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Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters

N. Daneshvar[a,*], D. Salari[a,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

Acid Red 14 (AR14), commonly used as a textile dye, could be photocatalytically degraded using TiO_2 suspensions irradiated by a UV-C lamp (30 W). The experiments showed that TiO_2 and UV light had a negligible effect when they were used on their own. The semi-log plot of dye concentration versus time was linear, suggesting first order reaction ($K = 1.41 \times 10^{-2}\,\text{min}^{-1}$). The effects of some parameters such as pH, the amount of TiO_2 and initial dye concentration were also examined.

The photodegradation of AR14 was enhanced by the addition of proper amount of hydrogen peroxide, but it was inhibited by ethanol. From the inhibitive effect of ethanol it was deducted that hydroxyl radicals played a significant role in the photodegradation of dye, but a direct oxidation by positive holes was probably not negligible. Accordingly, it could be stated that the complete removal of color, after selecting optimal operational parameters could be achieved in a relatively short time, about 3.5 h.

Keywords: Advanced oxidation processes; Azo dyes; Acid Red 14; Titanium dioxide; Photodegradation; Photocatalysis

1. Introduction

Dye pollutants from the textile industry are an important source of environmental contamination. Indeed, these effluents are toxic and mostly nonbiodegradable and also resistant to destruction by physico-chemical treatment methods. Removing color from wastes is often more important than other colorless organic substances, because the presence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably [1–4].

Therefore, it is necessary to find an effective method of wastewater treatment in order to remove color from textile effluents. Various chemical and physical processes, such as chemical precipitation and separation of pollutants, electrocoagulation [5], elimination by adsorption on activated carbon etc., are currently used. 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 and further treatments are deemed necessary [6–8].

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 quickly and nonselectively, oxidizes a broad range of organic pollutants [9,10].

The aim of the present work is to investigate the influence of various parameters on photocatalytic decomposition of an azo dye, called Acid Red 14 (AR14) (Fig. 1), in the presence of TiO_2 irradiated by the UV-C light. 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 about the mechanisms and reactive species involved in the reaction.

2. Experimental

2.1. Reagents

The hydrogen peroxide solution (30%), sulfuric acid and ethanol were obtained from Merck, Germany. Sodium hydroxide was purchased from Fluka, Switzerland. TiO_2–P25

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[*] 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.: +98-411-4421850.

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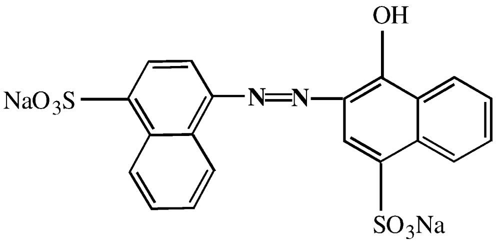

Fig. 1. Structure of Acid Red 14 (C.I. no. 14720).

was used as received. The azo dye, Acid Red 14 (AR14), was obtained from Rang Azar company (Iran) and used without further purification. Its structure is given in Fig. 1.

2.2. Photoreactor and light source

As for UV/TiO_2 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 TiO_2 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. Having adjusted the suspension pH values at the desired level using dilute NaOH and H_2SO_4, we measured the pH values by pH meter (Philips PW 9422). Then, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension homogenous, and the suspension was sampled after an appropriate illumination time. The concentration of dye in each degraded sample was determined by a spectrophotometer (UV-Vis Spectrophotometer Perkin–Elmer 55 OSE) at $\lambda_{max} = 515$ nm and a calibration curve (Fig. 2). By this method conversion percent of AR14 can be obtained in different intervals. The photodegradation efficiency (X) is given by Eq. (1)

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

where C_0 = initial concentration of AR14, C = concentration of AR14 at time t.

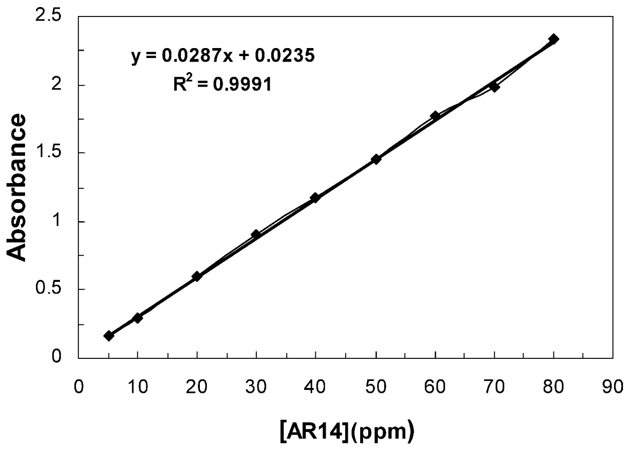

Fig. 2. Calibration curve in wavelength 515 nm.

3. Results and discussion

3.1. UV-Vis spectra changes

The changes in the absorption spectra of AR14 solution during the photocatalytic process at different irradiation times are shown in the Fig. 3. 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 indicates a rapid degradation of azo dye. The decrease is also meaningful with respect to the nitrogen to nitrogen double bond (–N=N–) of the azo dye, as the most active site for oxidative attack. Complete discolouration of dye was observed after 3.5 h in the optimized conditions.

3.2. Effect of UV irradiation and TiO_2 particles

Fig. 4 shows the effect of UV irradiation and TiO_2 particles on photodegradation of AR14. It can be seen from the figure that in the presence of both TiO_2 and light, 88.0% of dye was degraded at the irradiation time of 2.5 h. This was contrasted with 14.0% degradation for the same experiment performed in the absence of TiO_2, and the negligible 0.20% 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 TiO_2 were needed for the effective destruction of AR14. This is due to the fact that when TiO_2 is illuminated with the light of $\lambda < 390$ nm, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron–hole pairs. The valence band (h^+_{VB}) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e^-_{CB}) potential is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO_2. It causes photooxidation of pollutants according to the following reactions (Eq. (2)–(7)) [11–13].

$$TiO_2 + h\nu(\lambda < 390\,\text{nm}) \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \quad (2)$$

$$h^+_{VB} + H_2O_{(ads)} \rightarrow H^+ + {}^{\bullet}OH_{(ads)} \quad (3)$$

$$h^+_{VB} + OH^-_{(ads)} \rightarrow {}^{\bullet}OH_{(ads)} \quad (4)$$

$$e^-_{CB} + O_{2(ads)} \rightarrow {}^{\bullet}O^-_{2(ads)} \quad (5)$$

$$^{\bullet}OH_{(ads)} + \text{dye} \rightarrow \text{degradation of the dye} \quad (6)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet+} \rightarrow \text{oxidation of the dye} \quad (7)$$

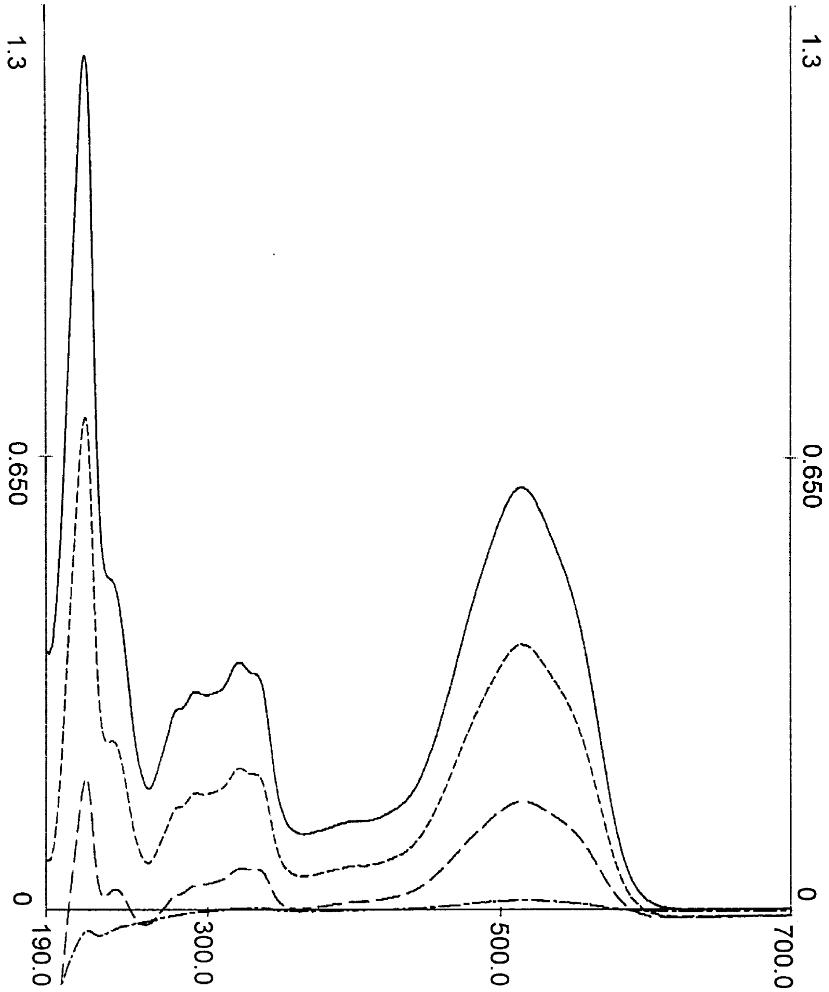

Fig. 3. UV-Vis spectra changes of AR14 (20 ppm) in aqueous TiO_2 dispersion (TiO_2 40 ppm) irradiated with a mercury lamp light at pH neutral, at times: (1) zero (2) 0.5 h (3) 1.5 h (4) 3.5 h.

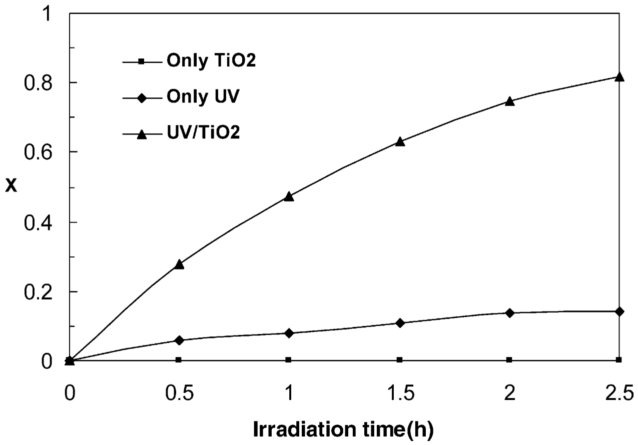

Fig. 4. Effect of UV light and TiO_2 on photocatalytic degradation of AR14. $[AR14]_0 = 20$ ppm, $TiO_2 = 40$ ppm, pH neutral.

3.3. Effect of the amount of photocatalyst

The effect of the amount of TiO_2 on the AR14 removal was studied as shown in Figs. 5 and 6. The photodegradation efficiency increases with an increase in the amount of photocatalyst, reaches the higher value of catalyst amount (40 ppm) and then decreases. The most effective decomposition of AR14 was observed with 40 ppm of TiO_2. The reason of this observation is thought to be the fact that when all dye molecules are adsorbed on TiO_2, the addition of higher quantities of TiO_2 would have no effect on the degradation efficiency. Another cause for this is supposedly an increased opacity of the suspension, brought about as a result of excess of TiO_2 particles [14].

3.4. Effect of initial AR14 concentration

The effect of initial AR14 concentration on photodegradation efficiency is shown in Fig. 7. It was observed that the photodegradation conversion of AR14 decreases with

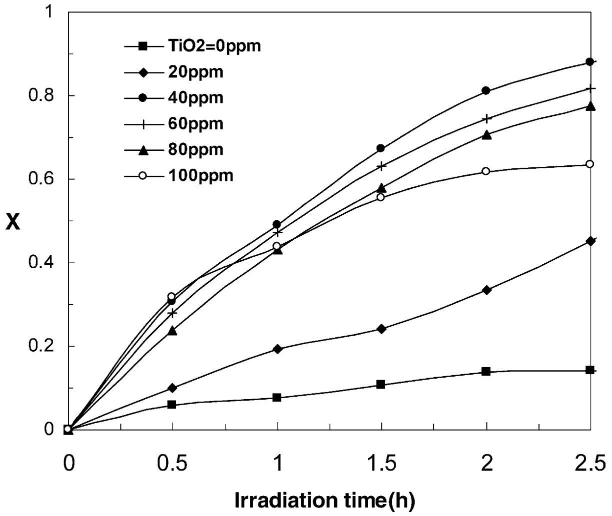

Fig. 5. Effect of the amount of TiO_2 on photodegradation efficiency of AR14. $[AR14]_0 = 20$ ppm, pH neutral.

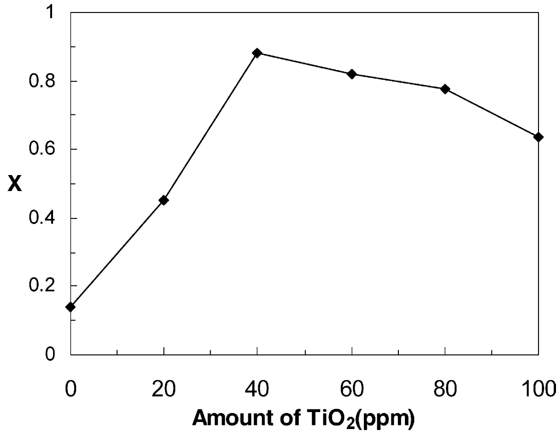

Fig. 6. Effect of the amount of TiO_2 on photodegradation efficiency of AR14 at irradiation time of 2.5 h. $[AR14]_0 = 20$ ppm, pH neutral.

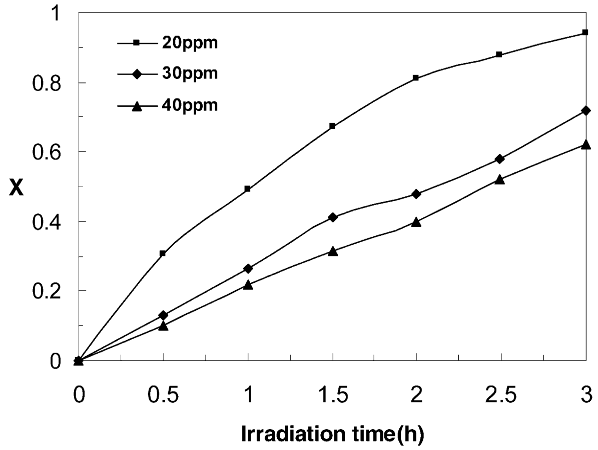

Fig. 7. Effect of initial AR14 concentration on photodegradation efficiency. $TiO_2 = 40$ ppm, pH neutral.

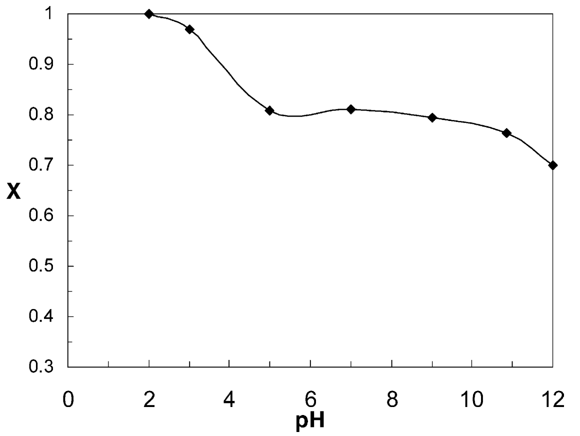

Fig. 8. Effect of pH on photodegradation efficiency of AR14 at the irradiation time of 2 h. $[AR14]_0 = 20$ ppm, $TiO_2 = 40$ ppm.

an increase in the initial concentration of AR14. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2. The large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with photogenerated holes or hydroxyl radicals, because of the lack of any direct contact between them. Once the concentration of dye is increased, it also causes the dye molecules to adsorb light and the photons never reach the photocatalyst surface, thus the photodegradation efficiency decreases.

3.5. *Effect of pH*

According to the authorities [15,16], pH value is one of the factors influencing the rate of degradation of some organic compounds in the photocatalytic process. It is also an important operational variable in actual wastewater treatment. Fig. 8 demonstrates the photodegradation of AR14 at different pH from 2 to 12, which clearly shows that the best results were obtained in acidic solution, ($pH = 2$, $X = 100\%$). According to the zero point of charge of TiO_2, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution [17,18]. Since the dye has a sulfuric group in its structure, which is negatively charged, the acidic solution favors adsorption of dye onto photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of AR14 in acidic solutions, which is probably due to the formation of $OH^{\bullet}$ as it can be inferred from the following reactions (Eqs. (8)–(11)) [19].

$$e^-_{CB} + O_{2(ads)} \rightarrow {}^{\bullet}O^-_{2(ads)} \tag{8}$$

$$^{\bullet}O^-_{2(ads)} + H^+ \rightarrow HO_2{}^{\bullet} \tag{9}$$

$$2HO_2{}^{\bullet} \rightarrow O_2 + H_2O_2 \tag{10}$$

$$H_2O_2 + {}^{\bullet}O^-_{2(ads)} \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{11}$$

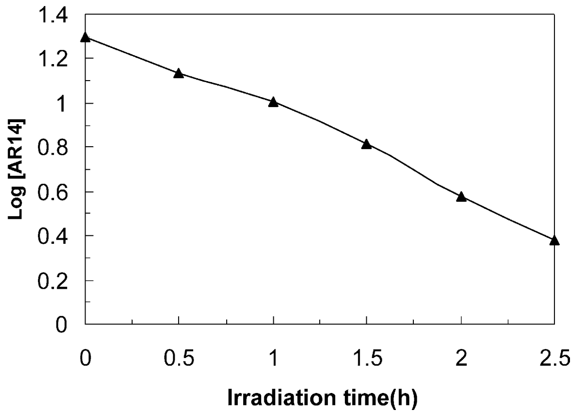

Fig. 9. Relationship between log[AR14] and irradiation time on photocatalytic degradation of AR14. $[AR14]_0 = 20$ ppm, $TiO_2 = 40$ ppm, pH neutral.

Because the difference between the degree of photodegradation of AR14 in acidic solution ($pH = 2$) and neutral ($pH = 7$) amounts to only 19%, the following experiments were carried out with neutral pH. It is the natural reaction of AR14 solution and does not require addition of extra agent (H_2SO_4) to regulate the pH of the solution.

3.6. Kinetics of photcatalytic 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 (Fig. 9). Rate constant ($K = 1.41 \times 10^{-2}\ \mathrm{min}^{-1}$) was estimated from the slope of the log[dye] versus time plot in the optimized conditions.

3.7. Addition of ethanol

Alcohols such as ethanol are commonly used to quench hydroxyl radicals. The rate constant of reaction between hydroxyl radical and ethanol is $1.9 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ [20]. As it was observed in the experiments, small amounts of ethanol inhibited the photocatalytic degradation of AR14 (Fig. 10). This may enable us to draw the conclusion that hydroxyl radicals play a major role in photocatalytic oxidation. It should be noted that the photodegradation efficiency decreases with an increase in the amount of ethanol, to be more exact, with 0.02% (v/v) of ethanol the photodegradation efficiency decreases to 12.40% at the irradiation time of 2 h, but it does not come to a full stop and remains constant at a minor amount (Fig. 11). Thus, hydroxyl radicals are not sole cause of degradation. 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 (Eq. (7)).

3.8. Addition of hydrogen peroxide

The photocatalytic degradation of AR14 was at focus in our experiment at different hydrogen peroxide concentrations, the results of which are given in Fig. 12. The degradation rate of AR14 increased with increasing H_2O_2 concentration up to 10 mmol/l, but above it, there was a decrease in the degradation rate. Similar results have been reported for photocatalytic oxidation of polyvinyl alcohol [19], phenyl azonaphtol [7] and cationic azo dye [21].

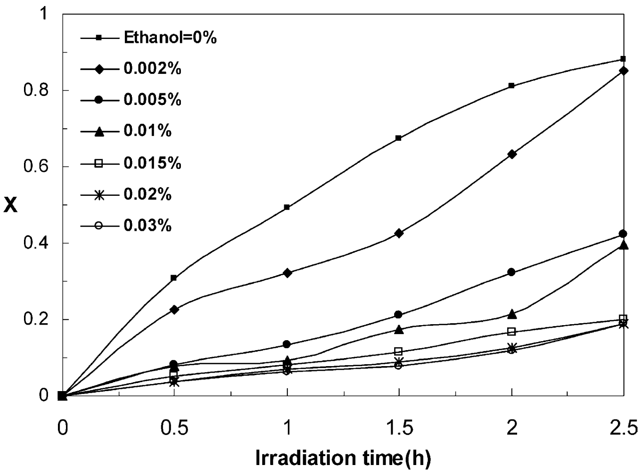

Fig. 10. Inhibition of photodegradetion of AR14 (20 ppm) by ethanol. $TiO_2 = 40$ ppm, pH neutral.

The higher reaction rates after the addition of peroxide were attributed to the increase in the concentration of hydroxyl radical. At low concentration of hydrogen peroxide, it inhibits the electron–hole recombination, according to Eq. (12) and it could act as an alternative electron acceptor to oxygen (Eq. (13)), because hydrogen peroxide is a better electron acceptor than molecular oxygen [22]. Hydrogen peroxide may also be split photolytically to produce hydroxyl radical directly, as cited in the studies of homogeneous photooxidation using UV/H_2O_2 (Eq. (14)) [22].

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + {}^\bullet OH \qquad (12)$$

$$^\bullet O_2^- + H_2O_2 \rightarrow OH^- + {}^\bullet OH + O_2 \qquad (13)$$

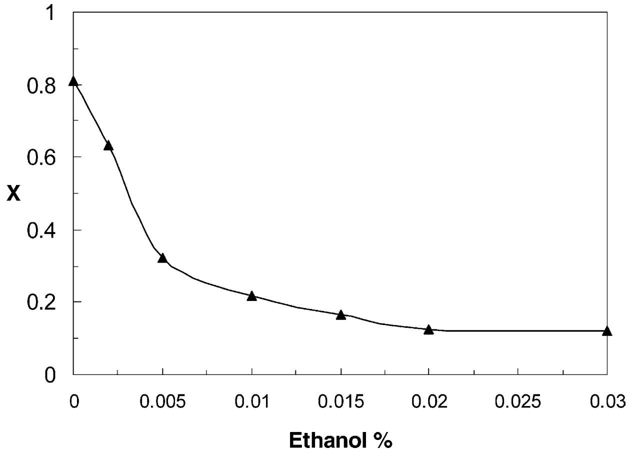

Fig. 11. Inhibitory effect of ethanol on photodegradation efficiency of AR14 at the irradiation time of 2 h. $[AR14]_0 = 20$ ppm, $TiO_2 = 40$ ppm, pH neutral.

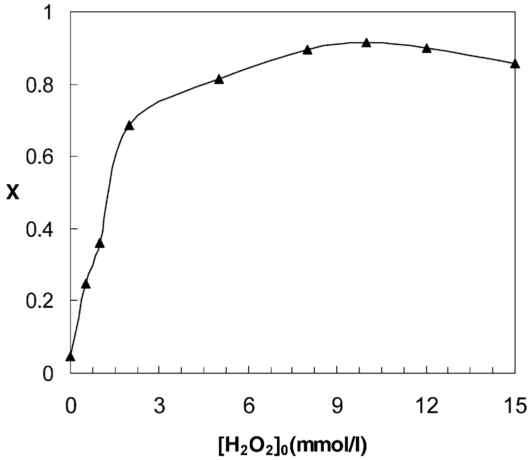

Fig. 12. Effect of H_2O_2 addition on photodegradation efficiency of AR14 in UV/TiO_2 process. $[AR14]_0 = 20$ ppm, $TiO_2 = 40$ ppm, pH neutral.

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad (14)$$

But at high concentration, H_2O_2 is a powerful $OH^{\bullet}$ scavenger [7,23]. The experiments showed that Eqs. (15) and (16) became predominant above 10 mmol/l (Fig. 12).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2{}^{\bullet} + H_2O \quad (15)$$

$$HO_2{}^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (16)$$

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 concentration of hydrogen peroxide according to the kinds and the concentrations of the pollutants.

4. Conclusion

The results of our study showed that UV/TiO_2 process could be efficiently used to degrade the Acid Red 14. Photodegradation efficiency of dye was small when photolysis was carried out in the absence of TiO_2 and negligible in the absence of the UV light. The results indicated that the degree of degradation of AR14 were obviously affected by the initial dye concentration, pH and the amount of TiO_2. We also learned that the optimal amount of photocatalyst was 40 ppm, with dye concentration of 20 ppm.

From the inhibitive effect of ethanol, it was concluded that hydroxyl radicals were the main reactive species, but probably positive holes were also involved. The addition of proper amount of hydrogen peroxide could improve the photodegradation rate. However, at high concentration, H_2O_2 would quench the hydroxyl radicals.

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References

[1] H. Chun, W. Yizhong, Chemosphere 39 (1999) 2107.
[2] S. Ledakowicz, M. Solecka, R. Zylla, J. Biotechnol. 89 (2001) 175.
[3] S. Ledakowicz, M. Gonera, Water Res. 33 (1999) 2511.
[4] J. Grzechulska, A.W. Morawski, Appl. Catal. B 36 (2002) 45.
[5] M. Yousuf, A. Molla, R. Schennach, J.R. Parga, D.L. Cocke, J. Hazard. Mater. B 84 (2001) 29.
[6] Y.M. Slokar, A.M.L. Marechal, Dyes Pigments 37 (1998) 335.
[7] C. Galindo, P. Jacques, A. Kalt, Chemosphere 45 (2001) 997.
[8] O. Tunay, I. Kabdasli, G. Eremektar, D. Orhon, Water Sci. Technol. 34 (1996) 9.
[9] W.S. Kuo, P.H. Ho, Chemosphere 45 (2001) 77.
[10] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.
[11] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[12] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C Photochem. Rev. 1 (2001) 1.
[13] C. Galindo, P. Jacques, A. Kalt, J. Photochem. Photobiol. A 130 (2000) 35.
[14] 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.
[15] H. Gupta, S. Tanaka, Water Sci. Technol. 31 (1995) 47.
[16] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, Water Res. 35 (2001) 3927.
[17] O.E. Kartal, M. Erol, H. Oguz, Chem. Eng. Technol. 24 (2001) 645.
[18] J. Fernandez, J. Kiwi, C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, J. Photochem. Photobiol. A 151 (2002) 213.
[19] Y. Chen, Z. Sun, Y. Yang, Q. Ke, J. Photochem. Photobiol. A 142 (2001) 85.
[20] A.A. Khodja, T. Sehili, J.F. Pihichowski, P. Boule, J. Photochem. Photobiol. A 141 (2001) 231.
[21] Z. Sun, Y. Chen, Q. Ke, Y. Yang, J. Yuan, J. Photochem. Photobiol. A 149 (2002) 169.
[22] S.R. Cater, M.I. Stefan, J.R. Bolton, A. Safarzadeh-Amiri, Environ. Sci. Technol. 34 (2000) 659.
[23] T. Sauer, G.C. Neto, H.J. Jose, R.F.P.M. Moreira, J. Photochem. Photobiol. A 149 (2002) 147.