

Photocatalytic degradation of triazinic ring-containing azo dye (Reactive Red 198) by using immobilized TiO₂ photoreactor: Bench scale study

Niyaz Mohammad Mahmoodi^{a,*}, Mokhtar Arami^{a,b}, Nargess Yousefi Limaee^a

^a Environmental Science and Engineering Department, Iran Color Research Center, Tehran, Iran

^b Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran

Received 28 June 2005; received in revised form 30 August 2005; accepted 29 September 2005

Available online 17 November 2005

Abstract

The decolorization and degradation of triazinic ring-containing azo dye by using TiO₂-immobilized photoreactor is reported. A simple and easy method was used for the immobilization of photocatalyst. Reactive Red 198 (RR 198) was used as model compound. Photocatalytic degradation processes were performed using a 5 L (bench scale) solution containing dye. Batch mode immersion type method was used for the treatment of dye solution. UV-vis, ion chromatography (IC) and chemical oxygen demand (COD) analyses were employed to evaluate the results of the photocatalytic degradation of RR 198. Dye solution was completely decolorized in relatively short time (35 min) after UV irradiation in combination with hydrogen peroxide. The results verified that all of the dye molecules were destructed. Kinetics analysis indicates that the dye photocatalytic decolorization rates followed first order model ($R^2 = 0.99$). Ion chromatography analysis was used to investigate the formation and destruction of aliphatic carboxylic acids and formation of inorganic anions during the process. Formate and oxalate anions were detected as main aliphatic carboxylic intermediates, which were further oxidized slowly to CO₂. UV/TiO₂/H₂O₂ process proved to be capable of successful decolorization and degradation of the RR 198.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Reactive Red 198; Photocatalytic degradation; Immobilized TiO₂ photoreactor; Triazinic ring-containing compounds

1. Introduction

The presence of the synthetic and non-biodegradable compounds such as triazine-containing azo dyes in textile effluents are of environmental concern. This is because of their widespread use, their potential producing of toxic aromatic amines and low removal rate during various waste treatment methods. It is reported that, 700,000 tons of dyes are produced in the world and about 50% among them are azo dyes [1]. Large amounts of these dyes are discharged in the watercourses, due to the hydrolysis, low fixation rate, etc. in developing countries. Thus there is an urgent need for textile wastewater to develop effective methods of treatment.

The photocatalytic degradation process is an emerging technology aimed at the degradation of air, water and wastewater

pollutants, especially refractory organic substances [2–10]. The advantages of photocatalytic process over competing processes are: (1) complete mineralization, (2) no waste disposal problem, (3) low cost and (4) only mild temperature and pressure conditions are necessary [5]. The mechanism of heterogeneous photocatalytic degradation of dyes was investigated in detail [11–14].

Irradiation of semiconductors like titanium dioxide (TiO₂) in suspended or fixed to various supports, in aqueous solutions containing organic pollutants, creates a redox environment, which is able to destroy these pollutants.

The use of suspended TiO₂ powder is efficient due to the large surface area of catalyst available for reaction. However, in the large-scale applications, the use of suspended powder requires the separation and recycling of the ultrafine catalyst from the treated wastewater prior to the discharge and can be a time-consuming and expensive process. In addition, the depth of penetration of UV light is limited because of strong absorptions by catalyst particles [15]. Above problems can be avoided by

* Corresponding author. Tel.: +98 21 77706373; fax: +98 21 22535206.
E-mail address: nm.mahmoodi@yahoo.com (N.M. Mahmoodi).

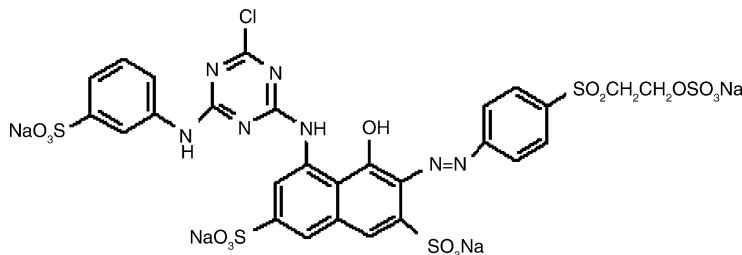


Fig. 1. The chemical structure of Reactive Red 198.

immobilization of photocatalyst over suitable supports. Thus, the use of immobilized photocatalysts is gaining importance in the elimination of pollutants from wastewaters.

Triazine-containing azo dyes are one of the most important classes of dyes, which are widely used in textile industries and the well-known resistance of the s-triazine to light induced fading. In the present article, it was attempted to determine the feasibility of the total decolorization and mineralization of bench scale (5 L) dye solution by a photocatalytic treatment of Reactive Red 198 (RR 198) using immobilized-TiO₂ photoreactor.

2. Experimental

2.1. Reagents

Reactive Red 198 (98% ≤ purity) was obtained from (Hoechst) and used without further purification. Reactive Red 198 is one of the most representative and commonly used dyes to dyeing the textile goods. This dye has several functional groups such as vinylsulfone (–SO₂–CH₂–CH₂–O–SO₃Na) and monochlorotriazine. The chemical structure of RR 198 was shown in Fig. 1. HCOONa, Na₂C₂O₄, Na₂SO₄ and NaNO₃, NaCl, NaHCO₃, Na₂CO₃ and H₂O₂ were purchased from Merck. Titanium dioxide (Degussa P25) was utilized as a photocatalyst. Its main physical data are as follows: average primary

particle size around 30 nm, purity above 97% and with 80:20 anatase to rutile.

2.2. Immobilized TiO₂ photoreactor

Experiments were carried out in a batch mode immersion rectangular immobilized photoreactor made of Pyrex glass, which is shown in Fig. 2. The radiation source was two UV-C lamps (15 W, Philips). The apparatus employed in the photocatalytic experiments has been described in detail elsewhere [16,17].

The photocatalyst (TiO₂) powder was immobilized by a UV resistant polymer in the inner surface of the reactor. The formulation of this polymer was unknown. Inner surfaces of reactor walls were cleaned with acetone and distilled water to remove any organic or inorganic material attached to or adsorbed on the surface and was dried in the air. A pre-measured mass of TiO₂ powder was attached over the inner surfaces of reactor walls using a thin layer of a UV resistant polymer. Immediately after preparation, the inner surface reactor wall–polymer–TiO₂ system was placed in the room temperature (25 °C) for at least 60 h for complete drying of the polymer.

In order to verify the activity of used catalyst and to check out its lifetime, two more experiments of decolorization process were conducted. Results did not show significant changes in decolorization time.

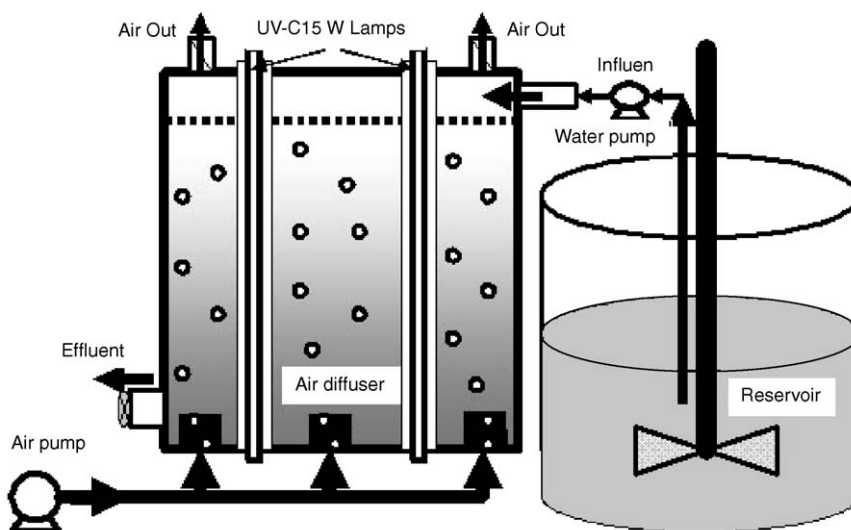


Fig. 2. Scheme of the immobilized TiO₂ photoreactor for photocatalytic dye degradation.

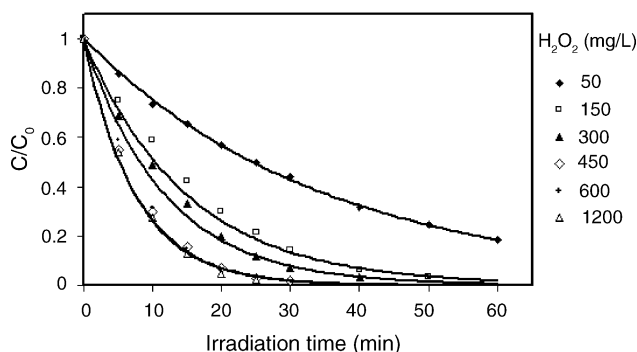


Fig. 3. Decolorization of RR 198 (50 mg/L) in the presence of different concentration of H_2O_2 at 525 nm.

2.3. Methods and analyses

RR 198 is a strongly absorbing dye in the UV–vis region. The chromophore containing azo linkage had absorption in the visible region while benzene and naphthalene rings in the UV region, and naphthalene ring absorption wavelength is higher than that of benzene ring.

Different groups in the dye molecule have different absorbance peaks. The absorbance peaks at 286.5, 371.5 and 520 nm are, respectively, attributed to benzene, naphthalene rings and azo linkage [18,19].

Photocatalytic decolorization processes performed using a 5 L solution containing dye with different concentration of hydrogen peroxide was shown in Fig. 3. The degradations were carried out at 298 K and at natural pH value (5.8). The initial concentration of dye solution was 50 mg/L. Samples were withdrawn from sample point at certain time intervals and their concentration was analyzed for decolorization of colored solutions by UV–vis CECIL2021 spectrophotometer.

Also, absorbance measurements of the samples at 254 nm were taken as an indication of the aromatic compounds content in the solution [20] (Fig. 4).

Ion chromatograph (METROHM 761 Compact IC) was used to determine formate, oxalate, SO_4^{2-} , NO_3^- , Cl^- ions

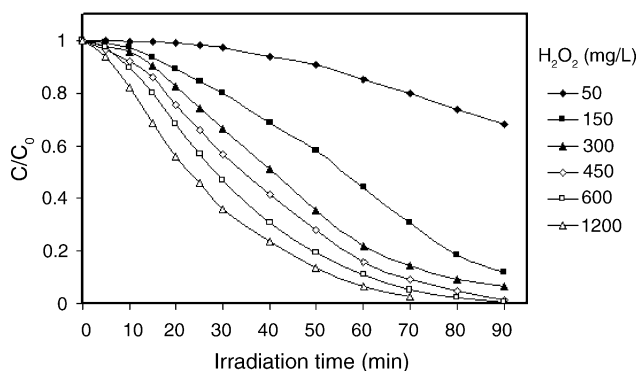


Fig. 4. The aromatic ring destruction of RR 198 by UV/ H_2O_2 / TiO_2 at 254 nm (dye 50 mg/L and H_2O_2 450 mg/L).

formed during the degradation and mineralization of RR 198 using an METROSEP Anion Dual 2, flow 0.8 mL/min, 2 mM NaHCO_3 /1.3 mM Na_2CO_3 as eluent, temperature 20 °C, pressure 3.4 MPa and conductivity detector.

The COD tests were carried out according to close reflux, colorimetric method [21] using a DR/2500 spectrophotometer (Hach, USA) and COD reactor (Hach, USA).

3. Results and discussion

3.1. Decolorization and aromatic ring destruction

The results from the radiation tests of the RR 198 solution (50 mg/L) using H_2O_2 (450 mg/L) in the immobilized TiO_2 photoreactor are shown in Fig. 5. The disappearance of the visible band within first minutes is due to the fragmentation of the azo band, which is the result of hydroxyl radical ($\bullet\text{OH}$) attack. This process is the first step in the degradation of azo dye. The color destruction of dye solutions was completed after 35 min of irradiation. The results of decolorization tests of dye solutions with different concentration of hydrogen peroxide were shown in Fig. 3.

After 130 min of irradiation, all absorbance peaks ($250 \leq \lambda \leq 700$ nm) have been disappeared and there is no absorbance peaks in UV–vis spectrum of solutions. So it may be claimed that RR 198 was degraded photocatalytically into aromatic intermediates. Finally these intermediates can be further oxidized and mineralized to produce CO_2 , H_2O , SO_4^{2-} , NO_3^- , etc.

3.2. Decolorization kinetics

The results of decolorization process were fitted by first-order kinetics ($R^2 > 0.99$). The kinetics of disappearance of RR 198 was followed by first-order kinetic model. This kinetic model is shown as $-\ln C/C_0 = kt$, where C_0 , C , t and k are initial dye concentration, dye concentration at t (min), decolorization time (min) and rate constant (1/min), respectively. The linear fit between the $-\ln C/C_0$ and irradiation time and different con-

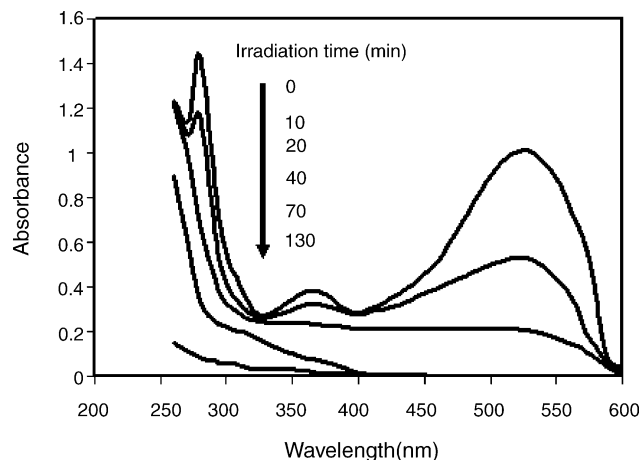


Fig. 5. Changes in the absorption spectrums of RR 198 (50 mg/L) with H_2O_2 (450 mg/L)/ TiO_2 /UV at different time intervals of irradiation.

Table 1

The parameters k (rate constant, 1/min) and R^2 (correlation coefficient) of decolorization process at different H_2O_2 concentrations

H_2O_2 (mg/L)	k	R^2
50	0.0283	0.999
150	0.0668	0.990
300	0.0849	0.993
450	0.1351	0.990
600	0.1324	0.996
1200	0.1486	0.991

concentrations of H_2O_2 can be approximated as first-order kinetics. The parameters k (rate constant, 1/min) and R^2 (correlation coefficient) of decolorization process were shown in Table 1. These results are in good agreement with previous works [14].

3.3. H_2O_2 effect

Hydrogen peroxide has different effects on the photocatalytic dye decomposition, depending on its concentration and nature of reductants [12]. At optimal concentration, H_2O_2 increases the formation rate of hydroxyl radicals in two ways. Firstly, the reduction of H_2O_2 at the conduction band would produce hydroxyl radicals. Secondly, the self-decomposition by illumination would also produce hydroxyl radicals [12,19]. As seen in Fig. 4, the decolorization rate increased when H_2O_2 concentration changed from 0 to optimal concentration (450 mg/L). There were not appreciable changes at decolorization rate when the concentration of H_2O_2 further increased. However, at high concentration, H_2O_2 can also become a scavenger of valence bond holes and hydroxyl radicals [8,12,22].



3.4. Initial dye concentration effect

The time dependencies of RR 198 during the photocatalytic degradation were investigated at the various initial concentra-

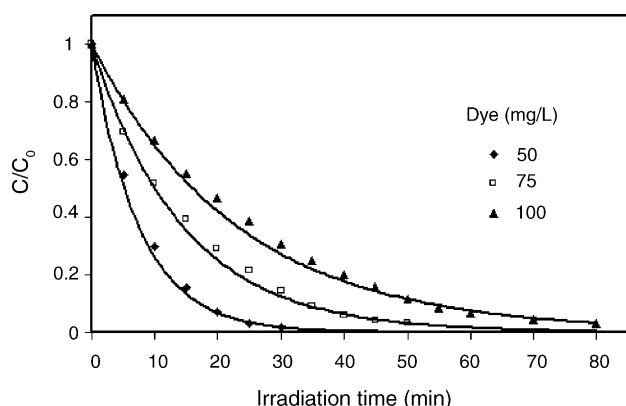


Fig. 6. The effect of initial concentration of dye on the time dependence of unconverted fraction of dye (H_2O_2 450 mg/L).

tions of dye. Fig. 6 shows the time dependence of unconverted fraction of RR 198 (C/C_0) for the various initial concentrations (50, 75 and 100 mg/L). Clearly, Fig. 6 shows that the first-order kinetic relative to dye is operative. However, the apparent first-order rate constant depends on the initial concentration of dye. As expected by increasing the dye concentration, the rate constant (k) (1/min) is decreased (0.1344 ($R^2 > 0.994$), 0.0691 ($R^2 > 0.992$) and 0.0432 ($R^2 > 0.993$) for 50, 75 and 100 mg/L respectively).

With the increase in the dye concentration, less photon reaches the photocatalyst surface, resulting in slower production of hydroxyl radicals (OH^\bullet). In combination with this, the fewer OH^\bullet available are required to oxidize more dye molecules [23].

Another possible cause is the interference from intermediates formed upon degradation of the parental dye molecules. Such suppression would be more pronounced in the presence of an elevated level of degradation intermediates formed upon an increased initial dye concentration [12].

3.5. Degradation of RR 198

During the photocatalytic degradation of RR 198, various organic intermediates were produced. Consequently, destruction of the dye should be evaluated as an overall degradation process, involving the degradation of both the parent dye and its intermediates.

The chemical oxygen demand (COD) gives a measure of degradation of dye and generated intermediates during the irradiation [24] and also a measure of the oxygen equivalent of the organic content in a sample that is susceptible to oxidation by strong oxidant. The rate of COD removal efficiency of RR 198 was shown in Fig. 7. This figure shows that after 3 h irradiation, 80% reduction in the COD of the sample was achieved. Also, the S-shape of the COD removal curve denotes the formation of by-products.

Further hydroxylation of aromatic intermediates products leads to the cleavage of the aromatic ring resulting in the formation of oxygen-containing aliphatic compounds [1,25]. The intermediates (organic carboxylic acids) generated during the degradation process were analyzed by IC and identified by comparison with commercial standards. Formate and oxalate were

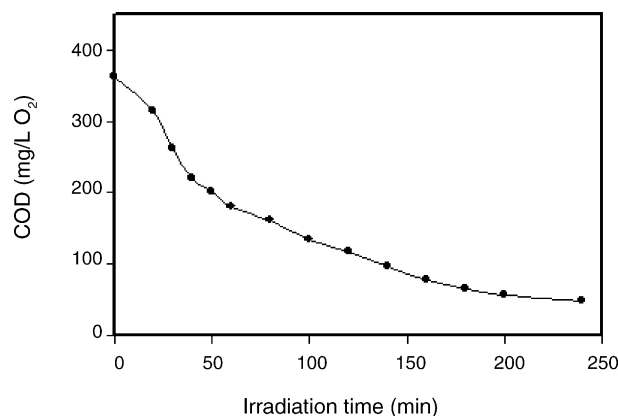


Fig. 7. COD removal of the solution during photocatalytic degradation of RR 198 (dye 50 mg/L and H_2O_2 450 mg/L).

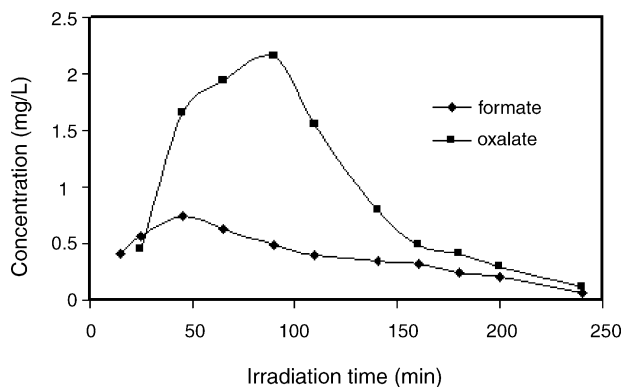


Fig. 8. Changes of formate and oxalate concentrations during photocatalytic degradation of RR 198 (dye 50 mg/L and H₂O₂ 450 mg/L).

detected as important aliphatic intermediates during degradation of RR 198 (Fig. 8). The formation of oxalate initially increased with the illumination time, and then sharply dropped. Carboxylic acids can react directly with holes generating CO₂ according to the “photo-Kolbe” reaction:



Also, in order to investigate the photocatalytic mineralization of RR 198, some inorganic ions arising from the dye degradation were followed with irradiation time. The degradation leads to

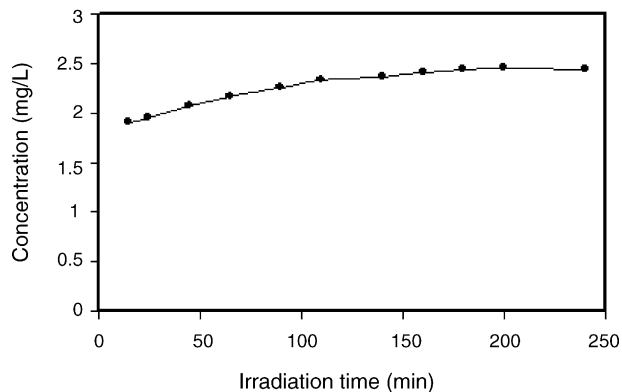


Fig. 9. Formation of Cl⁻ from the photocatalytic degradation of RR 198 (dye 50 mg/L and H₂O₂ 450 mg/L).

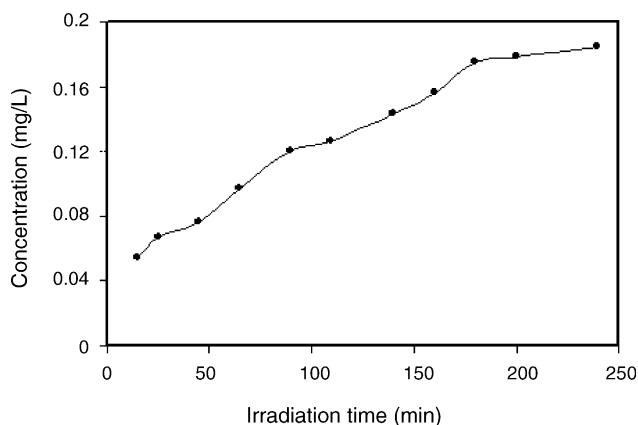


Fig. 10. Formation of NO₃⁻ from the photocatalytic degradation of RR 198 (dye 50 mg/L and H₂O₂ 450 mg/L).

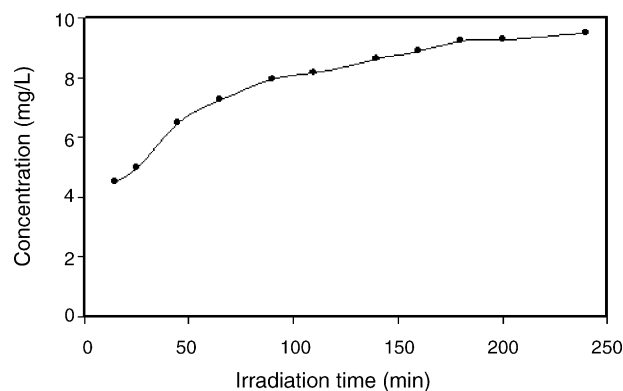


Fig. 11. Formation of SO₄²⁻ from the photocatalytic degradation of RR 198 (dye 50 mg/L and H₂O₂ 450 mg/L).

the conversion of organic carbon into harmless gaseous CO₂ and that of nitrogen and sulfur heteroatoms into inorganic ions, such as nitrate and sulfate ions, respectively [13]. The formation of inorganic ions including Cl⁻, NO₃⁻ and SO₄²⁻ from dye mineralization is reported for an irradiation period of 240 min in Figs. 9–11, respectively. The overall photocatalytic degradation process of RR 198 can be shown as follows:

Dye molecule (RR 198) → aromatic intermediates

→ organic carboxylic acids + inorganic anions

→ final products (SO₄²⁻, NO₃⁻, Cl⁻, H₂O and CO₂)

4. Conclusions

The photocatalytic degradation of RR 198 having different chemical groups was successfully performed. The decolorization of RR 198 was followed by first-order kinetic model ($R^2 = 0.99$) at optimal H₂O₂ concentration (450 mg/L). Decolorization and degradation of dye were tested by UV–vis, IC and COD analyses. In the photocatalytic degradation of azo dye, azo linkage was broken and substituted aromatic intermediates were produced, they can be further oxidized and finally mineralized to produce CO₂, H₂O, etc. Knowledge of the decolorization kinetics and formation and degradation of reaction intermediates is important from practical point of view. Immobilization of TiO₂ is an easy method to resolve the problems of suspended photocatalyst powder such as filtration and recovery of fine particles. Hence, this technique may be valuable for the treatment of large-scale textile wastewater and reuse of treated water.

References

- [1] C. Bauer, P. Jacques, A. Kalt, Photooxidation of an azo dye induced by visible light incident on the surface of TiO₂, J. Photochem. Photobiol. A: Chem. 140 (2001) 87–92.
- [2] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahneman, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.
- [3] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar/UV-induced photocatalytic degradation of three commercial textile dyes, J. Hazard. Mater. B 89 (2002) 303–317.

- [4] A.L. Linsebigle, G. Lu, J.T. Yates, Photocatalysis on TiO₂ surfaces: principles, mechanisms and selected results, *Chem. Rev.* 95 (1995) 735–758.
- [5] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental applications—a review, *J. Chem. Technol. Biotechnol.* 77 (2001) 102–116.
- [6] D.F. Oills, E. Pellizzetti, N. Serpone, Destruction of water contaminants, *Environ. Sci. Technol.* 25 (1991) 1523–1529.
- [7] Y. Xu, C.H. Langford, UV or Visible-light induced degradation of X3B on TiO₂ nanoparticles: the influence of adsorption, *Langmuir* 17 (2001) 897–902.
- [8] K. Vinodgopal, I. Bedja, S. Hotechandani, P.V. Kamat, Photocatalytic approach for the reductive decolorization of textile azo dyes in colloidal semiconductor suspensions, *Langmuir* 10 (1994) 1767–1771.
- [9] M. Saquib, M. Muneer, TiO₂-mediated photocatalytic degradation of triphenyl-methane dye (gentian violet) in aqueous suspensions, *Dyes Pigments* 56 (2003) 37–49.
- [10] I. Arsalan, I.A. Balcioglu, D.W. Babnemann, Advanced chemical oxidation of reactive dyes in simulated dye house effluents by ferrioxalate—Fenton UV-A and TiO₂/UV-A processes, *Dyes Pigments* 47 (2000) 207–218.
- [11] M. Vautier, C. Guillard, J.M. Herrmann, Photocatalytic degradation of dyes in water: case study of indigo and of indigo carmine, *J. Catal.* 201 (2001) 46–59.
- [12] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation, *Chemosphere* 46 (2002) 905–912.
- [13] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B: Environ.* 31 (2001) 145–157.
- [14] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—a review, *Appl. Catal. B: Environ.* 49 (2004) 1–14.
- [15] A.K. Ray, A.A.C.M. Beenackers, Novel photocatalytic reactor for water treatment, *AIChE* 44 (2) (1998) 477–483.
- [16] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, N. Salman Tabrizi, Decolorization and aromatic ring degradation kinetics of Direct Red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO₂ as a photocatalyst, *Chem. Eng. J.* 112 (1–3) (2005) 191–196.
- [17] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, N. Salman Tabrizi, Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized TiO₂ photocatalytic reactor, *J. Colloid Interface Sci.* (in press).
- [18] W. Feng, D. Nansheng, H. Helin, Degradation mechanism of azo dye C.I. Reactive Red 2 by iron powder reduction and photooxidation in aqueous solutions, *Chemosphere* 41 (2000) 1233–1238.
- [19] J.M. Lee, M.S. Kim, B. Hwang, W. Bae, B.W. Kim, Photodegradation of Acid Red 114 dissolved using a photo—Fenton process with TiO₂, *Dyes Pigments* 56 (2003) 59–67.
- [20] D. Georgiou, P. Melidis, A. Aivasidis, K. Gimouhopoulos, Degradation of azo reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide, *Dyes Pigments* 52 (2002) 69–78.
- [21] APHA, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1989.
- [22] S. Malato, J. Blanco, C. Richter, B. Braun, M.I. Maldonado, Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species, *Appl. Catal. B: Environ.* 17 (1998) 347–356.
- [23] C. Tang, V. Chen., The photocatalytic degradation of reactive black 5 using TiO₂/UV in an annular photoreactor, *Water Res.* 38 (2004) 2775–2781.
- [24] J. Li, C. Chen, J. Zhao, H. Zhu, J. Orthman, Photodegradation of dye pollutants on TiO₂ nanoparticles dispersed in silicate UV—vis irradiation, *Appl. Catal. B: Environ.* 37 (2002) 31–338.
- [25] K. Tanaka, S.M. Robledo, T. Hisanaga, R. Ali, Z. Ramli, W.A. Bakar, Photocatalytic degradation of 3,4-xylyl *N*-methylcarbamate (MPMC) and other carbamate pesticides in aqueous TiO₂ suspensions, *J. Mol. Catal. A: Chem.* 144 (1999) 425–430.