.1.

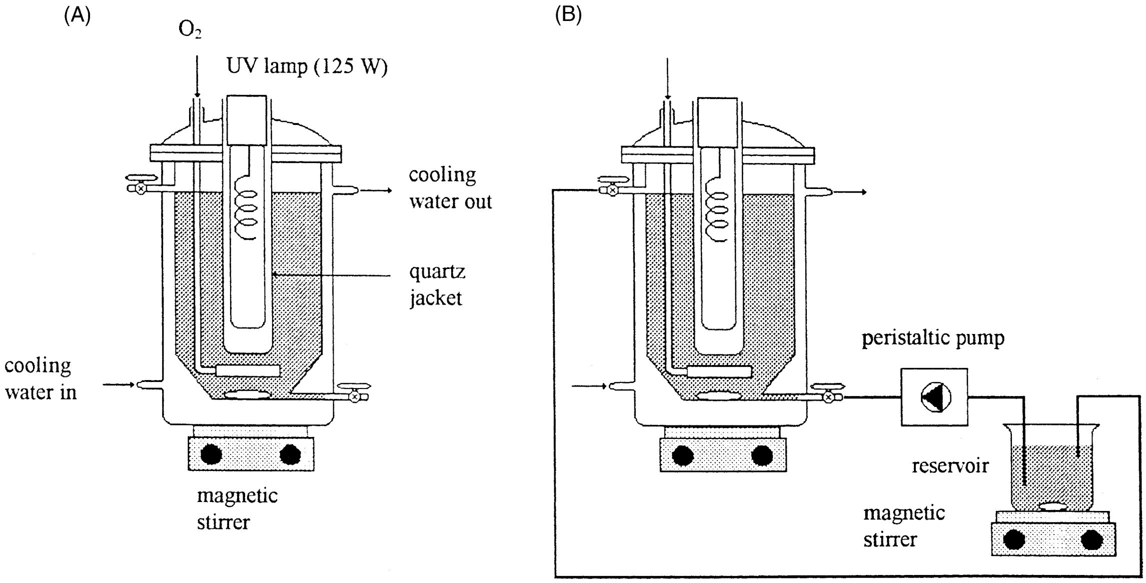

Fig. 2. Scheme of the photoreactor configurations used in TiO_2 and ZnO photodiscoloration of RB-19. The reactor A was used in all the optimization experiments and the reactor B in the toxicity, TOC and EE/O determinations.

2.3. Chemical analysis

The filtered samples obtained from the photochemical reactions were analyzed in a Shimadzu 1603 spectrophotometer. The maximum at 592 nm was recorded during the course of the reaction and reported as percent of color removal. The dye concentration was determined by using a spectrophotometric calibration curve obtained with commercial product (Aldrich).

Total organic carbon determinations were carried out in a Shimadzu 5000 A TOC analyzer. Acute toxicity was measured as EC_{50}, where the concentration was expressed in ppm units, in a Microtox *m* 500 toxicity analyzer. The bacteria *Vibrio fischeri* was used as toxicity indicator. The toxicity units are defined as $100/EC_{50}$.

2.4. Multivariate experimental design

Factorial design was performed following the methodology described by Box et al. [17]. The polynomial equations and response surfaces were obtained using the software FATORIAL provided by Professor R. Bruns from the State University of Campinas, Brazil [18].

In the multivariate design of the photocatalytic reaction using TiO_2 and ZnO, three variables were changed simultaneously: the initial pH (7–10), the catalyst concentration (0.5–1.5 $g\,l^{-1}$) and the dye concentration (30–70 ppm). For n variables and two levels (low and high) the total number of experiments was 17, determined by the expression: $2^n + 2n + 3$.

3. Results and discussion

3.1. Photocatalysis in the reactor without recycling

3.1.1. Preliminary results

Preliminary experiments of RB-19 discoloration were carried out in the reactor shown in Fig. 2A. Using $1\,g\,l^{-1}$ of the catalysts (TiO_2 or ZnO) at their natural pH (5.6 and 6.6, respectively), the kinetic profiles of discoloration were obtained and shown in Fig. 3. Very low photolytic degradation of RB-19 was observed until 30 min of irradiation. The photocatalytic degradation process was very efficient with TiO_2 as well as ZnO. A very similar discoloration profile was obtained for both catalysts, reaching 90% discoloration after 20 min of irradiation. It means

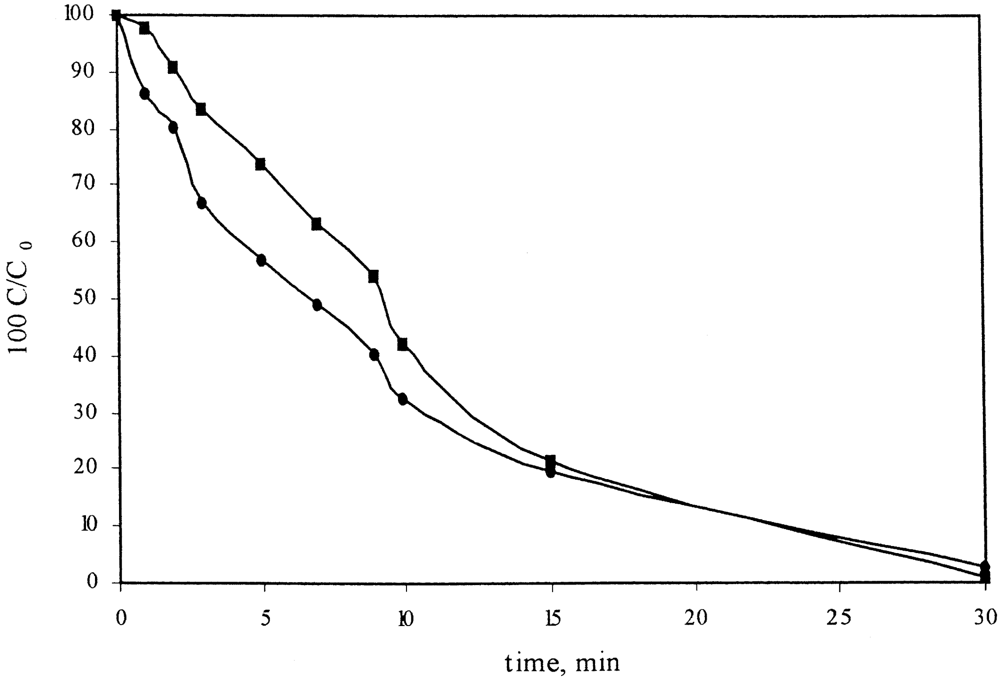

Fig. 3. Discoloration of RB-19 by $1\,g\,l^{-1}$ ZnO (■) and TiO_2 (●) photocatalysis. The pH of the solutions were 6.6 and 5.6, for ZnO and TiO_2, respectively.

that the photocatalytic process can be used as a rapid discoloration technique.

When the photocatalysis was carried out in 1 l reactor at natural pH and $1\,g\,l^{-1}$ of catalyst (see Fig. 3), there was no significant difference between the two catalysts. It can be concluded that the only valid comparison must be made under optimized conditions for each system.

An experimental factorial design of the reaction systems were performed to find the optimal conditions for accelerating the discoloration of RB-19 dye during the photocatalysis with TiO_2 and ZnO.

3.1.2. Dye degradation by TiO_2 photocatalysis

The use of a factorial design yields optimized parameters from a minimum set of experiments. Using codified values of the variables under study it is possible to obtain a polynomial expression that empirically describes the reaction yield. Previous studies have optimized the photo-Fenton discoloration of RB-19 [19] and photocatalytic treatment of cellulose effluents [20] using this mathematical methodology.

The variables under study were the catalyst concentration (x_1), the initial pH (x_2) and the initial dye concentration (x_3). The reaction was optimized to yield 90% of discoloration in a minimum period of time. This response factor (Y) was defined as a target to be achieved.

A matrix of experimental data was constructed for the TiO_2 catalyst. In Table 1, experimental and codified values of the 17 experiments performed are shown. The total number of assays includes the factorial design experiments (8), geometrically placed at the vertices of a cube, six experiments on the outer side of the cube faces and three points placed in the geometric center of the cube. With these 17 experiments, the statistical validity of the mathematical model is assessed. The last column of the table shows the minimum time required to remove the initial color in one order of magnitude, defined as the response factor (Y).

Solving the matrix of data presented in Table 1 with the software FATORIAL, a second grade polynomial was obtained. This mathematical expression is shown

Table 1
Numerical results of the factorial experimental design of RB-19 discoloration assisted by TiO_2

Experiment	$[TiO_2]$ (x_1)	pH (x_2)	[RB-19] (x_3)	Y[a]
1	0.5 (−1)	7 (−1)	30 (−1)	22.5
2	1.5 (+1)	7 (−1)	30 (−1)	11.5
3	0.5 (−1)	10 (+1)	30 (−1)	2.0
4	1.5 (+1)	10 (+1)	30 (−1)	5.5
5	0.5 (−1)	7 (−1)	70 (+1)	30.0
6	1.5 (+1)	7 (−1)	70 (+1)	28.0
7	0.5 (−1)	10 (+1)	70 (+1)	4.5
8	1.5 (+1)	10 (+1)	70 (+1)	4.2
9	1.0 (0)	8.5 (0)	50 (0)	12.5
10	1.0 (0)	8.5 (0)	50 (0)	11.5
11	1.0 (0)	8.5 (0)	50 (0)	14.5
12	0.16 (−1.68)	8.5 (0)	50 (0)	23.5
13	1.84 (+1.68)	8.5 (0)	50 (0)	11.5
14	1.0 (0)	5.6 (−1.68)	50 (0)	25.5
15	1.0 (0)	11.0 (+1.68)	50 (0)	7.5
16	1.0 (0)	8.5 (0)	16 (−1.68)	7.5
17	1.0 (0)	8.5 (0)	80 (+1.68)	31.5

[a] Response factor.

in Eq. (1), and it describes the photodiscoloration of RB-19 under given conditions, and are not valid for a different dye or a different set of conditions. The coefficients in the polynomial represents the weight of each variable (x_1, x_2, x_3) and the interactions between them.

$$\begin{aligned} Y_{TiO_2} = {} & 11.24(\pm 2.88) - 2.07x_1(\pm 1.36) \\ & -5.97x_2(\pm 1.40) + 5.15x_3(\pm 1.42) \\ & +0.94x_2^2(\pm 0.87) + 2.52x_3^2(\pm 1.63) \\ & +2.45x_1x_2(\pm 1.77) \end{aligned} \qquad (1)$$

In the polynomial, x_1, x_2 and x_3 represent the codified values for the amount of catalyst, the initial pH and the dye concentration, respectively. The values in parentheses indicate the relative error of each calculated coefficient. When this error was higher or equal than the coefficient, the effect of the variable is not shown.

Considering only the first-order effect, the discoloration reaction was improved at high catalyst concentration (x_1), high initial pH (x_2) and low dye concentration (x_3). The last two variables have most effect on the response factor. A low quadratic effect for the initial pH and a moderate quadratic effect for dye concentration were observed.

Although the first-order effect shows that increases in both variables x_1 and x_2 favor discoloration, an antagonistic effect was observed between these two parameters. The simultaneous increase of x_1 and x_2 is adverse for the reaction, as shown by the second-order effect of the last term in the polynomial expression. This means that at high pH, a minimal amount of TiO_2 catalyst must be used.

Fig. 4 shows a graphical 3D representation of the polynomial obtained from the matrix. To built this response surface, dye concentration was fixed at 50 ppm. The coordinates of the graph show the initial pH and TiO_2 concentration. The vertical axis represents the time required to remove 90% of the initial color. As predicted by the polynomial, the optimal conditions for rapid discoloration of 50 ppm dye solution are high pH and low concentrations of TiO_2. The amount of catalyst is critical when the initial pH is close to neutral. In this case the concentration of catalyst must be increased dramatically ($>1.5\,g\,l^{-1}$) to get 90% of color removal in <15 min. On the other hand, when the reaction is carried out at high pH (>10) and low TiO_2 concentration ($<0.5\,g\,l^{-1}$) almost complete discoloration is achieved in <5 min.

The optimal values to minimize the time of reaction, were determined solving the polynomial for the TiO_2 concentration and initial pH, fixing the dye concentration at 50 ppm. The optimal TiO_2 concentration calculated was $0.5\,g\,l^{-1}$ at optimal initial pH 11. These optimal values were used in the calculus of energy consumption to degrade the color by one order of magnitude (electric energy per order, EE/O), as shown below.

3.1.3. *Dye degradation by ZnO photocatalysis*

Photocatalytic discoloration of RB-19 was also carried out using ZnO as a catalyst. This semiconductor has been reported as very efficient in degrading cellulose effluents [21] and several other organic compounds [22,23]. Due to the solubility of ZnO in aqueous suspensions at pH <6.5, it is necessary to work at neutral or alkaline pH. The cellulose mill as well as the textile processes that use reactive dyes, normally produce effluents with very alkaline pH, and this condition is favorable for the use of zinc oxide as a catalyst.

The multivariate approach was performed studying simultaneously the ZnO concentration (0.5–$1.5\,g\,l^{-1}$), initial pH (7–10), and dye concentration in the

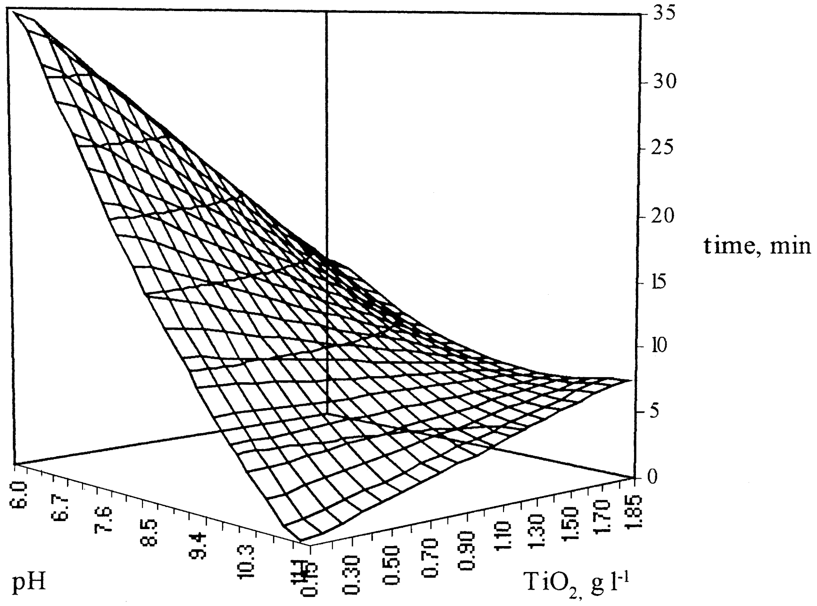

Fig. 4. Response surface showing the time required to reduce 90% of the 50 ppm RB-19 initial color by photocatalysis, as a function of pH and TiO_2 concentration.

30–70 ppm range. Table 2 shows the experimental and codified values for the experiments. As in the case of the TiO_2 catalysis, the response factor was the minimum time required to remove 90% of the initial color from the dye solution. A polynomial expression (Eq. (2)) of the reaction system was obtained using the FATORIAL software to solve the matrix:

$$\begin{aligned} Y_{\mathrm{ZnO}} = {} & 12.69(\pm 2.88) - 1.13x_2(\pm 1.10) \\ & + 7.46x_3(\pm 1.42) + 2.23x_1^2(\pm 1.48) \\ & - 2.29x_2^2(\pm 1.50) + 2.41x_3^2(\pm 1.63) \\ & - 2.47x_2x_3(\pm 1.76) \end{aligned} \tag{2}$$

The polynomial shows that the variable x_1 (concentration of ZnO) does not have a first-order effect but exerts a negative quadratic influence (x_1^2) in the RB-19 degradation rate. This indicates that the reaction performance is improved at intermediates values in the chosen range of concentrations. Very high or very low values for the ZnO concentration are detrimental for the discoloration rate. The effect of the initial pH (x_2) is less pronounced than for TiO_2-catalysis, but the favorable quadratic effect (x_2^2) indicates that the degradation rate is improved at very low or high pH. Finally, the most significant first-order effects derive from the initial concentration of RB-19 (x_3). Although ZnO concentration exerts no first-order effect, a synergistic influence in combination with pH was observed, as evident from the last term in the polynomial equation.

Table 2
Numerical results of the factorial experimental design of RB-19 discoloration assisted by ZnO

Experiment	[TiO_2] (x_1)	pH (x_2)	[RB-19] (x_3)	Y[a]
1	0.5 (−1)	7 (−1)	30 (−1)	7.5
2	1.5 (+1)	7 (−1)	30 (−1)	4.5
3	0.5 (−1)	10 (+1)	30 (−1)	7.0
4	1.5 (+1)	10 (+1)	30 (−1)	8.5
5	0.5 (−1)	7 (−1)	70 (+1)	27.5
6	1.5 (+1)	7 (−1)	70 (+1)	27.5
7	0.5 (−1)	10 (+1)	70 (+1)	15.5
8	1.5 (+1)	10 (+1)	70 (+1)	21.0
9	1.0 (0)	8.5 (0)	50 (0)	12.5
10	1.0 (0)	8.5 (0)	50 (0)	11.0
11	1.0 (0)	8.5 (0)	50 (0)	12.5
12	0.16 (−1.68)	8.5 (0)	50 (0)	22.5
13	1.84 (+1.68)	8.5 (0)	50 (0)	23.0
14	1.0 (0)	6.6 (−1.25)	50 (0)	15.5
15	1.0 (0)	11.0 (+1.68)	50 (0)	4.5
16	1.0 (0)	8.5 (0)	16 (−1.68)	10.0
17	1.0 (0)	8.5 (0)	80 (+1.68)	30.5

[a] Response factor.

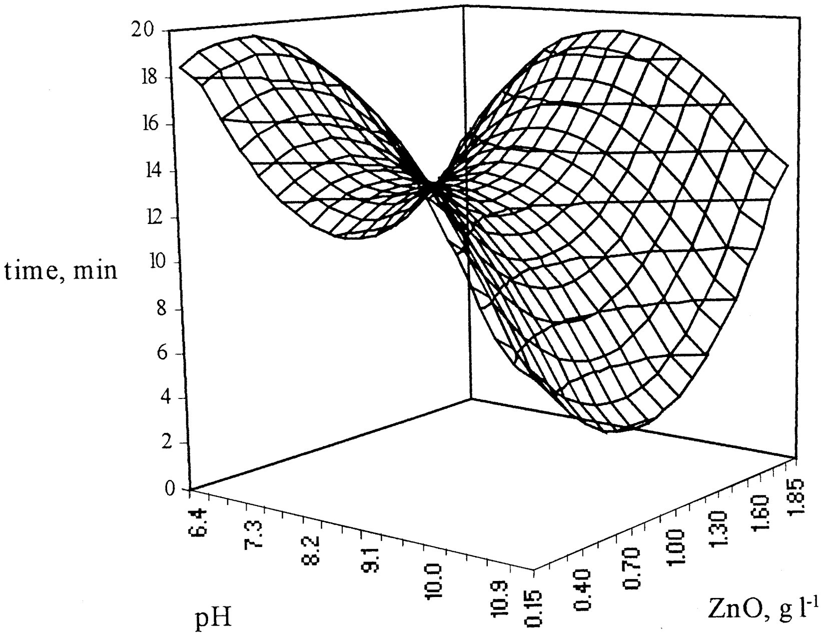

Fig. 5. Response surface showing the time required to reduce 90% of the 50 ppm RB-19 initial color by photocatalysis, as a function of pH and ZnO concentration.

The three dimensional representation of the polynomial is shown in Fig. 5. The response surface was very different from that the TiO_2 reaction system. As the time required to degrade the color by 90% must be minimized, the most favorable ranges for improving the reaction are shown in the lower part of the response surface. The best conditions for fast discoloration are obtained at high initial pH and at intermediate values of ZnO concentration in the range studied. Optimal values are $0.8\,g\,l^{-1}$ ZnO and pH 11, derived from the polynomial (Eq. (2)) at fixed dye concentration (50 ppm). As in the case of TiO_2 photocatalysis, the optimized values are used below.

3.1.4. Effect of the RB-19 initial concentration

The photocatalytic degradation of most organic compounds is well described by a pseudo-first-order kinetic for diluted solutions [23]. The kinetic follows a Langmuir–Hinshelwood (L–H) mechanism supporting the heterogeneous catalytic character of the reaction system. The linearized form of the L–H model is shown in Eq. (3), where r_0 is the initial rate of disappearance of the organic substrate and C_0 is the equilibrium bulk-solute concentration. K represents the equilibrium constant for monolayer adsorption of the substrate on the catalyst surface and k_0 the limiting rate of reaction at maximum coverage for the experimental conditions:

$$\frac{1}{r_0} = \frac{1}{k_0} + \frac{1}{k_0 K C_0} \tag{3}$$

In order to demonstrate the concordance of our reaction systems (using TiO_2 and ZnO) with the L–H kinetic model, k_0 values were calculated from the straight line slope of Fig. 6A and B, for TiO_2 and ZnO, respectively. The calculated values were: $k_0 = 2 \times 10^{-6}\,l\,mol^{-1}\,min^{-1}$ and $K = 1 \times 10^{6}\,l\,mol^{-1}$, for the TiO_2 system reaction, and $k_0 = 1 \times 10^{-5}\,l\,mol^{-1}\,min^{-1}$ and $K = 2 \times 10^{4}\,l\,mol^{-1}$, for the ZnO system. These calculations take into consideration the dye content of the Aldrich preparation (∼50%). There is a significant difference between the adsorption properties of TiO_2 and ZnO, reflected visually in the high adsorption of the dye over titania. The magnitude of the adsorption constant K determined for RB-19 on TiO_2 and ZnO, is in agreement

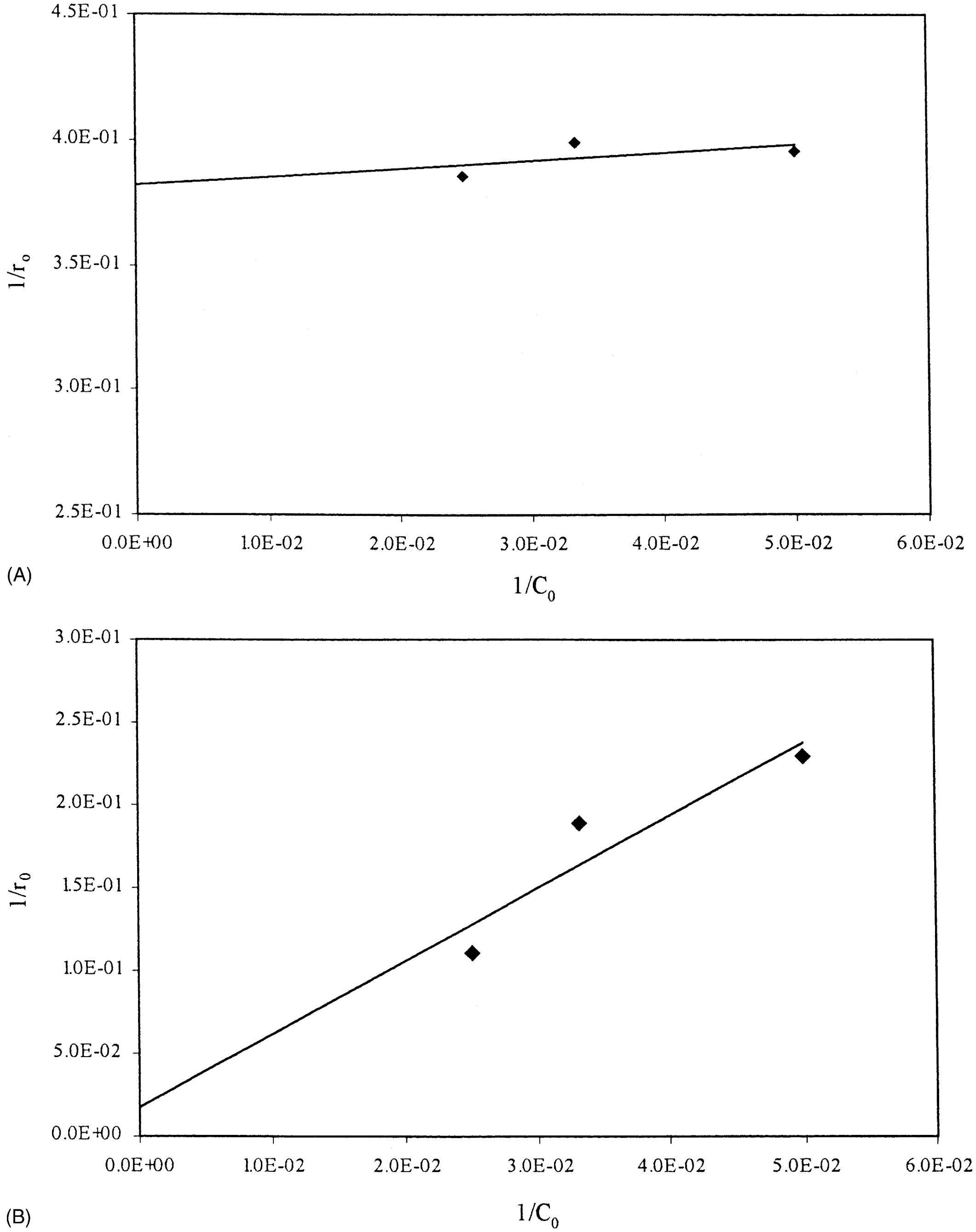

Fig. 6. L–H plot for RB-19 under optimized conditions determined for (A) TiO_2 ($[TiO_2] = 0.5\,g\,l^{-1}$, pH = 11) and (B) ZnO photocatalysis ($[ZnO] = 0.8\,g\,l^{-1}$, pH = 11).

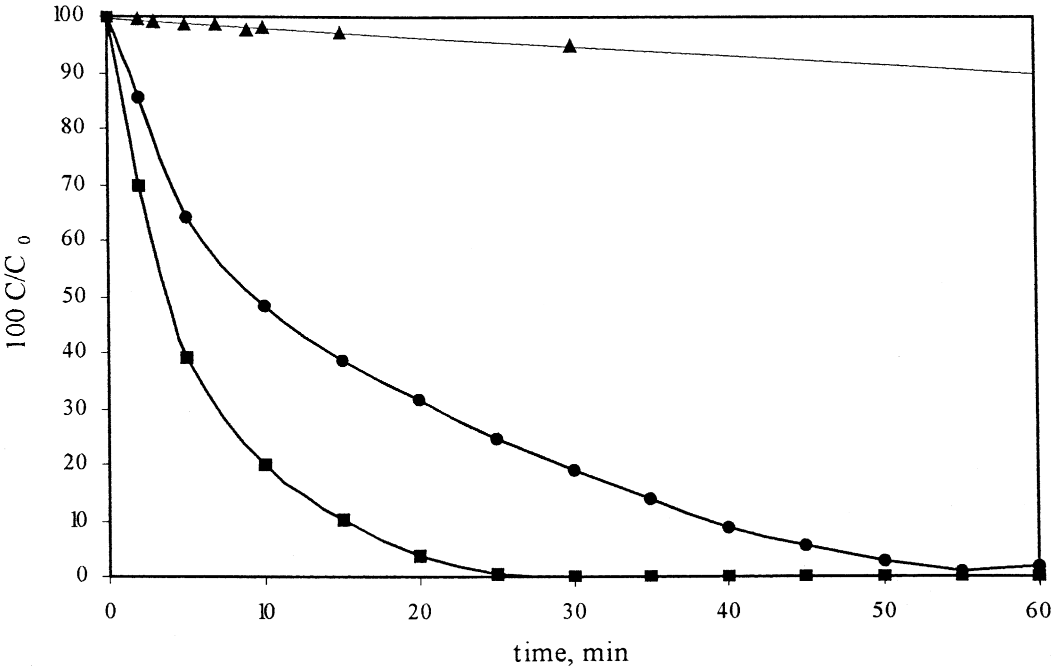

Fig. 7. Kinetic profile of 50 ppm RB-19 solution discoloration by photocatalysis carried out under optimized conditions in the reactor B with recycling (total volume = 4 l). (▲)UV light, pH = 11; (●) $[TiO_2] = 0.5\,g\,l^{-1}$, pH = 11; (■) $[ZnO] = 0.8\,g\,l^{-1}$, pH = 11.

with that reported for photocatalytic degradation of Acid Blue 74 [24].

3.2. Photocatalysis in the reactor with recycling

Once the best conditions for the discoloration by photocatalysis with TiO_2 and ZnO had been assessed, the reaction system was modified. In order to enhance accuracy of data obtained from the optimized reaction, the volume of the suspension was increased to 4 l in the system operated with recycling in the reactor shown in Fig. 2B.

3.2.1. Degradation of RB-19 under optimized conditions

The discoloration profiles with TiO_2 and ZnO at optimized operations conditions are shown in Fig. 7. The comparison is valid in the studied ranges for the variables pH and catalyst amount for both catalysts. It can be clearly observed that the initial rate discoloration of RB-19 is significantly high when ZnO was used, compared with TiO_2 photocatalysis. In fact, discoloration of the 4 l suspension by one order of magnitude was achieved in ca. 15 min when $0.8\,g\,l^{-1}$ zinc oxide was used at pH 11. At the optimized conditions for TiO_2 ($0.5\,g\,l^{-1}$, pH = 11), 90% color removal was achieved in ca. 40 min. Total color removal was achieved at different times in the two systems: 25 and 50 min, for ZnO and TiO_2, respectively, following an expected pseudo-first-order kinetic.

Arslan and Balcioglu [25] stated that the surface of the semiconductor TiO_2 is highly hydroxylated at alkali pH, then the reaction driven by hydroxyl attack is favored and overall rate is enhanced. On the other hand, a similar enhancement in the degradation of 2-phenylphenol was observed by Khodja et al. [22] when ZnO was used as catalyst, attributing this rate increase to a more efficient formation of OH radical from OH^-.

In a recent publication, Poulios and Aetopoulou [26] described very similar behavior of both catalysts acting on the reactive dye Orange 16. According to Kormann et al. [27], one possible explanation for the high photocatalytic activity of ZnO could be the higher production of hydrogen peroxide production on the catalyst surface compared with TiO_2 when illuminated.

3.2.2. Electric energy determination

The electrical energy consumption of the advanced oxidation process has been proposed as figure-of-merit for comparing the cost of each technology. The EE/O has been defined as the “electrical energy in kilowatt hours (kWh) required to bring about the degradation of a contaminant by one order of magnitude in 1000 l of contaminated water or air” [28]. In this work we define the EE/O as the energy required to remove the initial color in one order of magnitude.

In a previous study we have reported the EE/O for RB-19 in two different non-optimized reactions. Comparing TiO_2 immobilized in glass rings with suspended TiO_2, values of 139 and 104 kWh m^{-3} were obtained. Arslan et al. [29] calculated the EE/O in 20-fold diluted synthetic dye-house effluent for six different reactive dyes, obtaining values of 0.22, 0.72 and 4.85 kWh m^{-3}, respectively, for the O_3, O_3/H_2O_2 and UV/H_2O_2 systems.

The electric dose (kWh m^{-3}) necessary to reduce the color at different times was calculated from the kinetic data obtained at optimized conditions (Fig. 8). The calculated dose considers the electric power of the lamp (125 W) and the total volume of the reactor (4 l) at different times of reaction working in batch conditions. Fig. 8 shows a logarithmic plot of C/C_0 versus electric energy dose. The EE/O for both catalysts ZnO and TiO_2 under optimized conditions was determined from this graph. The values 7.6 and 22.4 kWh m^{-3} were determined for ZnO and TiO_2, respectively, using the intercept of the straight line for each catalyst with the one order of magnitude color removal line.

In conclusion, the use of the of experimental design methodology to optimize the operational parameters of the reaction can be extremely helpful in reducing the energetic cost of waste water treatment.

3.2.3. Toxicity and TOC depletion

The analysis of acute toxicity during the course of the 50 ppm RB-19 photocatalyzed degradation was carried out in the circulating reactor, with optimized conditions, in order to determine the formation of toxic products in the course of the reaction. The initial dye solution did not present any toxicity against the bacteria *V. fischeri*, as shown in Fig. 9. After 10 min of irradiation in the presence of ZnO or TiO_2, the acute toxicity increased significantly, reaching values of 50 and 30 toxicity units, respectively. The toxicity units

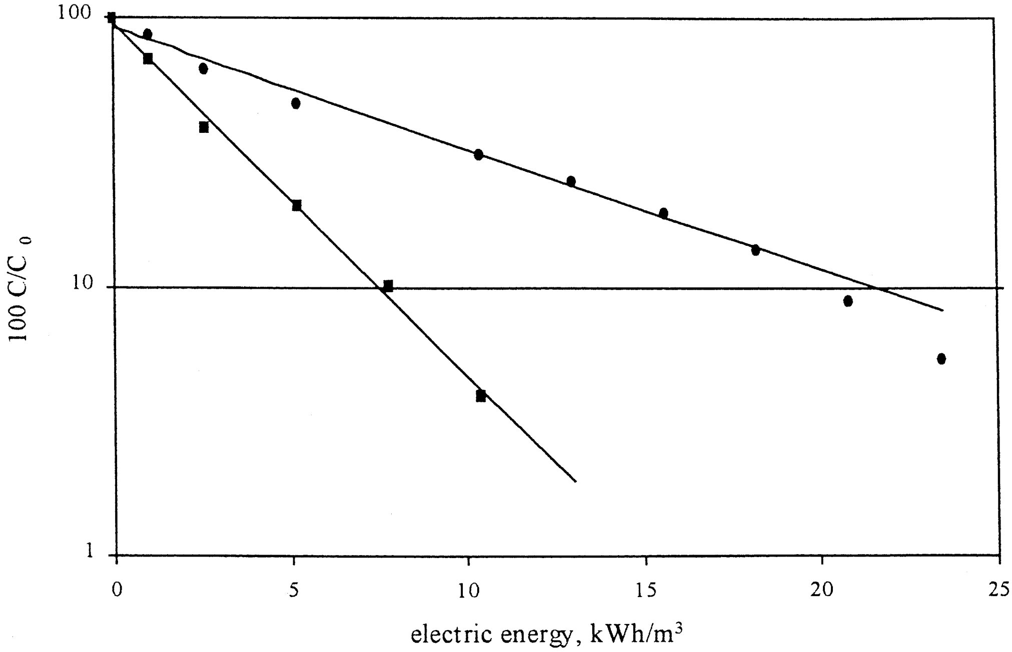

Fig. 8. EE/O determined for the photocatalytic systems working under optimized conditions in the reactor B (4 l), operated with recycling of the suspension. (●) $[TiO_2] = 0.5\,g\,l^{-1}$, pH = 11; (■) $[ZnO] = 0.8\,g\,l^{-1}$, pH = 11.

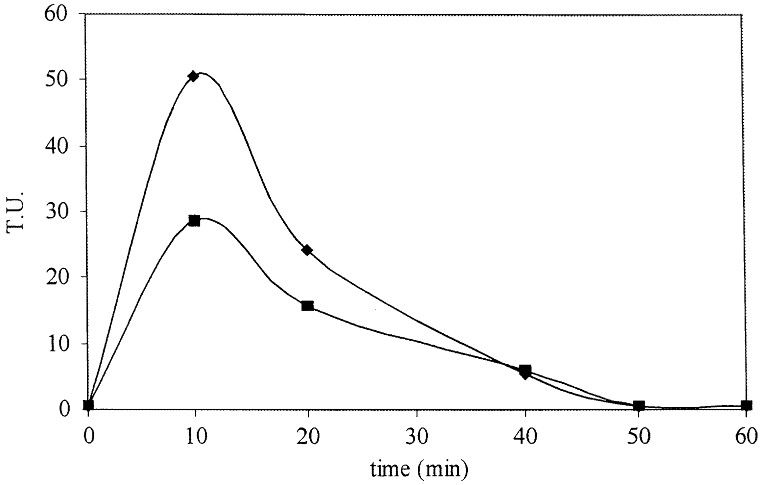

Fig. 9. Acute toxicity during the course of the photocatalytic reactions determined by Microtox, for TiO_2 (■) and ZnO (◆). Reactions were performed in the reactor B (4 l), with suspension recycling. $[TiO_2] = 0.5\,g\,l^{-1}$, pH = 11; $[ZnO] = 0.8\,g\,l^{-1}$, pH = 11).

were previously defined as $100/EC_{50}$. The high accumulation of toxic intermediates in the ZnO photo-assisted catalysis is in agreement with the higher initial rate for the ZnO-catalyzed reaction, indicated above (Fig. 8). Apparently, due to their high initial rate, more concentrated toxic intermediates are formed during the first stages of the reaction. This initial toxicity induced by photodegradation of RB-19 was depleted at times over 10 min, always being higher in the ZnO photocatalytic reaction. After 20 min of irradiation the toxicity was reduced to half of that observed at 10 min. At longer times of irradiation the acute toxicity was almost completely removed. At present, efforts are being made to determine the structures of the intermediates to be correlated with the initial increase of the toxicity.

On the other hand, the TOC was moderately removed by using both catalysts. The initial value of TOC (32 ppm) was reduced in 46% and 60% after 1 h of irradiation under optimized conditions for TiO_2 and ZnO, respectively. It is important to remark that just around 50% of the commercial preparation used in the experiments correspond to dye.

4. Conclusions

The optimization of photocatalytic process by means of response surface is an appropriate tool for reducing both the number of experiments and the energy consumption involved in the RB-19 discoloration. The photocatalytic process follows an L–H mechanism for the two catalysts studied, TiO_2 and ZnO.

Zinc oxide is a more efficient catalyst than TiO_2 in the color removal of RB-19 and its use is limited only by pH. Although toxicity increases during the first stages of the reaction, it was completely removed on achievement of thorough discoloration.

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