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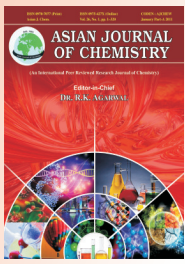

Photocatalytic Degradation of Reactive Red 198 Dye Using Zinc Oxide and Titanium Dioxide Nanocatalysts

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Photocatalytic destruction of reactive red 198 using zinc oxide and titania nanoparticles was investigated in the presence of UV light irradiation. The photocatalytic experiments were carried out in a batch mode using 8 W UV lamp which emits a peak wavelengths of 254 and 375 nm. The effect of parameters such as the effect of incident wavelength and the effect of pH were conducted. For nano ZnO there was a slight decrease of degradation at neutral pH and decreased again in alkali medium. Reactive red 198 dye degradation was found to be more favorable in mild acidic and neutral medium on TiO_2 surface. The photocatalytic degradation reaction accords with a pseudo-first order kinetics. The reusability of the nanocatalysts was also investigated. Total organic carbon analysis indicated complete mineralization of reactive red 198 on ZnO and TiO_2 surfaces.

Keywords: Textile wastewater, Degradation, Organic contaminants, Nanoparticle, Photocatalyst.

INTRODUCTION

One of the most serious problems affecting people throughout the world is inadequate access to clean water and sanitation. Water pollution is mainly due to demand and shortage of clean water sources, the fastest development of industrialization and its toxic organic chemical wastes, long-term droughts, rapid increase in the use of pesticides, herbicides, dyes, solvents and agricultural development around the world[1,2]. The disposal of toxic contaminants specifically dyes and phenolic compounds which are harmful to the environment, hazardous to humans and difficult to degrade by natural way. It is seriously associated with industrial development are frequently found in the industrial effluents[3]. Amongst the different industrial wastewaters with different types of color-causing substances, synthetic textile organic dye wastes occupy a prominent position. Almost every industry uses dyestuffs to dye their products. Over 7×10^5 tons and approximately 10,000 different types of dyes and pigments are produced worldwide annually. Of these, the azo dyes constitute about 60-70 % of the total dyes used in the industries. It is estimated that 10 to 15 % of the dye is lost in the effluent during the dyeing process.

Hence there is a need to develop water treatment processes that are more effective in replacing organic contaminants from wastewater by conventional chemical treatment systems[4]. The traditional techniques for the treatment of effluents in wastewater are usually non-destructive, inefficient, costly and transfers pollutants from water to another phase[5]. Efficient photocatalytic process is essential to solve society's greatest challenges and tackling environmental pollution[6]. Heterogeneous photocatalysis using ZnO, TiO_2, WO_3, SnO_2, ZrO_2, CeO_2, CdS and ZnS as catalysts in the presence UV light irradiation is utilized to achieve mineralization of toxic pollutants present in wastewater[7]. Among them, nano ZnO and TiO_2 have been the most dominant photocatalysts[8]. The most important semiconductor with direct band gap (3.3 eV) and a large exciton binding energy (60 meV) is zinc oxide (ZnO) nanoparticle and it has gained intense interests due to their potential applications in optoelectronic devices[9], ultraviolet laser devices, chemical sensors, solar cells. It has a significant attention in the photodegradation and complete mineralization of environmental pollutants[10]. Titanium dioxide nanoparticle has been extensively used as the photocatalytic material due to its self-cleaning ability[11], water purifying capacity and antibacterial property and it gives effective approach to settle various environmental problems. Current researches show that nano ZnO and TiO_2 are used as a very efficient semiconductor photocatalysts for the water purification process[12].

In this paper, it is reported that the photocatalytic degradation studies of reactive red 198 in the presence of UV light on nano ZnO and TiO_2 surface were carried out. The effect of the incident wavelength and the effect of pH were conducted. Kinetics of photocatalytic degradation reaction of nano ZnO and TiO_2 was studied. The reusability of the nanophotocatalysts was also tested.

EXPERIMENTAL

Zinc acetate dihydrate, oxalic acid dihydrate, ethanol, titanium(IV) isopropoxide, glacial acetic acid and all the organic reagents were analytical grade purchased from Merck, SRL and Qualigens, India. Double distilled water was used for all the measurements. Zinc oxide and TiO_2 nanoparticles were synthesized by sol-gel method as mentioned in the references with some modifications[13,14]. Reactive red 198 was one of the textile dye purchased from Thirupur, Tamilnadu, India without any further purification.

Photocatalytic reactor and its studies: The photodegradation study of reactive red 198 dye solution was carried out in a suspended particle vertical catalytic reactor in the batch mode. In this nano ZnO or TiO_2 particles were suspended in the solution column through aeration. Thereafter configuration and operating conditions for the photocatalytic degradation have been optimized by preliminary trial experiments with respect to (i) the total batch volume of reactant solution, (ii) the stirring speed and (iii) the time for adsorption equilibrium prior to exposure to UV light. The typical experimental procedure consisted of aerating a mixture of 250 mL of dye solution of known concentration and the photocatalyst for 0.5 h to allow pre-adsorption followed by irradiation with the UV light. The lamp emits 8 W of UV radiation with a peak wavelength of 254 and 375 nm. A sample of 3 mL was withdrawn at periodic intervals of irradiation time followed by centrifugation. The residual concentration of dye solution was measured at 532 nm using the UV-visible spectrophotometer. After the analysis the solutions were returned to the reactor. In the presence of UV light, all the studies have been carried out at 30 ºC and the pH of the solution was adjusted to desired values between 4 and 10 by using dilute solutions of HCl or NaOH. The radiation intensity of the UV light used in the experimental study was determined by ferri oxalate actinometry was found to be 3.32×10^{19} quanta/second. The decolorization efficiency (%) has been calculated as:

$$\text{Decolorization efficiency (\%)} = \frac{(C_0 - C)}{C_0} \times 100$$

where C_0 is the initial concentration of dye and C is the concentration of dye after photo irradiation.

The reusability of the ZnO and TiO_2 nanoparticles evaluated by reclaiming the catalyst after reaction in the batch mode, washing drying in air at 110 °C and using it for the dye degradation under similar experimental conditions. During the photocatalytic degradation of dye solution the estimation of total organic carbon was done by subjecting the dye solution to oxidize all the components in a closed reactor to convert the organic carbon to carbon dioxide[15]. Cary-50 ultraviolet spectrophotometer (Varian) was used in the measurements of absorbance of reactive red 198 dye in aqueous solution at different incident wavelengths and pHs and at an incident wavelength, λ_{max} of 532 nm.

Operational parameters: In heterogeneous photocatalytic water treatment system, the operating parameters the effect of incident wavelength and pH were taken for photodegradation investigation. Because the parameters affect the charge on the catalyst particles, size of catalyst aggregates and the positions of conductance and valence bands. Due to the nature of nanophotocatalyst, any variation in the operating pH is known to affect the isoelectric point or the surface charge of the photocatalyst used. Many reports used the point of zero charge (PZC) of nanophotocatalyst to study the pH impact on the photocatalytic oxidation performance[16]. The photocatalytic degradation study was used the pH range of 4 and 10. The photonic nature of the photocatalysis reaction was outlined the dependency of the overall photocatalytic rate on the light source used. And light intensity is one of the parameters that affect the degree of photocatalytic reaction on organic substrates such as dye solution. For this investigation the incident wavelengths 254 and 375 nm of UV light irradiation was taken and compared their photodedegradable efficiency.

RESULTS AND DISCUSSION

Particle size and structural properties of nanophotocatalysts: The synthesized ZnO and TiO_2 nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The experimental results showed that the crystallite sizes of ZnO and TiO_2 nanoparticles calcined at 500 ºC were found to be 26.3 and 13.2 nm. The SEM micrograph of nano ZnO consisted of average particle size of 17.5 ± 5 nm with homogeneous and spherical shape of the nanoparticle with large agglomeration. The SEM micrograph of TiO_2 nanoparticles consisted of uniform particle with spherical shape and the particle size was found to be 15 ± 5 nm.

Effect of wavelength of incident light on the photocatalytic degradation of reactive red 198: The photocatalytic degradation of reactive red 198 was investigated by exposing the dye solution to light of incident wavelengths 375 and 254 nm and in the presence of nano ZnO. The photocatalytic degradation of reactive red 198 dye in the presence of nano ZnO involves the light absorption of wavelength (380 nm) higher than band gap energy of 3.2 eV. A sample of 100 μM of the dye solution on irradiation with 254 nm light was found to undergo complete mineralization within 165 min. Under similar conditions, with 375 nm light, only 20-30 % of the degradation was observed. The effect of incident light wavelength on the photodegradability of reactive red 198 dye as a function of time is shown in Fig. 1. The improved effectiveness of 254 nm light compared to 375 nm light may be due to the fact that the shorter wavelength light is absorbed more strongly by the nanophotocatalyst particles than the longer wavelength light. Hence the penetration distance of photons into the particle was shorter and photoelectrons and holes were formed closer to the surface of the particle. Therefore they take less time to migrate to the surface of the particle and hence have less time to participate in wasting recombination reactions before useful surface reaction take place. Many organic molecules were excited by 254 nm light and are degraded as result of direct action. In the case of reactive red 198 dye there is adsorption at but not at 380 nm. But the direct degradation rate is very small compared to the rate in the presence of a photocatalyst. Similar observation has been reported by Mathews and McEvoy[17]. Therefore the photocatalytic degradation studies were carried out at incident light of wavelength 254 nm.

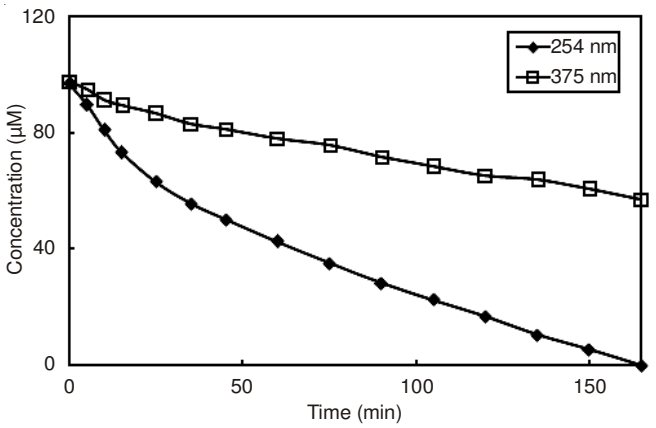

Fig. 1. Effect of wavelength of incident light on the photocatalytic degradation of reactive red 198 dye. [Reactive red 198] = 100 μM; pH = 7.0 ± 0.1; weight of nano ZnO catalyst = 1 g/L; temperature = 30 ± 0.1 °C; absorbance measured at 532 nm

Photodegradability of nano ZnO and TiO_2 catalysts: The photocatalytic activities of prepared nanocatalysts ZnO and TiO_2 were evaluated by the degradation of reactive red 198 dye in aqueous solution. In addition to experiments with the photocatalysts and UV light irradiation, both blank experiments in the absence of UV light irradiation with the photocatalysts or in the presence of UV light irradiation without the photocatalysts were investigated. Blank experiment results showed that the dye solution could not be degraded without the photocatalysts or UV light irradiation as shown in the Fig. 2. In the presence of UV light irradiation and with nano ZnO and nano TiO_2, the dye in aqueous solution was easily degraded completely within 165 and 90 min. Therefore this experiment demonstrated that both UV light and a photocatalyst were needed for the effective destruction of water effluent such as reactive red 198 in aqueous solution. The photo-degradation mechanism of dye solution using nano ZnO could be similar to that of nano TiO_2, which has been reported by several authors. When the photocatalyst is irradiated with ultraviolet (UV) radiation, it produces electron-holes pairs on or near the surface through electron transfer from the valence band to the conduction band across the band gap of the semiconductor. This state is referred as the semiconductor's photo-excitation state. The electron-hole pair quickly diffuses to the surface. These photogenerated electron-hole pairs can recombine within a time scale of nanoseconds to radiate heat. Band gap-illumination of a nanocatalyst leads to vectorial transfer of generated electrons and holes which results in improved photocatalytic efficiency[18]. In TOC analysis carbon dioxide determined experimentally was found to tally with theoretical value on the basis of molecular weight and concentrations employed. The percentage of carbon photo-oxidised in aqueous suspensions is 98 % of the theoretical value.

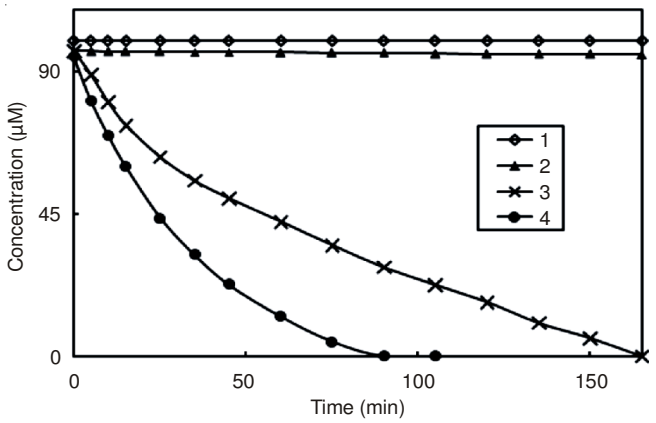

Fig. 2. Photocatalytic degradability of reactive red 198 dye. [Reactive red 198] = 100 μM; pH = 7.0 ± 0.1; Weight of nano ZnO and TiO_2 catalyst = 1 g/L; temperature = 30 ± 0.1 °C; absorbance measured at 532 nm [1 = Dye solution irradiated with UV light in the absence of nano ZnO; 2 = Dye solution treated with 1.0 g/L of nano ZnO in the dark; 3 = Dye solution irradiated with UV light in the presence of nano ZnO; 4 = Dye solution irradiated with solar light in the presence of nano ZnO]

Effect of pH: The pH of the solution is one of the most important parameters for the degradation of dye solution. The dye wastewater from textile industries usually has a wide range of pH values. In this experiment the effect of pH on the photo-degradation of dye solution in the presence of nano ZnO and TiO_2 particles was investigated over the pH range of 3-10. The influence of initial pH generally depends on the type of pollutant and the zero point charge (zpc) of photocatalyst used in the oxidation process[19]. The pH of dye solution influenced the surface charge properties of the photocatalyst and it had significant effects on the electrostatic interaction between the nanocatalyst surface and the dye molecules. Figs. 3 and 4 illustrates the effect of pH on the photocatalytic degradation of dye solution in the presence of fixed amount of nano ZnO and TiO_2 (1 g/L), respectively and concentration of dye solution (100 μM) at 30 ± 0.1 ºC on the catalyst surface. In the presence of nano ZnO, the percentage degradation of reactive red 198 dye solution was found to decrease with increase in pH. At mild, acidic and natural pH the percentage degradation was found to be fast, increased steadily in degradation and almost equal. At neutral pH there was a slight decrease of degradation. At higher pH, dye molecule existed as negatively charged species. Therefore, the adsorption of dye molecules on the catalyst surface decreased. However, at higher pH 10 slight decreases in degradation might be due to higher concentration of hydroxyl ions. Therefore dye degradation was more favourable in mild, acidic and neutral pH on the surface of ZnO[20]. The effect of pH on nano TiO_2, a high percentage degradation of dye solution was observed at lower pH from 3 to 5.6

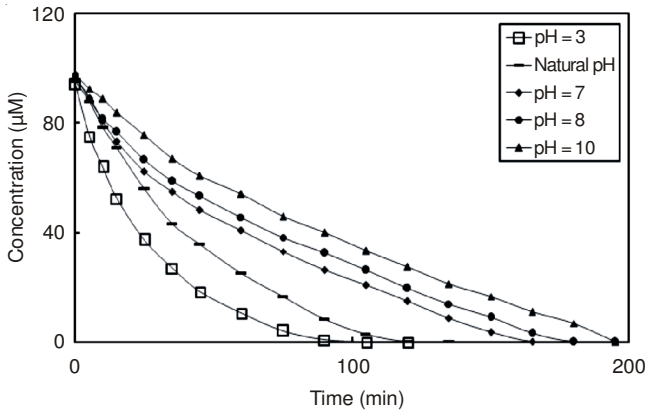

Fig. 3. Effect of pH on the photocatalytic degradation of reactive red 198; [Reactive red 198] = 100 μM; weight of nano ZnO catalyst = 1 g/L; temperature = 30 ± 0.1 °C; absorbance measured at 532 nm

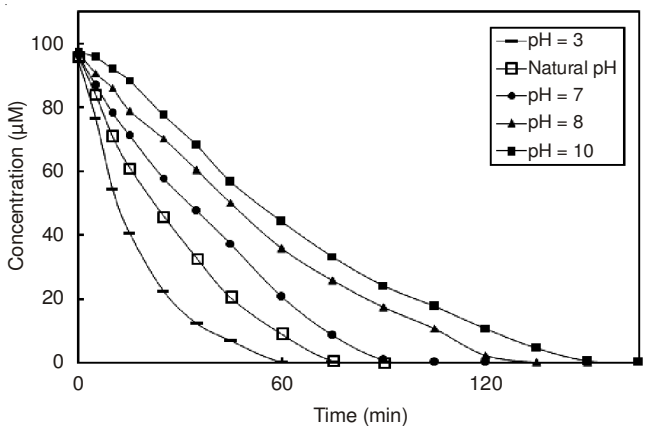

Fig. 4. Effect of pH on the photocatalytic degradation of reactive red 198; [Reactive red 198] = 100 μM; weight of nano TiO_2 catalyst = 1 g/L; temperature = 30 ± 0.1 °C; absorbance measured at 532 nm

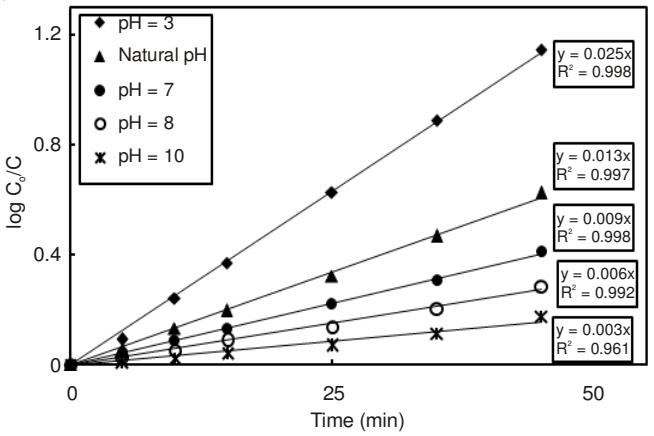

Fig. 6. Plot of C_o/C *vs.* time for reactive red 198. pH = 7; weight of nano TiO_2 = 1 g/L; concentration = 100 μM; temperature = 30 ± 0.1 °C; absorbance measured at 532 nm

(natural pH) is shown in Figure. This is attributed to the fact that TiO_2 is amphoteric in aqueous solution. The effect of pH of dye solution in the presence of nano TiO_2 showed that the initial degradation increased from pH 3 to 5.7 and decreased slightly with further increase of pH. The degradation was maximum at 3 to natural pH (5.7) and started decreased with increase of pH from 7 to 10. At pH values higher than 3, the surface becomes negative charge and the opposite occurs for pH values greater than pHpzc.

Kinetics study: Under constant conditions of catalyst weight and photon flux the effect of pH of the dye solution on its photocatalytic degradability has been studied. The photocatalytic degradation of dye solution in the presence of nano ZnO and TiO_2 follows first order kinetics. $\ln (C_o/C) = kt$, where C_o is the initial concentration, C is the concentration at any time, t and k is pseudo first order constant. The plot of $\log (C_o/C)$ *vs.* t gave a straight line as shown in the Figs. 5 and 6. From the kinetic study it was found that rate constant values were found to decrease with increase of pH values. The observed k value is listed in Table-1. The reaction proceeds *via* hydroxylation and the intermediates adsorbed on nano ZnO were found to decrease the rate of oxidation of dye molecules. The reduction of COD shows the extent of photodegradation of the dye molecules in wastewater was investigated under optimized conditions as a function of irradiation time using

TABLE-1
OBSERVED k VALUE FOR THE ZnO AND TiO_2 NANOPARTICLES IN PHOTOCATALYTIC DEGRADATION OF REACTIVE RED 198

Nano photocatalyst	pH				
	3.0	5.6	7.0	8.0	10.0
ZnO	0.0345	0.0207	0.0161	0.0115	0.0092
TiO_2	0.0575	0.0299	0.0207	0.0138	0.0069

UV light irradiation. From the investigation it was found that COD removal with photodegradation of reactive red 198 showed higher efficiency than the degradation of reactive red 198.

Reusability of nanocatalysts: Reusability of nanocatalysts for the degradation of dye solution by photocatalysis was evaluated. The solution resulting from the photocatalytic degradation of dye was filtered, washed and the photocatalyst was dried at 100 °C. The dried catalyst samples are used for the degradation of dye, employing similar experimental conditions and procedures. The filtrate was subjected to AAS analysis to assess the loss of Zn^{2+} or Ti^{4+} to solution as a result of dissolution of nano ZnO or TiO_2. Under the present investigation it was observed that dissolution of catalyst was found to be negligible (0.04 % loss of zinc or titanium was observed during 2 h of reaction time). Catalyst samples showed considerably reproducible photocatalysis activity up to four cycles for the degradation of dye is shown in Fig. 7. The loss in activity and loss of

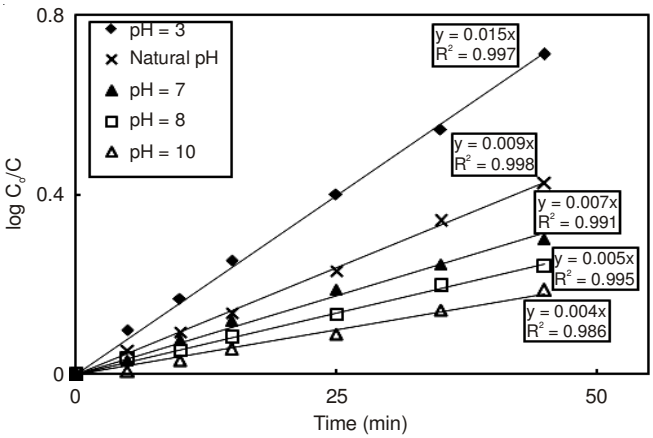

Fig. 5. Plot of C_o/C *vs.* time for reactive red 198. pH = 7; weight of nano ZnO = 1 g/L; concentration = 100 μM; temperature = 30 ± 0.1 °C; absorbance measured at 532 nm

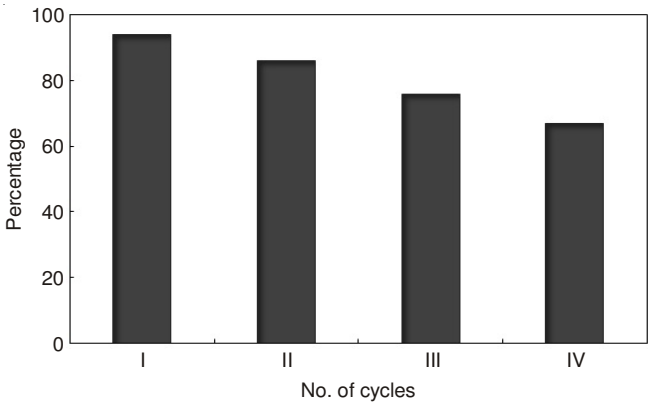

Fig. 7. Resuability of nano ZnO particles at 100 °C. pH = 7; weight of nano ZnO = 1 g/L; concentration = 100 μM; temperature= 30 ± 0.1 °C; absorbance measured at 532 nm

zinc as zinc ions or titanium as titanium ions was more pronounced only after the 5th cycle of reuse[15]. The decrease in the degradation percentage was explained by adsorption of organic intermediates and by-products of the photodegradation process in the cavities and on the surface of the photocatalyst that influences the surface activity of the nanocatalysts[21]. The repetitive uses of the nanocatalysts, a loss occurred in the amount of the reused nanophotocatalyst particles. The major advantage of the use of heterogeneous catalytic materials is their easy recovery.

Conclusion

One of the textile industrial pollutant reactive red 198 was studied effectively using UV light irradiation in the presence of ZnO and TiO_2 nanoparticles as the photo catalysts. Nanoparticles showed higher photodegradation efficiency at 254 than 375 nm. Introduced at comparatively acidic and natural medium nano TiO_2 was done the effective photodegradation. ZnO nanoparticle was showed a steady increase of degradation from 3 to 5.6. The photocatalytic degradation of dye solution can be described with pseudo-first order reaction kinetics. A demonstrated ability to use nano ZnO and TiO_2 systems at a pilot scale for effluent purification processes would certainly benefit the environment.

REFERENCES

1. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev*., **95**, 69 (1995).
2. A.L. Linsebigler, G. Lu and J.T. Yates Jr., *Chem. Rev*., **95**, 735 (1995).
3. S. Malato, P. Fernandez Ibanez, M.I. Maldonado, J. Blanco and W. Gernjak, *Catal. Today*, **147**, 1 (2009).
4. N. Sobana and M. Swaminathan, *Sep. Purif. Technol*., **56**, 101 (2007).
5. I.K. Konstantinou and T.A. Albanis, *Appl. Catal. B*, **49**, 1 (2004).
6. W. A. Zeltner and D. T. Tompkin, Ashrae Transactions vol. III, vol. 2, American Society of Heating and Air-Conditioning Engineers, Atlanta, Ga, USA (2005).
7. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, *Chemosphere*, **46**, 1173 (2002).
8. M. Sleiman, C. Ferronato and J.M. Chovelon, *Environ. Sci. Technol*., **42**, 3018 (2008).
9. O. Carp, C.L. Huisman and A. Reller, *Solid State Chem*., **32**, 33 (2004).
10. C. Guillard, J. Disdier, M. Herrmann, C. Lehaut, T. Chopin, S. Malato and J. Blanco, *Catal. Today*, **54**, 217 (1999).
11. M. Cristina Yeber, J. Rodríguez, J. Freer, N. Durán and H. D. Mansilla, *Chemosphere*, **41**, 1193 (2000).
12. T. Yazawa, F. Machida, K. Oki, A. Mineshige and M. Kobune, *Ceram. Int*., **35**, 1693 (2009).
13. C. Hariharan, *Appl. Catal. A*, **304**, 55 (2006).
14. M. Hamadanian, A. Reisi-Vanani and A. Majedi, *J. Iran Chem. Soc*., **7**, 52 (2010).
15. S. Lathasree, A.N. Rao, B. Siva Sankar, V. Sadasivam and K. Rengaraj, *J. Mol. Catal. Chem*., **223**, 101 (2004).
16. M.N. Chong, B. Jin, H.Y. Zhu, C.W.K. Chow and C. Saint, *Chem. Eng. J*., **150**, 49 (2009c).
17. R.W. Matthews and S.R. McEvoy, *J. Photochem. Photobiol. Chem*., **66**, 355 (1992c).
18. T. Yazawa, F. Machida, K. Oki, A. Mineshige and M. Kobune, *Ceram. Int*., **35**, 1693 (2009).
19. P.R. Gogate and A.B. Pandit, *Adv. Environ. Res*., **8**, 501 (2004).
20. H.C. Akyol, M. Yatmaz and M. Bayramoglu, *Appl. Catal. B*, **54**, 19 (2004).
21. E. Sanatgar-Delshade, A. Habibi-Yangjeh and M. Khodadadi-Moghaddam, *Monatsh. Chem*., **142**, 119 (2011).