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# Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to $TiO_2$

N. Daneshvar [a,*], D. Salari [b,1], A.R. Khataee [a,2]

[a] *Water and Wastewater Treatment Research Laboratory, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*
[b] *Laboratory of Petroleum Technology, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*

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**Abstract**

The degradation of acid red 14 (AR14), commonly used as a textile dye, can be photocatalysed by ZnO. Using advanced oxidation processes (AOPs), zinc oxide appears to be a suitable alternative to $TiO_2$ for water treatment. In this study, a detailed investigation of photocatalytic degradation of acid red 14 is presented. Photodegradation efficiency was small when the photolysis was carried out in the absence of ZnO and it was also negligible in the absence of UV light. The semi-log plot of dye concentration versus time was linear, suggesting first order reaction ($K = 0.0548\,min^{-1}$). The effects of some parameters such as pH, amount of photocatalyst, hydrogen peroxide and ethanol concentration were also examined.

The addition of proper amount of hydrogen peroxide improved the decolorization, while the excess hydrogen peroxide could quenched the formation of hydroxyl radicals ($^{\bullet}OH$). As our results indicated that ethanol inhibited the photodegradation of dye, we concluded from the inhibitive effect of ethanol that hydroxyl radicals played a significant role in the photodegradation of dye. This should not undermine direct oxidation caused by positive holes.


*Keywords:* Advanced oxidation processes; Heterogeneous photocatalysis; Azo dyes; Acid red 14; Zinc oxide

## 1. Introduction

The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Azo dyes, such as acid red 14 (AR14), are widely used in the textile industry [1,2].

Various chemical and physical processes, such as chemical precipitation and separation of pollutants, coagulation, electrocoagulation [3], elimination by adsorption on activated carbon, etc. are applied for color removal from textile effluents. One difficulty with these methods, is that they are not destructive but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced which calls for further treatment [4–6]. In recent years an alternative to conventional methods, is "advanced oxidation processes" (AOPs), based on the generation of very reactive species such as hydroxyl radicals, that oxidizes a broad range of organic pollutants quickly and non-selectively [7,8].

AOPs include photocatalysis systems such as a combination of a semiconductor ($TiO_2$, ZnO, etc.) and UV light. Due to a faster electron transfer to molecular oxygen, $TiO_2$ is found to be more efficient for photocatalytic degradation of pollutants [9]. However, widespread use of $TiO_2$ and platinum catalyst is uneconomic for large-scale water treatment operations. ZnO appears to be a suitable alternative to $TiO_2$ since its photodegradation mechanism has been proven to be similar to that of $TiO_2$ [10,11]. ZnO has been reported, sometimes, to be more efficient than $TiO_2$. Its efficiency has been reported to be particularly noticeable in the advanced oxidation of pulp mill bleaching wastewater [12], the photooxidation of 2-phenylphenol [13] and photocatalysed oxidation of phenol [14,15].

In our previous works we reported the effect of operational parameters on photocatalytic degradation of acid red 14 [1] and sodium dodecylbenzene sulfonate (DBS) [16] by $UV/TiO_2$ process, so the aim of the present work is to study the photocatalytic degradation of an azo dye (acid red 14), extensively used by the textile industry, in the presence of

* Corresponding author. Tel.: +98-411-5275825/5212096/3393146; fax: +98-411-3340191.
*E-mail addresses:* nezam_daneshvar@yahoo.com (N. Daneshvar), salari_d@yahoo.com (D. Salari), ar_khataee@yahoo.com (A.R. Khataee).
[1] Tel.: +98-411-3308639; fax: +98-411-3340191.
[2] Tel.: +98-411-3393165; fax: +98-411-3340191.

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ZnO as a suitable alternative to $TiO_2$ irradiated by UV-C light (UV/ZnO process). The effect of UV light irradiation, pH and the amount of photocatalyst were both examined. The effect of the addition of $H_2O_2$ was also studied for enhancing the elimination of azo dye. The inhibitive influence of ethanol, commonly used to quench hydroxyl radicals, provides information on reactive species involved in the reaction.

## 2. Experimental

### 2.1. Materials

Acid red 14, zinc oxide, hydrogen peroxide, sulfuric acid, sodium hydroxide and ethanol were of laboratory reagent grade and used without further purification. Structure of acid red 14 (Chromotrope FB) is given in Fig. 1.

### 2.2. Photoreactor and light source

For UV/ZnO process, irradiation was performed in a batch photoreactor of 500 ml in volume with a mercury lamp Philips 30 W (UV-C).

### 2.3. Procedures

For the photodegradation of AR14, a solution containing known concentration of dye and ZnO was prepared and it was allowed to equilibrate for 30 min in the darkness, then 50 ml of the prepared suspension was transferred to a 500 ml pyrex reactor. The suspension pH values were adjusted at desired level using dilute NaOH and $H_2SO_4$ and then the pH values were measured with pH meter (Philips PW 9422). After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time. The concentration of dye in each degraded sample was determined with a spectrophotometer (UV/VIS Spectrophotometer, Perkin-Elmer 550 SE) at $\lambda_{max} = 515$ nm and a calibration curve. By this method conversion percent of AR14 can be obtained in different intervals. The degree of photodegradation ($X$) as a function of time is given by:

$$X = \frac{C_0 - C}{C_0} \quad (1)$$

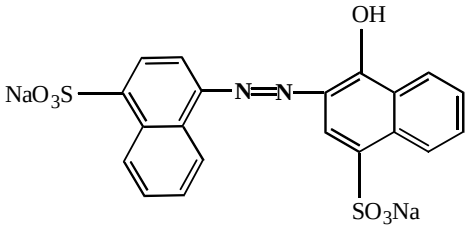


Fig. 1. Structure of acid red 14 (C.I. no. 14720).

where $C_0$ is the initial concentration of AR14, and $C$ the concentration of AR14 at time $t$.

## 3. Results and discussion

### 3.1. UV-Vis spectra changes

Fig. 2 shows a typical time-dependent UV-Vis spectrum of AR14 solution during photoirradiation. The absorption peaks, corresponding to dye, diminished and finally disappeared under reaction which indicated that the dye had been degraded. No new absorption bands appear in either the visible or ultraviolet regions. The spectrum of AR14 in the visible region exhibits a main band with a maximum at 515 nm. The decrease of absorption peaks of AR14 at $\lambda_{max} = 515$ nm in this figure indicated a rapid degradation of azo dye. It also indicates that the nitrogen to nitrogen double bond (–N=N–) of the azo dye, in this study, is the most active site for oxidative attack. Complete discoloration of dye was observed after 1 h in the optimized conditions.

### 3.2. Effect of UV irradiation and ZnO particles

It can be seen from Fig. 3 that in the presence of both ZnO and light, 70.4% of dye was degraded at the irradiation time of 3.5 h. This was contrasted with 14.3% degradation for

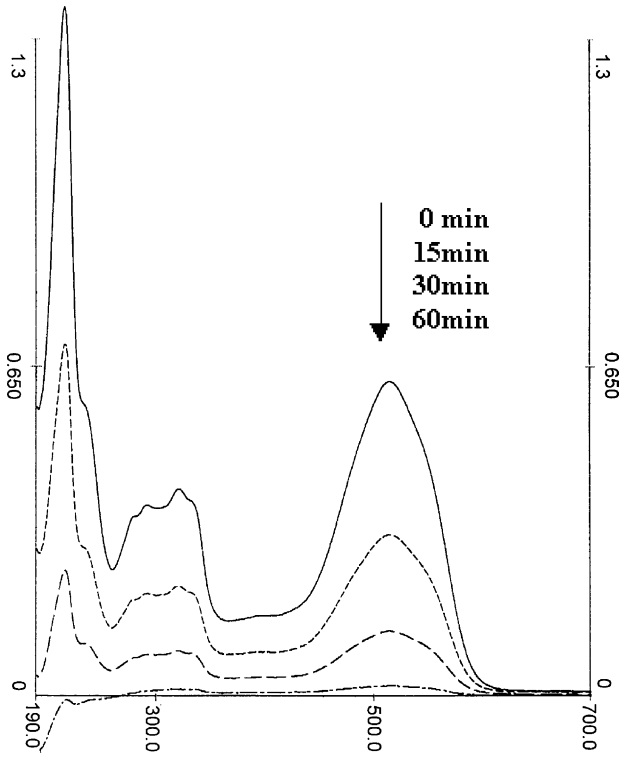


Fig. 2. UV-Vis spectra changes of AR14 (20 ppm) in aqueous ZnO dispersion (ZnO 160 ppm) irradiated with a mercury lamp light at pH neutral, at times: (1) zero, (2) 15 min, (3) 30 min, and (4) 60 min where ppm = mg/kg ≈ mg/L = g/m$^3$.

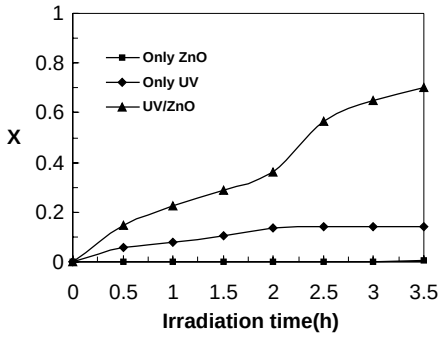


Fig. 3. Effect of UV light and ZnO on photocatalytic degradation of AR14. $[AR14]_0 = 20$ ppm, ZnO = 60 ppm, pH neutral.

the same experiment performed in the absence of ZnO, and the negligible 0.5% when the UV lamp had been switched off and the reaction was allowed to occur in the darkness. These experiments demonstrated that both UV light and a photocatalyst, such as ZnO were needed for the effective destruction of AR14. Because it has been established that the photocatalysed degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of catalyst (Eq. (2)).The high oxidative potential of the hole ($h^+_{VB}$) in the catalyst permits the direct oxidation of organic matter (dye) to reactive intermediates (Eq. (3)). Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. (4)) or by the reaction of the hole with $OH^-$ (Eq. (5)). The hydroxyl radical is an extremely strong, non-selective oxidant ($E^0 = +3.06$ V) which leads to the partial or complete mineralization of several organic chemicals.

$$ZnO + h\nu \rightarrow ZnO\left(e^-_{CB} + h^+_{VB}\right) \quad (2)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet +} \rightarrow \text{oxidation of the dye} \quad (3)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + {}^\bullet OH \quad (4)$$

$$h^+_{VB} + OH^- \rightarrow {}^\bullet OH \quad (5)$$

Electron in the conduction bond ($e^-_{CB}$) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (6)). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. (7)) or hydrogen peroxide (Eq. (8)).

$$e^-_{CB} + O_2 \rightarrow {}^\bullet O_2{}^- \quad (6)$$

$${}^\bullet O_2{}^- + \text{dye} \rightarrow \text{dye} - OO^\bullet \quad (7)$$

$${}^\bullet O_2{}^- + HO_2{}^\bullet + H^+ \rightarrow H_2O_2 + O_2 \quad (8)$$

Electrons in the conduction bond are also responsible for the production of hydroxyl radicals, species which have been indicated as the primary cause of organic matter mineralization (Eq. (9)) [15–17]. The mechanism is assumed up in Fig. 4.

$${}^\bullet OH + \text{dye} \rightarrow \text{degradation of the dye} \quad (9)$$

### 3.3. Effect of catalyst concentration

The effect of the amount of ZnO on the photodegradation efficiency was shown in Fig. 5. Experiments performed with different concentrations of ZnO showed that the photodegradation efficiency increases with an increase in ZnO concentration up to 160 ppm, and is then decreased. This

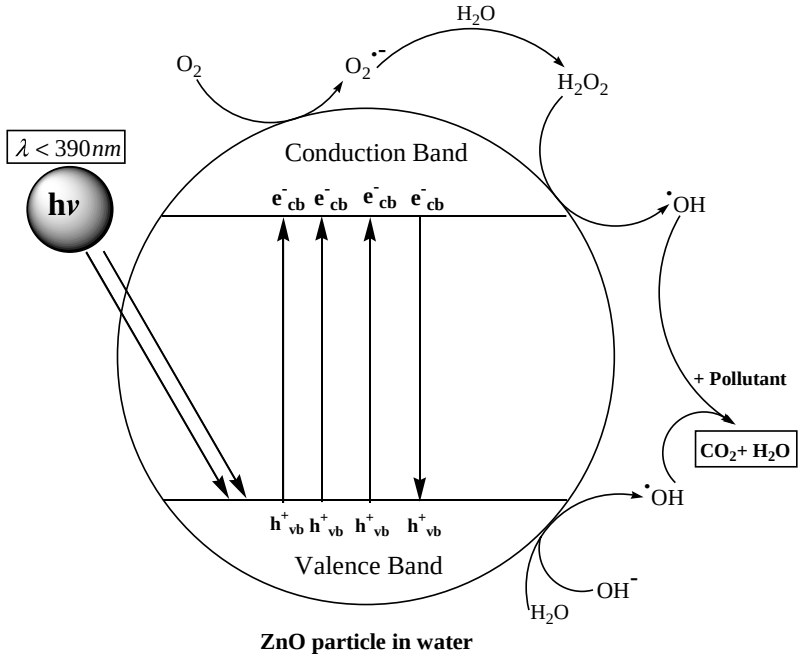


Fig. 4. General mechanism of the photocatalysis.

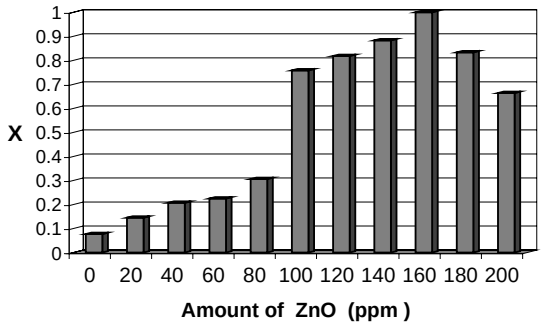


Fig. 5. Effect of ZnO amount on photodegradation efficiency of AR14 at irradiation time of 1 h. $[AR14]_0 = 20$ ppm, pH neutral.

observation can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension [18]. The total active surface area increases with increasing catalyst dosage. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases [19]. Since the most effective decomposition of AR14 was observed with 160 ppm of ZnO, the other experiments were performed in this concentration of ZnO.

### 3.4. Effect of pH

Fig. 6 shows the color removal efficiency of acid red 14 solution as a function of pH. The effect of pH on the photodegradation efficiency of AR14 was examined in the range 4–12 in an aqueous ZnO suspension. The results showed that a direct influence the pH of the solution, had on the heterogeneous photocatalysis process (Fig. 6). In acidic solutions photodegradation efficiency was more than that in alkaline solutions. It is because photodecomposition of ZnO takes place in acidic and neutral solutions. The photocorrosion of ZnO is complete at pH lower than 4. The formation of $Zn^{2+}$ is attributed to the oxidation of ZnO by $h^+_{VB}$ (Eq. (10)) [13,20].

$$ZnO + 2h^+_{VB} \rightarrow Zn^{2+} + O^* \quad (10)$$

At pH higher than 10, no photocorrosion of ZnO takes place. More efficient formation of hydroxyl radicals occurs in alkaline solution (Eq. (5)) [18]. AR14 has a sulfuric group in its structure, which is negatively charged in alkaline conditions, therefore, in the alkaline solution dye may not be adsorbed onto photocatalyst surface effectively.

In the light of the findings, it was deduced that the efficient condition for photodegradation of AR14 was neutral pH.

### 3.5. Kinetics of photocatalytic degradation of AR14

The plot log[dye] versus irradiation time for AR14 was linear suggesting that the photodegradation reaction approximately follows the first order kinetics. Rate constant ($K = 0.0548\,min^{-1}$) was estimated from the slope of the log[dye] versus time plot in the optimized conditions.

### 3.6. Effect of ethanol

According to the previous literature [5,16], alcohols such as ethanol, are commonly used to quench hydroxyl radicals. The rate constant of reaction between hydroxyl radical and ethanol is $1.9 \times 10^9\,M^{-1}\,s^{-1}$ [13]. It was observed that small amounts of ethanol inhibited the photocatalytic degradation of AR14. What it means could be that, hydroxyl radicals play a major role in photocatalytic oxidation. The photodegradation efficiency decreases with an increase in the amount of ethanol. With 8% (v/v) of ethanol the photodegradation efficiency decreases to 7.7% at the irradiation time of 1 h (Fig. 7). Thus the transformation is not only due to hydroxyl radicals. There must be another species involved which does not react with alcohols. The species is most probably the positive holes ($h^+_{VB}$) formed on the irradiated photocatalyst, which react with the adsorbed dye molecules (Eq. (3)).

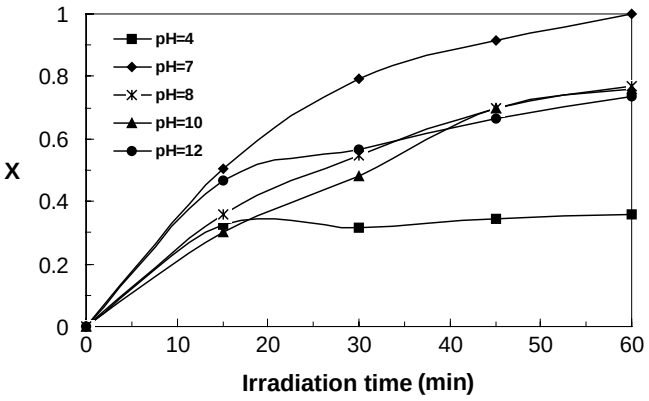


Fig. 6. Effect of pH on photodegradation efficiency of AR14 at different irradiation times. $[AR14]_0 = 20$ ppm, ZnO = 160 ppm.

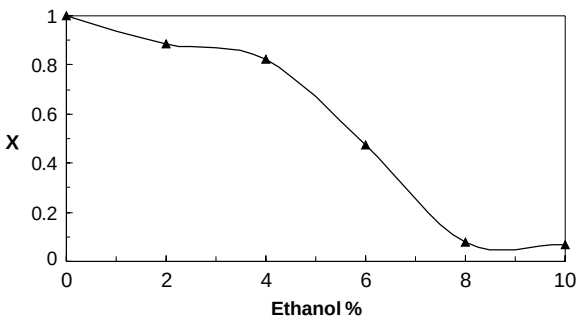


Fig. 7. Inhibitory effect of ethanol on photodegradation efficiency of AR14 at the irradiation time of 1 h. $[AR14]_0 = 20$ ppm, ZnO = 160 ppm, pH neutral.

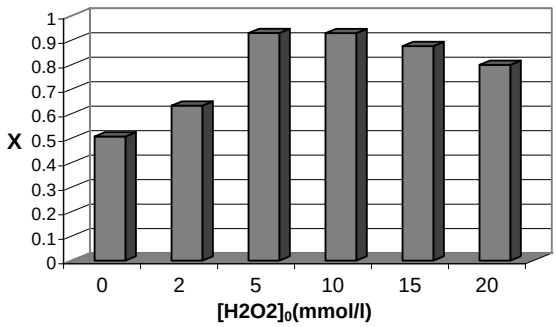


Fig. 8. Effect of $H_2O_2$ addition on photodegradation efficiency of AR14 in UV/ZnO process at the irradiation time of 15 min. $[AR14]_0 = 20$ ppm, ZnO = 160 ppm, pH neutral.

### 3.7. Effect of hydrogen peroxide

Limitation to the rate of photocatalytic degradation has been attributed, by most researches, to the recombination of photogenerated hole–electron pairs [21,22]. The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of peroxides [16,23,24].

The photocatalytic degradation of AR14 has been studied at different hydrogen peroxide concentrations. Results are given in Fig. 8. The degradation rate of AR14 increased with increasing $H_2O_2$ concentration up to 10 mmol/l, but above it, the degradation rate decreased. The higher reaction rates after the addition of peroxide were attributed to the increase in the concentration of hydroxyl radical. According to Eq. (11), at its low concentration of hydrogen peroxide inhibits the electron–hole recombination. Since hydrogen peroxide is a better electron acceptor than molecular oxygen it could act as an alternative electron acceptor to oxygen [1,13]. Hydrogen peroxide may also be split photocatalytically to produce hydroxyl radical directly, as cited in the studies of homogeneous photooxidation using UV/$H_2O_2$ (Eq. (12)) [25,26].

$$e^-_{CB} + H_2O_2 \rightarrow OH^- + {}^\bullet OH \quad (11)$$

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \quad (12)$$

But at high dosage, $H_2O_2$ is a powerful $^\bullet$OH scavenger [1,27]. The experiments showed that Eq. (13) became predominant above 10 mmol/l (Fig. 8).

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2{}^\bullet + H_2O \quad (13)$$

Therefore, the proper addition of hydrogen peroxide could accelerate the photodegradation rate of AR14. However, in order to keep the efficiency of the added hydrogen peroxide, it was necessary to choose the proper dosage of hydrogen peroxide, according to the kinds and the concentrations of the pollutants.

## 4. Conclusion

The results presented in this paper indicated that UV/ZnO process could be efficiently used to degrade the acid red 14. ZnO and UV light had a negligible effect when they were used on their own. The results indicated that degree of degradation of acid red 14 were obviously affected by illumination time, pH and photocatalyst amount. We also learned that optimal amount of photocatalyst was 160 ppm, with dye concentration of 20 ppm. ZnO can not be used in acidic solution. The photocatalytic decomposition of AR14 was most efficient in neutral solution. The complete removal of color, after selection of optimal operational parameters, could be achieved in a relatively short time of about 1 h.

The proper addition of hydrogen peroxide could improve the photodegradation rate, but it was inhibited by ethanol. It was concluded that hydroxyl radicals were the main reactive species, but positive holes were probably also involved.

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## References

[1] N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem. Photobiol. A 157 (2003) 111.
[2] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaoui, C. Guillard, J.M. Herrmann, Appl. Catal. B 39 (2002) 75.
[3] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, Sep. Purif. Technol. 31 (2003) 153.
[4] Y.M. Slokar, A.M.L. Marechal, Dyes Pigments 37 (1998) 335.
[5] C. Galindo, P. Jacques, A. Kalt, Chemosphere 45 (2001) 997.
[6] O. Tunay, I. Kabdasli, G. Eremektar, D. Orhon, Water Sci. Technol. 34 (1996) 9.
[7] W.S. Kuo, P.H. HO, Chemosphere 45 (2001) 77.
[8] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.
[9] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C, Photochem. Rev. 1 (2001) 1.
[10] B. Dindar, S. Icli, J. Photochem. Photobiol. A 140 (2001) 263.
[11] K. Pirkanniemi, M. Sillanpaa, Chemosphere 48 (2002) 1047.
[12] M.C. Yeber, J. Rodriguez, J. Freer, J. Baeza, N. Duran, H.D. Mansilla, Chemosphere 39 (1999) 10.
[13] A.A. Khodja, T. Sehili, J.F. Pihichowski, P. Boule, J. Photochem. Photobiol. A 141 (2001) 231.
[14] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, H. Hidaka, J. Photochem. Photobiol. A 85 (1995) 247.
[15] G. Marci, V. Augugliaro, M.J.L. Munoz, C. Martin, L. Palmisano, V. Rives, M. Schiavello, R.J.D. Tilley, A.M. Venezia, J. Phys. Chem. B 105 (2001) 1033.
[16] N. Daneshvar, D. Salary, M.A. Behnasuady, Iran J. Chem. Chem. Eng. 21 (2002) 55.
[17] C. Galindo, P. Jacques, A. Kalt, J. Photochem. Photobiol. A 130 (2000) 35.
[18] M.S.T. Goncalves, A.M.F. Oliveira-Campos, E.M.M.S. Pinto, P.M.S. Plasencia, M.J.R.P. Queiroz, Chemosphere 39 (1999) 781.
[19] O.E. Kartal, M. Erol, H. Oguz, Chem. Eng. Technol. 24 (2001) 645.
[20] J. Fernandez, J. Kiwi, C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, J. Photochem. Photobiol. A 151 (2002) 213.

[21] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[22] A.L. Linsebigler, G. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735.
[23] R. Bauer, G. Waldner, H. Fallmann, S. Hager, M. Klare, T. Krutzler, S. Malato, P. Maletzky, Catal. Today 53 (1999) 131.
[24] M.A. Fox, M.T. Dulag, Chem. Rev. 93 (1993) 341.
[25] M.I. Stefan, J.R. Bolton, Environ. Sci. Technol. 33 (1999) 870.
[26] S.R. Cater, M.I. Stefan, J.R. Bolton, A. Safarzadeh-Amiri, Environ. Sci. Technol. 34 (2000) 659.
[27] T. Sauer, G.C. Neto, H.J. Jose, R.F.P.M. Moreira, J. Photochem. Photobiol. A 149 (2002) 147.