Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 3(4), 2013, 181-189
ISSN 2277-2669

MBIR DOWEX-11 ASSISTED PHOTOCATALYTIC DEGRADATION OF AZO DYES: A REVIEW

HIMAKSHI, NEELAKSHI and R. C. MEENA*

Department of Chemistry, Jai Narain Vyas University, JODHPUR – 342001 (Raj) INDIA

(*Received : 18.10.2013; Revised : 30.10.2013; Accepted : 01.11.2013*)

ABSTRACT

Advanced oxidation process (AOP) is best for treatment of textile industries effluents (waste water). Methylene blue immobilized resin dowex-11, a newly developed photocatalyst is used for degradation of azo dyes. The mechanism of the photodegradation depends on the radiation used. The degradation of dyes depends on several parameters such as catalyst loading, dye concentration, pH, and light intensity. Activity of catalyst remains unaffected on continuous use. The process follows pseudo first order kinetics according to Langmuir Hinshelwood model. Carbon dioxide, water, nitrate, sulphate ions have been identified as mineralization products.

Key words: Degradation, Azo dyes, Methylene blue immobilized resin, Textile effluents, Dowex-11, Photocatalyst.

INTRODUCTION

Today most of water resources are polluted. Water pollution is increasing steadily, due to rapid population growth, industrialization, urbanization, increasing living standard and wide sphere of human activities. Large volume of discharge and effluents and wastewater of textile industries are most polluting among all industrial sectors[1]. Wastewater of textile industries cannot be treated successfully by conventional treatment methods and presently used methods give low quality water not suitable to use for domestic utilization. Organic dyes are present in textile wastewater and these dyes are synthetic and non-biodegradable so, biological treatment of wastewater alone is usually not effective and waters may result in poor water quality.[2]

Dyes are used mostly in the textile (fabric used in clothing) industry and paper industry. These industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. The annually world production of textile industry is about 30 million ton requiring 700,000 tons of different type dyes which causes considerable environmental pollution problems[3]. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Various chemical and physical processes such as adsorption, air stripping, flocculation, precipitation, reverse osmosis and ultra-filtration can be used for color removal from textile effluents[4-7]. Many textile manufacturers use dyes that release aromatic amines (e.g. banzidine, toluidine). Dye bath effluents may contain heavy metals ammonia, alkali salts, toxic solids and large amounts of pigments, many of which are

---

*Author for correspondence; E-mail: vermahimakshi88@gmail.com

also toxic. Treatment of dye-based effluents is considered to be one of the challenging tasks in environmental fraternity. Dyes are complex aromatic compounds, which are normally used for coloration of various substrates like leather, textiles, papers etc. They are sometimes fused with heavy metals on the structural interface and are considered to have relatively bad consequence on the surrounding environment due to their toxic and inhibitory nature[8,9].

Ever since 1977, when Frank and Bard[10,11] first examined the possibilities of using TiO_2 to decompose cyanide in water, there has been increasing interest in environmental applications. Treatment plants have applied additional processes like coagulation, or adsorption for the removal of the contaminants[12-14]. In recent years, TiO_2 photocatalyst has been successfully applied to remove organic and inorganic pollutants[15], to inactivate microorganisms[16] and to control disinfection byproduct formation[17,18]. TiO_2 photocatalyst was found to be effective for the destruction of a wide variety of environmental contaminants present in water and wastewater, this technology has not yet been successfully commercialized in past because of the costs and problems connected to the separation of TiO_2 particles from the suspension after treatment. In order to solve this problem, supported photocatalysts have been developed[19-26]; in particular, titanium powder has been immobilized on supports transparent to UV/VIS radiation. Unfortunately, the surface area of active catalyst exposed to solution is lower in supported systems than in suspended systems, reducing the catalytic activity.

For this reason, methylene blue immobilized resin Dowex-11 photocatalyst has been studied as an alternative to conventional processes. Recently, there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non-selectively[27,28]. AOPs include photocatalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Heterogeneous photocatalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive dyes[29-32].

EXPERIMENTAL

Photocatalytic degradation mechanism

The detailed mechanism of the process has been discussed previously in literature[1,2,33-44] and will be only briefly summarized here –

$$\text{Dye} \longrightarrow \text{Dye}^{*1}$$

$$\text{Dye}^{*1} \xrightarrow{\text{ISC}} \text{Dye}^{*3}$$

$$\text{Dye}^{*3} + \text{I–R} \longrightarrow \text{Dye}^{+} + \text{I–R}\ (e^{-})$$

$$\text{I-R}\ (e^{-}) + O_2 \longrightarrow \text{I–R} + O_2^{-}$$

$$\text{Dye}^{+} + OH^{-} \longrightarrow \text{Dye} + {}^{\bullet}OH$$

$$\text{Dye/Dye}^{+} + {}^{\bullet}OH\ /(O_2^{-}) \longrightarrow \text{Product}$$

Methylene blue can act as sensitizer for light induced process. Due to sensitization of photocatalyst, electron migrates from valance band (VB) to conduction band (CB) and holes are formed in valance band;

these holes can generate hydroxyl radicals, which are highly oxidizing in nature. Probably hole can react with dye molecule and abstract electron from dye molecule and process of degradation start.

When the solution of the dye was exposed to light, in presence of photocatalyst, initially the dye molecules are excited to first excited singlet state (dye^{*1}). Then these excited molecules are transferred to the triplet state through inter system crossing (ISC). The triplet dye (dye^{*3}) may donate its electron to the photocatalyst (I-R) and the dye becomes positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of the semiconductor thus, regenerating the semiconductor. The positively charged molecules of the dye (dye^{+}) will immediately react with OH^{-} ions to form $OH^{\bullet}$ radicals that will convert the dye molecules into products[45,46].

The azo dyes that have been already studied for their MBIR Dowex-11 assisted photocatalytic degradation are summarized in Table 1.

Table 1: Summary of MBIR Dowex-11 mediated photocatalytic degradation studies of some azo dyes

Azo dyes	No. of azo bonds	Wavelength (nm)	References
Acid red 73	2	507	41
Direct red 81	2	508	42
Ponceau-BS	2	508	38
Acid red 186	1	455	40
Chicago sky blue 6B	2	618	37
Acid red 27	1	520	1
Methyl orange	1	460	33
Ponceau S	2	514	36
Sudan iv	2	520	2
Direct red 23	2	508	39
Acid orange 7	1	483	43
Direct red 5B	2	510	44
Amido black 10B	2	620	35
Acid orange 6	1	387	34

FTIR spectra of photocatalyst (MBIR-11)

The IR spectrum of Dowex-11 resin (Pure) shows peak in the region 3100-3000 cm^{-1} is attributed to =C-H stretching vibration. Another strong and sharp peak show in the region 1650-1600 cm^{-1} denotes –C=C- stretching vibration. Two peaks in the region 1600-1450 cm^{-1} show aromatic –C=C-stretching vibration. Following peak is shown in Fig. 1[38,39].

In order to examine the differences between immobilized Resin Dowex-11 and pure Resin Dowex-11, the FT-IR spectra were applied to the study. The FTIR spectrum of immobilized Resin Dowex-11 exhibit many alterations from that of pure Resin Dowex-11. The major differences where 3650-3400 cm^{-1} to >N-H stretching vibration and 3100-2900 cm^{-1} stretching vibration of =C-H (Methylene) group. Due to immobilization and another strong and sharp peak of N-H bending in the region 1550-1510 cm^{-1}, these peaks are shown in Fig. 2.

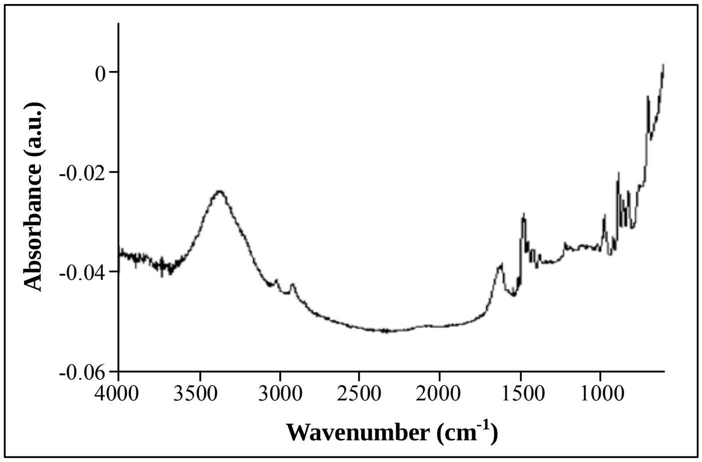

Fig. 1: FTIR spectra of Dowex-11 resin without immobilization

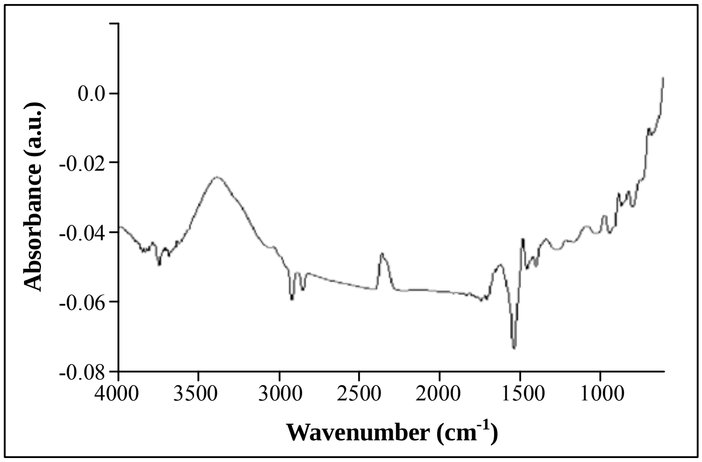

Fig. 2: FTIR spectra of immobilized Dowex-11 resin

Effect of irradiation time

The percentage degradation increases with increasing irradiation time. The light induced degradation proceeds with a slow kinetics after one hour irradiation. This indicates the formation of intermediates and its competitiveness with parent dye molecules in the photocatalytic degradation process. Bandara et al[47] have attributed the slow kinetics of dye degradation after certain time limit due to the difficulty in converting the N-atoms of dye into oxidized nitrogen compounds. This has been observed during photocatalytic degradation of C-N bonds in aliphatic compounds like form amide Mallard et al.[48] The photocatalytic degradation of the dye occurs on the surface of catalyst where $OH^{\bullet}$ and $O_2^{\bullet}$ radicals are available for photocatalytic degradation. Hydroxyl radicals are formed from the holes in valence band reacting with either water OH^- adsorbed on the catalyst surface. The $OH^{\bullet}$ radicals are strong enough to break the different bonds in the dye molecules (N=N, C-C, C=N, C-N, C-S and C=N) adsorbed on the surface of catalyst, which lead to the formation of carbon dioxide and inorganic ions such as NH_4^+, NO_3^-, Cl^- and SO_4^{2-}. The formation of $OH^{\bullet}$ radicals and $O_2^{\bullet}$ increases with increase in irradiation time.

Effect of initial dye concentration

It is important both from a mechanistic and from an application point of view to study the dependence of the photocatalytic reaction rate on the substrate concentration. It is generally noted that the degradation rate increases with the increase in dye concentration to a certain level and a further increase in dye concentration leads to decrease the degradation rate of the dye[49-51]. The active surface on the catalyst available for reaction is very crucial for the degradation to take place, but as the dye concentration is increased and the catalyst amount is kept constant, results in fewer active sites for their action[52,53]. With increased dye molecules the solution became more intense colored and the path length of photons entering the solution decreased thereby only fewer photons reached the catalyst surface. And therefore, the production of hydroxyl and superoxide radicals was limited. At still higher concentration of the dye, the path length was further reduced and the photodegradation was found to be negligible.

Effect of catalyst loading

The amount of catalyst is one of the main parameter for the degradation studies. The degradation efficiency increases with increase in the catalyst loading upto certain limit. The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose[54]. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase of catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface[55]. The availability of active sites increases with the suspension of catalyst loading, but the light penetration, and hence, the photo-activated volume of the suspension shrinks. Moreover, the decrease in the percentage of degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules.

Effect of light intensity

An increase in light intensity increases the rate of photocatalytic degradation[56,57]. As the intensity of light increases, the number of photons striking per unit area of the photocatalyst also increases. Linear behavior between light intensity and the rate of reaction was observed. Ollis et al.[58] reviewed the studies reported for the effect of light intensity on the kinetics of the photocatalysis process and stated that (i) at low light intensities (0-20 m W/cm^2), the rate would increase linearly with increasing light intensity (first order), (ii) at intermediate light intensities beyond a certain value (approximately 25 mW/cm^2)[59], the rate would depend on the square root of the light intensity (half order), and (iii) at high intensity the rate is independent of light intensity. This is likely because at low light intensity reaction involving electron hole formation are pre dominant and electron hole recombination is negligible. However at increase light intensity electron hole pair separation competes with recombination, thereby causing lower effect on the reaction rate. In the studies reviewed here, the enhancement of the rate of degradation as the light intensity increased was also observed[60-62].

Effect of pH variation

The interpretation of the pH effect on the efficiency of dye photodegradation process is a very difficult task because of its multiple roles. Increase of pH of the dye solution from 3.5 to 7.5 increases the degradation of dye. Photocatalytic degradation of dye increases with increase in pH upto a pH value of 7.5 and then decreases again with increase in pH value above 7.5. This behavior may be explained on the basis that the increase in the rate of photocatalytic degradation may be due to the increased availability of OH^- at higher pH values[63-65]. By combining with holes, OH^- ions will generate more hydroxyl radicals ($OH^\bullet$), which are considered responsible for the photocatalytic degradation. Above a pH value of 7.5, the increased number of OH^- ions will compete with the electron rich dye. The OH^- ions will make the surface of the semiconductor negatively charged and as a consequence of repulsive force between two negatively charged species (OH^-) ions and the electron rich dye); the approach of dye molecules to the semiconductor surface will be retarded. This will result in a decrease in the rate of photocatalytic degradation of dye.

Effect of dissolved oxygen on degradation rate

As dissolved oxygen increases in dye solution rate of degradation also increases. When oxygen gas is passed through reaction mixture the rate of degradation also increases. When nitrogen or any other non-reacting gas is passed through this solution no effect is observed on rate of degradation. This effect may cause due to more availability of oxygen for formation of super oxide ions and hydroxyl radicals. These are highly oxidative in nature and increase the rate of degradation of dye molecules[40].

Recycling studies

In order to know the stability of the catalyst, the catalyst was recycled five times by using dye solutions at optimum conditions. After each experiment, the catalyst was separated from solution by filtration, washed with deionized water for several times, the catalyst was dried overnight and then used for next run. Noticeably, after five cycles of experimentation, the catalysis efficiency was still higher and the catalytic performance was not affected by the times of reuse[41,42].

Kinetic study

The photocatalytic degradation of dye follows pseudo-first-order kinetics[66,67]. The plot of 1 + log O. D. versus exposure time is a straight line. The rate constant (k) for the reaction was determined using the expression. Rate (k) = 2.303 × slope. The dye removal efficiency (X %) of dye solution is calculated by this equation.

$$X\ \% = (C_i - C_t / C_i) \times 100$$

Where, C_i and C_t are optical densities of dye solution at initial time and at time t, respectively.

CONCLUSION

As compared to solar photocatalytic systems with other catalyst, methylene blue immobilized-resin Dowex-11 used as solar photocatalyst gives very good results and successfully improved the degradation rate of organic dyes. It is believed that the improved color degradation capability is due to the fact that the visible region of the solar radiation excites the methylene blue immobilized resin, followed by a series of photosensitizing reactions. Degradation of textile azo dye by newly developed photocatalyst MBIR Dowex-11 is a cheap and a very good alternative to traditional technologies for industrial application. It provides a promising technology to improve the quality of effluents from textile waste water treatment plants.

ACKNOWLEDGEMENT

The authors are grateful to the authorities of the J. N. V. University, Jodhpur especially of the Chemistry Department, for encouragement.

REFERENCES

1. P. Yadav and R. C. Meena, Scholars Research Library, **2(3)**, 66-71 (2010).
2. R. C. Meena, R. B. Pachwarya, V. K. Meena and S. Arya, American J. Env. Sci., **5(3)**, 444-450 (2009).
3. A. M. Talarposhti, T. Donelly and G. K. Anderson, Water Res., **35**, 425-432 (2001).
4. T. F. Robinson, G. McMullan, R. Marchant and P. Nigam, Bioresour. Technol., **77**, 247-255 (2001).

5. P. P. Zamora, A. Kunz, S. G. Moraes, R. Pelegrini, P. C. Molerio, J. Reyes and N. Duran, Chemosphere, **38**, 835-852 (1999).

6. L. Ladakowicz, M. Solecka and R. Zylla, J. Biotechnol., **89**, 175-184 (2001).

7. D. Georgiou, P. Melidis, A. Aivasidis and K. Gimouhopoulos, Dyes Pigments, **52**, 69-78 (2002).

8. H. G. Kulla, FEMS Microbiol. Lett., **12**, 387-399 (1981).

9. V. M. Correia, T. Stephenson and S. J. Judd, Environ. Technol., **15**, 917-929 (1994).

10. S. N. Frank and A. J. Bard, J. Am. Chem. Soc., **99**, 303-304 (1977).

11. S. N. Frank and A. J. Bard, J. Phys. Chem., **81**,1484-1488 (1977).

12. D. Georgiou, A. Aivazidis, J. Hatiras and K. Gimouhopoulos, Water Res., **37**, 2248-2250 (2003).

13. S. P. Petrova and P. A. Stoychev, Desalination, **154**, 247-252 (2003).

14. P. C. C. Faria, J. J. M. Órfão and M. F. R. Pereira, Water Res., **38**, 2043-2052 (2004).

15. M. A. Aguado, M. A. Anderson and C. G. Hill, J. Mol. Cataly., **89**, 165-178 (1994).

16. A. G. Rincón and C. Pulgarin, Applied Cataly. B: Environ., **51**, 283-302 (2004).

17. M. Bekbolet, C. S. Uyguner, H. Selcuk, RizzoL, A. D. Nikolaou, S. Meric and V. Belgiorno, Desalination, **176**, 155-166 (2005).

18. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J. M. Hermann, Applied Cataly. B: Environ., **31**, 145-157 (2001).

19. A. Özkan, M. H. Özkan, R. Gürkan, M. Akçay and M. Sökmen, J. Photochem. Photobiol. A: Chem., **163**, 29-35 (2004).

20. G. Chester, M. Anderson, H. Read and S. Esplugas, J. Photochem. Photobiol. A: Chem., **71**, 291-297 (1993).

21. R. Franke and C. Franke, Chemosphere, **39**, 2651-2659 (1999).

22. C. M. Ling, A. R. Mohamed and S. Bhatia, Chemosphere, **57**, 547-554 (2004).

23. M. A. Anderson, M. J. Gieselmann and X. Qunyin, J. Membrane Sci., **39**, 243-258 (1998).

24. S. Matsuo, N. Sakaguchi, K. Yamada, T. Matsuo and H. Wakita, Applied Surface Sci., **228**, 233-244 (2004).

25. C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui and J. M. Hermann, J. Photochem. Photobiol. A: Chem., **158**, 27-36 (2003).

26. H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J. M. Hermann, Applied Cataly. B: Environ., **39**, 75-90 (2002).

27. S. Das, P. V. Kamat, S. Padmaja, V. Au and S. A. Madison, J. Chem. Soc., Perkins Trans., **2**, 1219-1224 (1999).

28. Y. Yang, D. Wyatt and M. Bahorsky, Textile Chem. Colorist, **30**, 27-35 (1998).

29. C. Galindo, P. Jacques and A. Kalt, J. Photochem. Photobiol. A: Chem., **141**, 47-56 (2001).

30. N. Serpone and E. Pelizzetti (Eds.), Wiley Interscience, New York (1989).

31. M. A. Fox and M. T. Dulay, Chem. Rev., **93**, 341-357 (1993).

32. A. A. Khodja, T. Sehili, J. F. Pilichowski and P. Boule, J. Photochem. Photobiol. A: Chem., **141**, 231 (2001).
33. V. K. Meena and R. C. Meena, J. Ind. Council Chem., **27(2)**, 180-184 (2010).
34. V. Kumar and R. C. Meena, J. Ind. Chem. Soc., 257-264 (2011).
35. R. B. Pachwarya and R. C. Meena, J. Scientific and Industrial Res., **68**, 730-734 (2009).
36. R. B. Pachwarya and R. C. Meena, Energy Source Part A, **33**, 1651-1660 (2011).
37. R. B. Pachwarya and R. C. Meena, Environ. Sci., **6(3)**, 1066-1074 (2011).
38. R. C. Meena and M. Meena, Environ. Sci., **7(6)**, 199-204 (2012).
39. Swati, R. C. Meena, Int. J. Sci. and Rec. Publication, **3(4)** (2013).
40. R. C. Meena, Swati and Munesh, Res. J. Chem. Sci., **2(9)**, 56-62 (2012).
41. Munesh, Swati and R. C. Meena, Scholars Res. Library, **4(1)**, 472-479 (2012).
42. R. C. Meena, R. S. Sindal, Munesh and Swati, Int. J. Basic Appl. Chem. Sci., **2(1)**, 46-49 (2012).
43. P. Yadav, Disha and R. C. Meena, Scholars Res. Library, **4(3)**, 1231-1239 (2012).
44. Disha and R. C. Meena, Int. J. Scientific Res. Publication, **3(2)** (2013).
45. M. Muneer, R. Philip and S. Das, Res. Chem. Intermed., **23**, 233 (1997).
46. C. Bauer, P. Jacques and A. Kalt, J. Photochem. Photobiol. A: Chem., **140(1)**, 87 (2001).
47. J. Bandara, V. Nadtochenko, J. Kiwi and C. Pulgarin, Water Sci. Tech., **35**, 87 (1997).
48. C. Maillard, C. Guillard, P. Pichat and M. A. Fox, New J. Chem., **16**, 821 (1992).
49. I. K. Konstantinou, Albanis, Applied Ctalysis B; Environmental, **49**, 1-14 (2004).
50. M. Saquib and M. Muneer, Dyes Pigments, **56**, 37-49 (2003).
51. S. Sakthivel, B. Neppolian, M. V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, Solar Cells, **77**, 65 (2003)
52. R. J. Davis, J. L. Gainer, G. O. Neal and I. W. Wu, Water Environ. Res., **66**, 50 (1994).
53. I. Poulios and I. Aetopoulou, Environ. Technol., **20**, 479 (1999).
54. A. Akyol, H. C. Yatmaz and M. Bayramoglu, Appl. Catal. B: Environment, **54**, 19 (2004).
55. M. S. T. Gonclaves, A. M. F. Oliveira-Campose, E. M. M. S. Pinto, P. M. S. Plasencia and M. J. R. P. Queiroz, Chemosphere, **39**,781-786 (1999).
56. W. S. Kuo and P. H. Ho, Chemosphere, **45**, 77 (2001).
57. S. Chakrabarti and B. K. Dutta, J. Hazard. Mater., **112**, 269 (2004).
58. D. F. Ollis, E. Pelizzetti and N. Serpone, Environ. Sci. Technol., **25**, 1523 (1991).
59. J. M. Hermann, Catalysis Today, **53**, 115 (1999).
60. C. M. So, M. Y. Cheng, J. C. Yu and P. K. Wong, Chemosphere, **46**, 905 (2002).
61. L. B. Reutergarth and M. Iangphasuk, Chemosphere, **35**, 585 (1997).
62. T. Sauer, G. C. Neto, H. J. Jose and R. F. P. M. Moreiara, J. Photochem. Photobiol. A: Chem., **149**, 147 (2002).

63. K. Hustert and R. G. Zepp, Chemosphere, **24**, 335 (1992).
64. C. Lizama, J. Freer, J. Baeza and H. D. Mansilla, Catal. Today, **76**, 235 (2002).
65. B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, Chemosphere, **4**, 1173 (2002).
66. M. A. Behnajady, N. Modirshahla and R. Hamzavi, J. Hazard. Mater., **133**, 226 (2006).
67. H. T. Chang, N. M. Wu and F. Zhu, Wat. Res., **34**, 407-416 (2000).