



TiO₂-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions

M. Saquib, M. Muneer*

Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India

Received 20 May 2002; received in revised form 15 June 2002; accepted 18 August 2002

Abstract

TiO₂-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet, 1), was investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV-spectroscopic analysis and decrease in total organic carbon (TOC) content as a function of irradiation time. The degradation of dye was studied under a variety of conditions such as pH, catalyst concentration, substrate concentration, different types of TiO₂ and in the presence of electron acceptors such as hydrogen peroxide (H₂O₂) and ammonium persulphate ((NH₄)₂S₂O₈) besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient as compared with other photocatalysts. The degradation products were analysed by GC–MS technique and probable pathways for the formation of the products were proposed.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Photocatalysis; Triphenylmethane dye; Gentian violet; Titanium dioxide

1. Introduction

Wastewater from the textile industry is highly coloured and of a complex and variable nature [1]. The large amount of dyestuffs used in the dyeing stage of textile manufacturing processes represent an increasing environmental danger due to their refractory nature [2,3]. A substantial amount of dyestuff is lost during the dyeing process in the textile industry [4], which poses a major problem for the industry as well as a threat to the environment [4–9]. Decolourization of dye effluents has

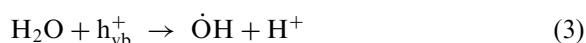
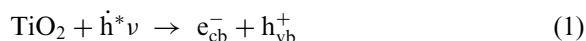
therefore acquired increasing attention. During the past two decades, photocatalytic process involving TiO₂ semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of waste water pollutants. Earlier studies [10–13] have shown that a wide range of organic substrates can be completely photomineralized in the presence of TiO₂ and oxygen.

There are several studies related to the use of semiconductors in the photomineralization of photostable dyes [14–30]. The photocatalysed degradation of various organic systems employing irradiated TiO₂ is well-documented in the literature [10]. The initial step in the TiO₂ mediated photocatalysed degradation is proposed to involve

* Corresponding author. Tel.: +91-571-700515; fax: +91-571-702758.

E-mail address: cht12mm@amu.nic.in (M. Muneer).

the generation of (e^-/h^+) pair leading to the formation of hydroxyl radical and superoxide radical anion [Eqs. (1)–(3)];

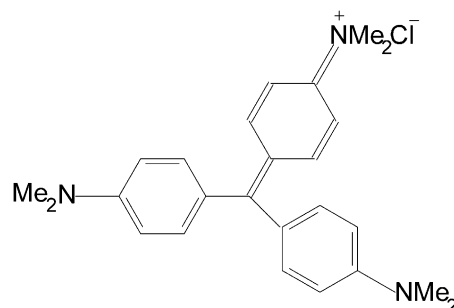


It has been suggested that the hydroxyl radicals and superoxide radical anions are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye and the efficiency of the degradation will depend upon the oxygen concentration, which determines the efficiency with which the conduction band electrons are scavenged and the (e^-/h^+) recombination is prevented. Alternatively, the electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of dye radical anion and subsequent reaction of the radical anion can lead to degradation of the dye.

An example of triphenylmethane dye (gentian violet) is extensively used in textile dyeing, paper printing, as a biological stain and as a dermatological agent [31,32]. Gentian violet is a mutagen, a mitotic poison and clastogen and has been used for many years in veterinary medicine and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus [33–36]. Littlefield et al. [37] found that gentian violet is carcinogenic in mice at several different organ sites. The carcinogenic effects of gentian violet in rodents has also been reported [38]. McDonald and Cerniglia [39] reported the reduction of gentian violet to leucogentian violet by human, rat and chicken intestinal microflora under anaerobic conditions. They showed that the major portion of the metabolites was often bound to the cells (up to 87% of the metabolite produced by human microflora). Because of its low cost, its effectiveness as an antifungal agent for commercial poultry feed, and its ready availability, the general public may be exposed to the dye and its metabolites through the consumption of treated poultry products. Therefore, there are both environmental

and human health concerns regarding the bioaccumulation of gentian and leucogentian violet.

Biological decolourization of triphenylmethane dyes including gentian violet is widely reported in the literature [40–46]. There are no reports dealing with the photocatalytic oxidation of the related system by titanium dioxide. With this view we have undertaken a detailed study on the photo-degradation of the triphenylmethane dye (gentian violet, 1) sensitized by TiO_2 in aqueous solution.



(1)

2. Experimental methods

2.1. Reagent and chemicals

Gentian violet was obtained from B.D.H., Poole, England and used as such without any further purification. The water employed in all the studies was double distilled. While the photocatalyst titanium dioxide, P25 (Degussa AG) was used in most of the experiment, other catalyst powders, namely Hombikat UV100 (Sachtleben chemie GmbH) and PC500 (Milenium inorganic chemicals), were used for comparative studies. P25 consists of 75% anatase and 25% rutile with a specific BET-surface area of $50 \text{ m}^2 \text{ g}^{-1}$ and primary particle size of 20 nm [47]. Hombikat UV100 consists of 100% anatase with a specific BET-surface area $> 250 \text{ m}^2 \text{ g}^{-1}$ and primary particle size of 5 nm [48]. The photocatalyst PC500 has a BET-surface area of $287 \text{ m}^2 \text{ g}^{-1}$ with 100% anatase and primary particle size of 5–10 nm [49]. The other chemical used in this study such as NaOH, HNO_3 ,

H₂O₂ and (NH₄)₂S₂O₈, were obtained from Merck.

2.2. Procedure

Stock solutions of the dye containing the desired concentration were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, a water circulating jacket and an opening for supply of molecular oxygen was used. For irradiation experiments 250 ml of the stock solution were taken into the photoreactor and the required amount of photocatalyst was added. The solution was stirred and bubbled with molecular oxygen for at least 30 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from a blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp. IR-radiation and short-wavelength UV-radiation were eliminated by a water jacket. Samples (10 ml) were collected before and at regular intervals during the irradiation. They were centrifuged by Remi-R23 Revolving Centrifuge before analysis.

2.3. Analysis

The mineralization of the dye was monitored by measuring the total organic carbon (TOC) content with a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solution whereas the degradation was monitored by measuring the absorbance using a Shimadzu UV-Vis Spectrophotometer (Model 1601). The absorbance of the dye was followed at 536 nm wavelength after 80% dilution of the irradiated solution. For each experiment the degradation rate for the mineralization and decomposition of the model pollutant was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of the TOC and absorbance of the dye as a function of irradiation time, i.e. First

order degradation kinetics. It was calculated in terms of $\text{ML}^{-1} \text{min}^{-1}$.

For the characterization of the intermediate products, aqueous solutions (250 ml) of the compound containing (P25, 1 g l) was taken in the immersion well photochemical reactor. The mixture was irradiated with a 125 W medium pressure mercury lamp for 120 min and the photocatalyst was removed through filtration. The filtrate was extracted with chloroform, which was subsequently dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC-MS. For GC-MS analysis a Hewlett Packard Gas chromatograph and mass spectrometer (G1800A) equipped with a 30 m HP-1 ($d=0.25$ mm) capillary column, operating temperature programmed (100–10–250–30–280) in splitless mode. An injection volume of 0.5 μl with helium as a carrier gas was used.

3. Results

3.1. Photolysis of TiO₂ suspensions containing gentian violet (1)

Fig. 1 shows the degradation and depletion in TOC for irradiation of an aqueous solution of gentian violet (1, 0.18 mM) in the presence of the photocatalyst (P25, 1 g l⁻¹) by the “Pyrex” filtered output of a 125 W medium pressure mercury lamp. It was observed that 99 and 85% decomposition and mineralization of the dye takes place, respectively, after 90 min of illumination. Both the mineralization and degradation curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. The degradation rate for the mineralization and decomposition of the dye was calculated using formula given below,

$$-d[\text{TOC}]/dt = kc^n$$

$$-d[A]/dt = kc^n$$

where: k = rate constant, c = concentration of the pollutant, n = order of reaction.

Blank experiments were carried out by irradiating the aqueous solution of the dye in the absence

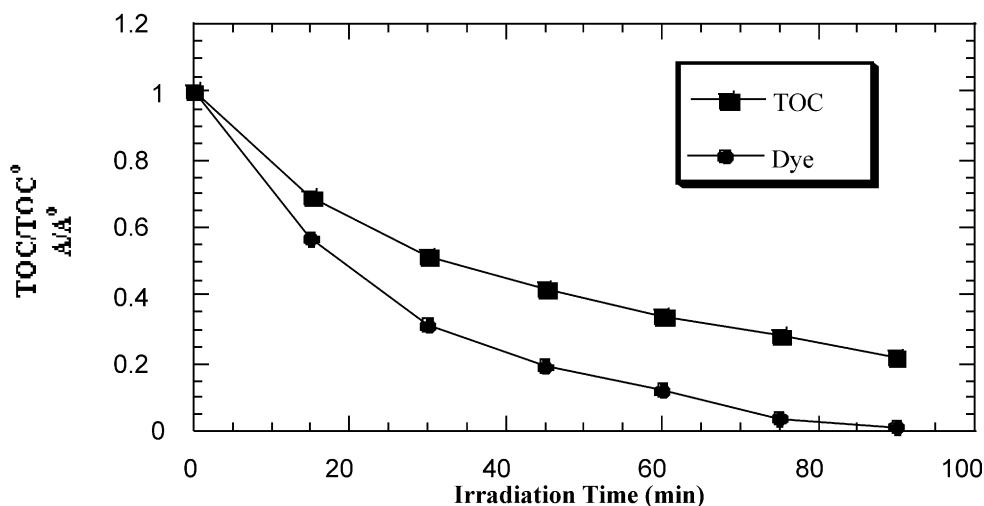


Fig. 1. Depletion in TOC and change in absorbance as a function of irradiation time for an aqueous solution of gentian violet in the presence of TiO_2 . Experimental condition: dye concentration (0.18 mM), $V=250$ ml, immersion well photoreactor, 125 W medium pressure Hg lamp, P25 (1 g l^{-1}), absorbance was followed at 536 nm after 80% dilution. cont. O_2 purging and stirring, irradiation time = 90 min.

of TiO_2 , where no observable loss of the dye was observed. Also no observable loss of the dye due to adsorption on the surface of the photocatalyst was observed in unirradiated blank solutions. The zero irradiation time readings were obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.2. Comparison of different photocatalysts

The influence of three different photocatalyst (namely P25, UV100 and PC500) on the degradation kinetics of gentian violet (**1**) was investigated and the results are shown in Fig. 2. It was observed that the mineralization and degradation of dye proceeds much more rapidly in the presence of P25 as compared with other photocatalysts.

In all following experiments, Degussa P25 was used as the photocatalyst since this material exhibited the highest overall activity for the degradation of the dye.

3.3. pH effect

Employing Degussa P25 as photocatalyst the decomposition and mineralization of gentian vio-

let (**1**) in the aqueous suspensions of TiO_2 was studied in the pH range between 3 and 11. The degradation rate for the TOC depletion and for the decomposition of the dye as a function of reaction pH is shown in Fig. 3. The efficiency of degradation rate for the decomposition of the dye was better at pH 3.5 and 11, whereas it was lower at pH values 5.8 and 9. In contrast, the degradation rate for the mineralization of the dye was found to decrease with the increase in pH from 3.5 to 9 and further increase in pH leads to increase in the efficiency of the degradation rate.

The adsorption of the dye on the surface of the photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h in a round bottomed flask containing varying amount of photocatalyst such as 0, 0.5, 1, 2 and 5 g l^{-1} at pH 3.5, 5.8, 9 and 11. Analysis of the sample after centrifugation indicates some observable loss of the dye at pH 3.5 and 4.6, whereas no adsorption was observed at pH 9 and 11.

3.4. Effect of substrate concentration

It is important both from a mechanistic and from an application point of view to study the

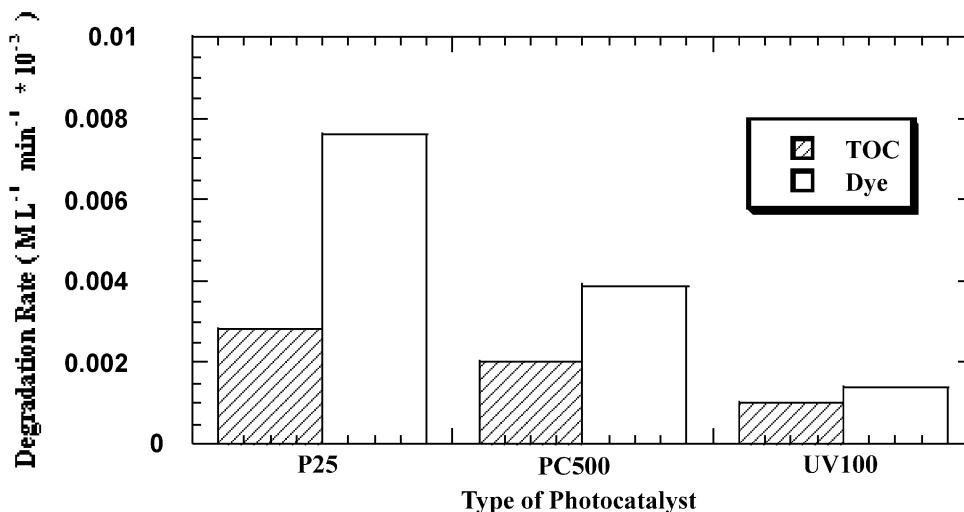


Fig. 2. Comparison of degradation rate for the mineralization and decomposition of gentian violet under different photocatalysts. Experimental conditions: dye concentration (0.18 mM), $V=250$ ml, P25 (1 g l^{-1}), Sachtleben Hombikat UV 100 (1 g l^{-1}) and PC 500 (1 g l^{-1}), immersion well photoreactor, 125W medium pressure Hg lamp), absorbance was followed at 536 nm after 80% dilution cont. O_2 purging, irradiation time = 90 min.

dependence of the photocatalytic reaction rate on the substrate concentration. Hence the effect of substrate concentration on the degradation of gentian violet was studied at varying concentrations such as 0.18, 0.25, 0.35 and 0.5 mM. Fig. 4 shows the degradation rate for the TOC depletion and decomposition of 1 as a function of substrate concentration employing Degussa P25 as a photocatalyst. It is interesting to note that the degradation rate increases with the increase in substrate concentration from 0.18 to 0.25 mM. A further increase in the substrate concentration from 0.25 to 0.5 mM leads to decrease in the degradation rate of the dye.

3.5. Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of gentian violet was investigated employing different concentrations of Degussa P25 varying from 0.5 to 5 g l^{-1} . As expected, the degradation rate for the TOC depletion and decomposition of the dye was found to increase with the increase in catalyst concentration (Fig. 5), which is the characteristic of heterogeneous photocatalyst and results are in agreement with the earlier studies.

3.6. Effect of electron acceptors

The effect of electron acceptors such as hydrogen peroxide and ammonium persulphate in addition to molecular oxygen on the degradation kinetics of the model compound was investigated as well. It was found that the model compound, gentian violet, undergoes oxidation in the presence of ammonium persulphate ion and TiO_2 in the dark, which was indicated by an instant colour change, decrease in total organic carbon content and absorption intensity. On the other hand the electron acceptor such as hydrogen peroxide was found to enhance the rate for the TOC depletion of gentian violet in the presence of P25, as shown in Fig. 6 (TOC vs time profile). Blank experiments were carried out by irradiating the aqueous solution of the dye containing hydrogen peroxide in the absence of the photocatalyst. Analysis of the sample after centrifugation showed no observable loss of the dye.

3.7. Intermediate product

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye in aqueous suspensions of

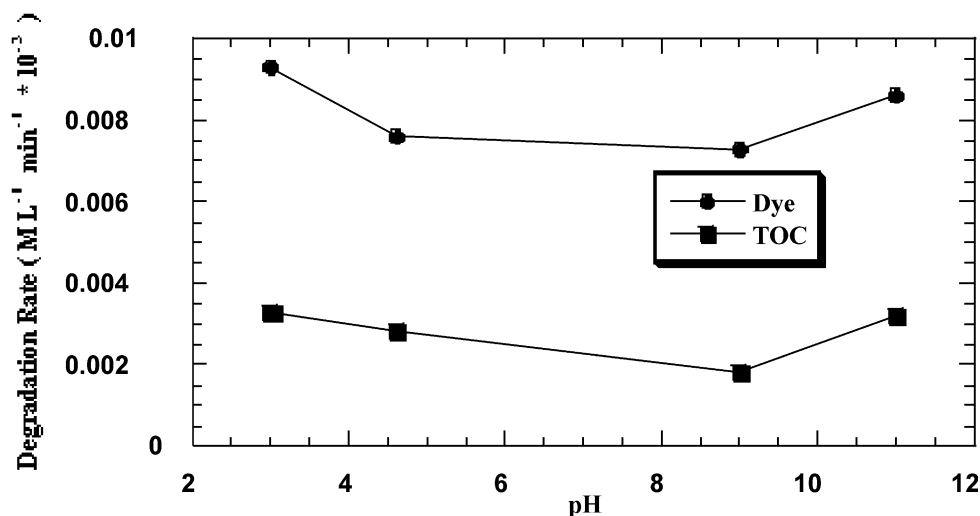


Fig. 3. Influence of pH on the degradation rate for the mineralization and decomposition rate of gentian violet. Experimental conditions: dye concentration (0.18 mM), $V=250$ ml, P25 (1 g l^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp), absorbance was followed at 536 nm after 80% dilution, cont. O_2 purging and stirring, irradiation time=90 min.

titanium dioxide through GC–MS analysis. The GC–MS analysis of the irradiated mixture of 1 showed the formation of several products. Out of which two products appearing at retention times (t_R) 8.45 min and 9.30 min could be assigned to *p*-aminobenzoic acid (**14**) and *N*-methylaniline (**8**)

was identified based on their molecular ion and mass spectrometric fragmentation peaks, as shown:

Compound **14**: 137 (M^+), 121, 107, 93, 86, 73, 69, 63, 55 and 49.

Compound **8**: 107 (M^+), 104, 83, 73, 71, and 51.

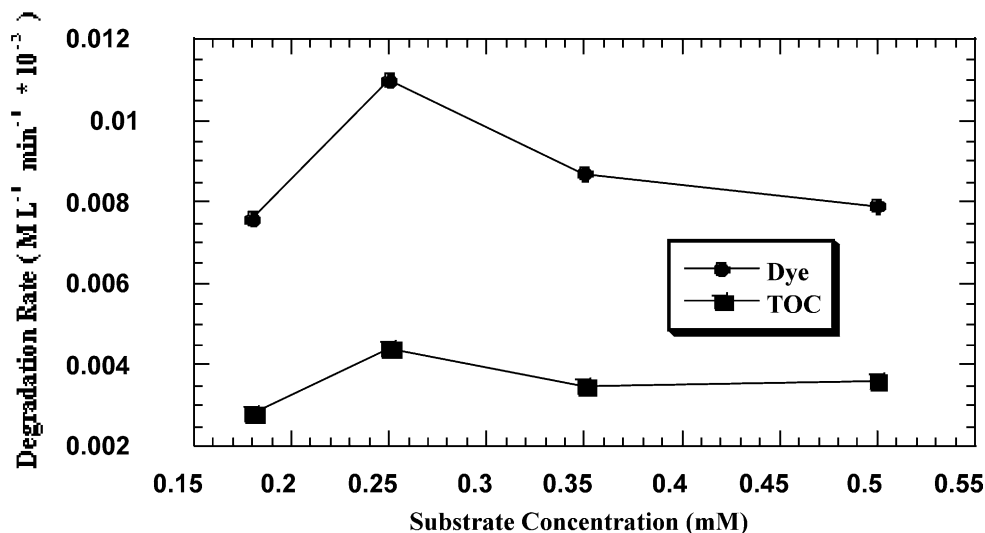


Fig. 4. Influence of substrate concentration on the degradation rate for the mineralization and decomposition rate of gentian violet. Experimental conditions: dye concentration (0.18, 0.25, 0.35 and 0.5 mM), $V=250$ ml, P25 (1 g l^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp), absorbance was followed at 536 nm after 80% dilution, cont. O_2 purging and stirring, irradiation time=90 min.

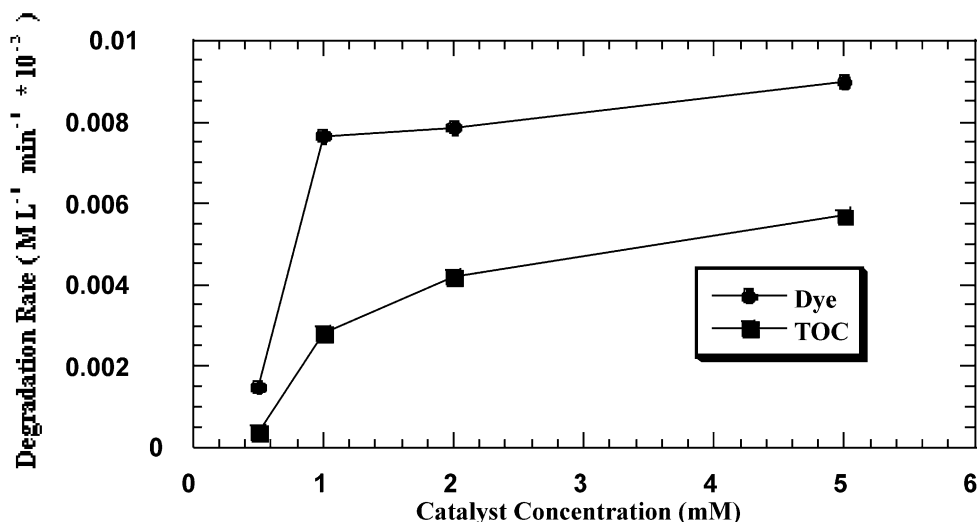


Fig. 5. Influence of catalyst concentration on the degradation rate for the mineralization and decomposition of gentian violet. Experimental conditions: dye concentration (0.18 mM), $V=250$ ml, P25 (0.5, 1, 2 and 5 g l⁻¹), immersion well photoreactor, 125 W medium pressure Hg lamp), absorbance was followed at 536 nm after 80% dilution, cont. O₂ purging and stirring, irradiation time = 90 min.

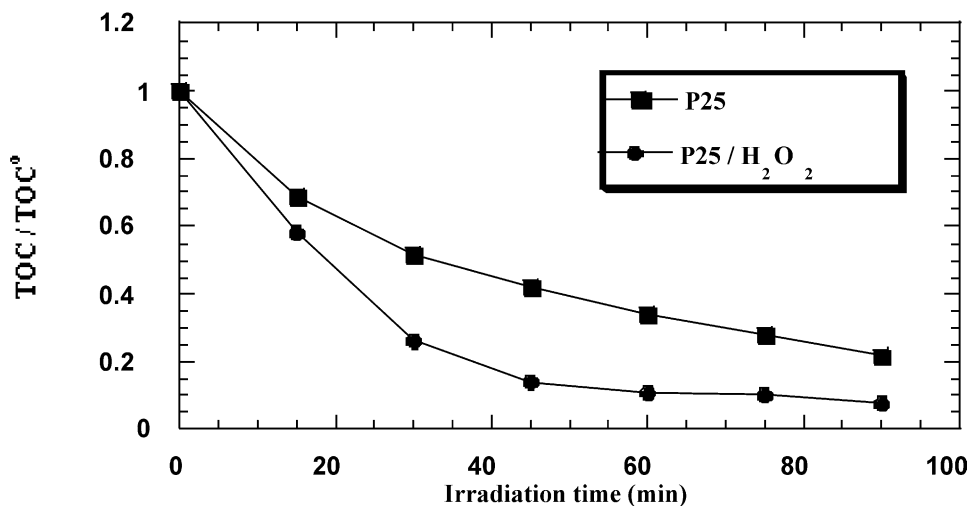


Fig. 6. Effect of hydrogen peroxide on the depletion in TOC as a function of irradiation time for the photocatalytic degradation of gentian violet. Experimental conditions: dye concentration (0.18 mM), $V=250$ ml, P25 (1 g l⁻¹), Electron Acceptor: H₂O₂ (10 mM) immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O₂ purging and stirring, irradiation time = 90 min.

4. Discussion

The results on the photodegradation of the model compound using different kinds of TiO₂ photocatalyst with different bulk and surface properties, i.e. BET-surface, impurities, lattice

mismatches or density of hydroxyl groups on the catalyst's surface, indicate that the latter is apparently not responsible for the photocatalytic activity or alternatively just compensate each other. It has been shown earlier that Degussa P25 owes its high photoreactivity due to slow recombination of

(e^-/h^+) pair whereas Sachtleben Hombikat UV100 has a high photoreactivity due to fast interfacial electron transfer rate [50]. Since, the photocatalyst P25 was found to be better for the degradation of the model compound, indicating the lifetime of the photogenerated (e^-/h^+) pairs being the rate-limiting step where higher concentration of electrons and holes are available for suitable reactants to initiate the photocatalytic reaction. Another reason for the better efficiency of Degussa P25 photocatalyst could be explained by a “quantum size effect” ([51,52] and references cited there in), when the particles become too small, there is a “blue shift” with an increase of band gap energy, detrimental to the near UV-proton adsorption, and an increase of the electron-hole recombination. Too high specific area as not beneficial for an optimum efficiency.

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. In the case of photocatalyst Degussa P25, the zero point of charge (pH_{zpc}) is at pH 6.5. Hence, at more acidic pH values, the particle surface is positively charged, while at pH values above 6.5, it is negatively charged [53]. In this study it has been shown that the degradation rate for the model compound under investigation is strongly influenced by the reaction pH, where the efficiency of degradation rate for the decomposition of the dye was better at pH 3.5 and 11, whereas it was lower at pH values 5.8 and 9. In contrast, the degradation rate for the mineralization of the dye was found to decrease with the increase in pH from 3.5 to 9 and further increase in pH leads to increase in the efficiency of the degradation rate. It is important to note that the degradation rate for TOC depletion and decomposition of the dye was found to be higher at pH values where significant adsorption of the dye takes place which decreases with the increase in pH. The results of these studies indicate that adsorption is a prerequisite for the degradation of organic pollutants in heterogeneous photocatalysis. A further increase in the degradation rate at higher pH value may be attributed to more efficient generation of hydroxyl radicals by TiO_2

with increasing concentration of OH^- . At the alkaline pH values, the hydroxyl radicals have to diffuse away and degrade the dye in the bulk solution.

The effect of substrate concentration on the degradation rate for the mineralization and decomposition of 1 (Fig. 4) was studied, as it is important both, from mechanistic and from the application point of view. As oxidation proceeds, less and less of the surface of the TiO_2 particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing illumination time. It has been agreed, with minor variation that the expression for the rate of photomineralization of organic substrates with irradiated TiO_2 follows the Langmuir–Hinshelwood (L–H) law for the four possible situations; (a) the reaction takes place between two adsorbed substances, (b) the reaction occurs between a radical in solution and an adsorbed substrate molecule, (c) the reaction takes place between a radical linked to the surface and a substrate molecule in solution, and (d) the reaction occurs with both the species being in solution. In all cases, the expression for the rate equation is similar to that derived from the L–H model, which has been useful in modeling the process, although it is not possible to find out whether the process takes place on the surface, in the solution or at the interface. Our results on the effect of the initial concentration on the degradation rate for the mineralization and decomposition of the dye 1 shown in Fig. 4 indicate that the rate increases with the increase in the substrate concentration from 0.18 to 0.25 mM and a further increase in the concentration of the pollutant leads to decrease in the degradation rate. This may be due to the fact that as the initial concentrations of the dye increases more and more dye molecules are adsorbed on the surface of the catalyst. Hence, the penetration of light to the surface of the catalyst decreases and the relative amount of $\cdot OH$ and O_2^- on the surface of the catalyst do not increase as the intensity of light and illumination time are constant. Conversely, their concentrations will decrease with an increase in concentration of the dye as the light photons are largely absorbed and

prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

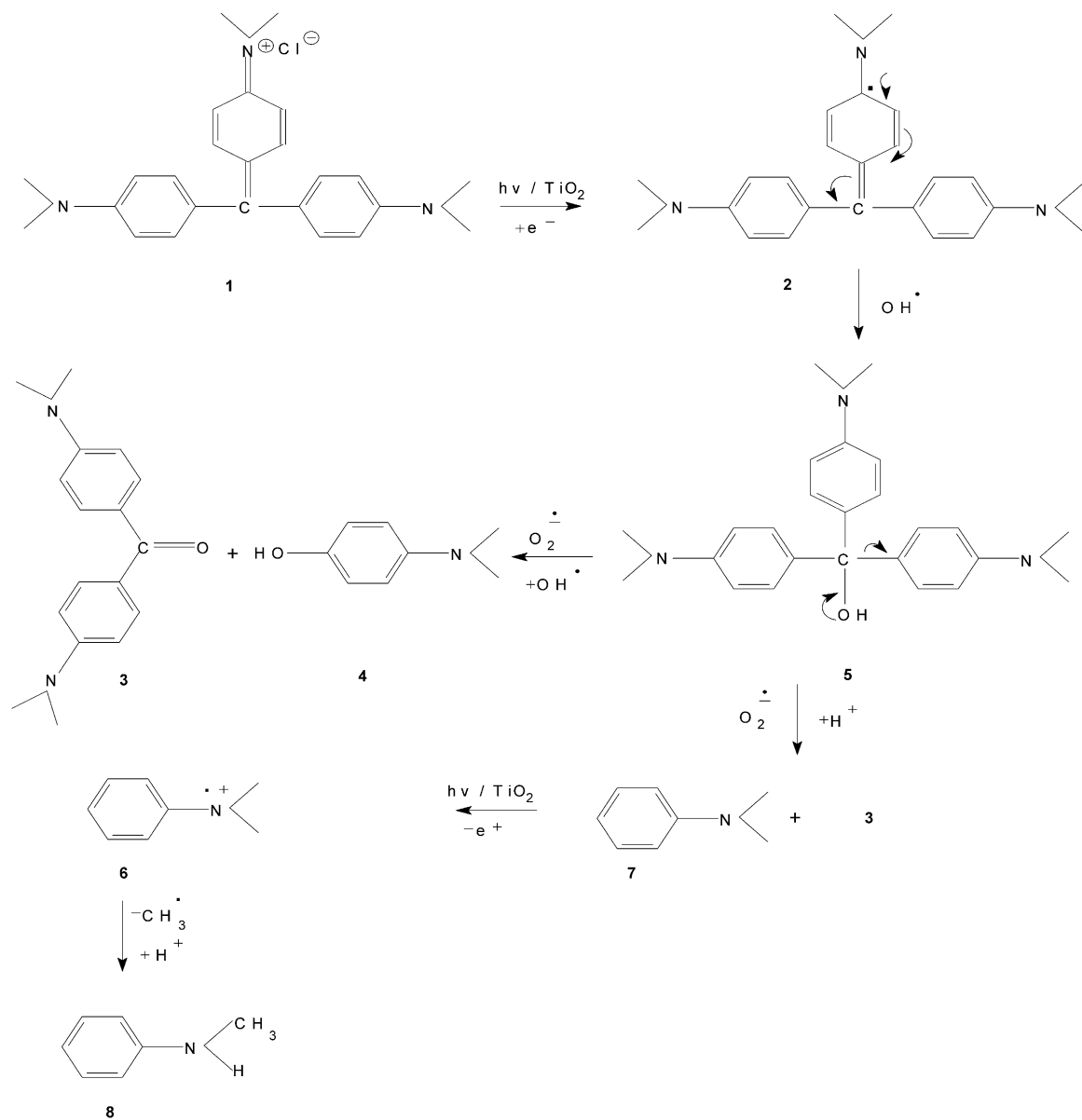
Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, it was observed that above a certain concentration, the reaction rate even decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO_2 in which all the particles, i.e. the entire surface exposed, are totally illuminated. When the catalyst concentration is very high, after travelling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration $[(\text{TiO}_2)_{\text{OPT}}]$ has to be found, in order to avoid excess catalyst and insure total absorption of efficient photons. Our results on the effect of catalyst concentration on the degradation rate for the decomposition and for the mineralization of dye, shown in Fig. 5, are in agreement with numerous studies reported in the literature.

One practical problem in using TiO_2 as a photocatalyst is the undesired electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and thus represent the major energy-wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron–hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as, i.e. (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds, and (4) to avoid problems caused by low oxygen concentration. It is pertinent to mention here that in highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of inorganic ions to enhance the organic degradation rate may often be justified. In this connection, we have studied the effect of electron acceptors such as

hydrogen peroxide and persulphate ions on the photocatalytic degradation of the model compound under investigation. It was observed that persulphate ion in the presence of TiO_2 oxidizes the model compound in the dark, which was shown by the decrease in TOC content and absorption intensity. On the other hand the electron acceptor such as hydrogen peroxide showed beneficial effect on the photocatalytic degradation of the triphenylmethane dye 1. A typical TOC vs time profile observed during the photocatalytic degradation of the dye in the presence of hydrogen peroxide containing TiO_2 shown in Fig. 6.

The enhanced degradation rate in the presence of H_2O_2 could be rationalized in terms of several reasons. Firstly, it increases the rate by removing the surface-trapped electrons, thereby lowering the electron–hole recombination rate and increasing the efficiency of hole utilization for reactions such as $(\text{OH}^- + \text{h}^+ \rightarrow \cdot\text{OH})$. Secondly, H_2O_2 may split photolytically to produce OH radicals directly, as cited in studies of homogeneous photooxidation using $\text{UV}/(\text{H}_2\text{O}_2 + \text{O}_2)$ [54]. Thirdly, the solution phase may at times be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer, peroxide addition thereby increases the rate towards what it would have been had an adequate oxygen supply been provided.

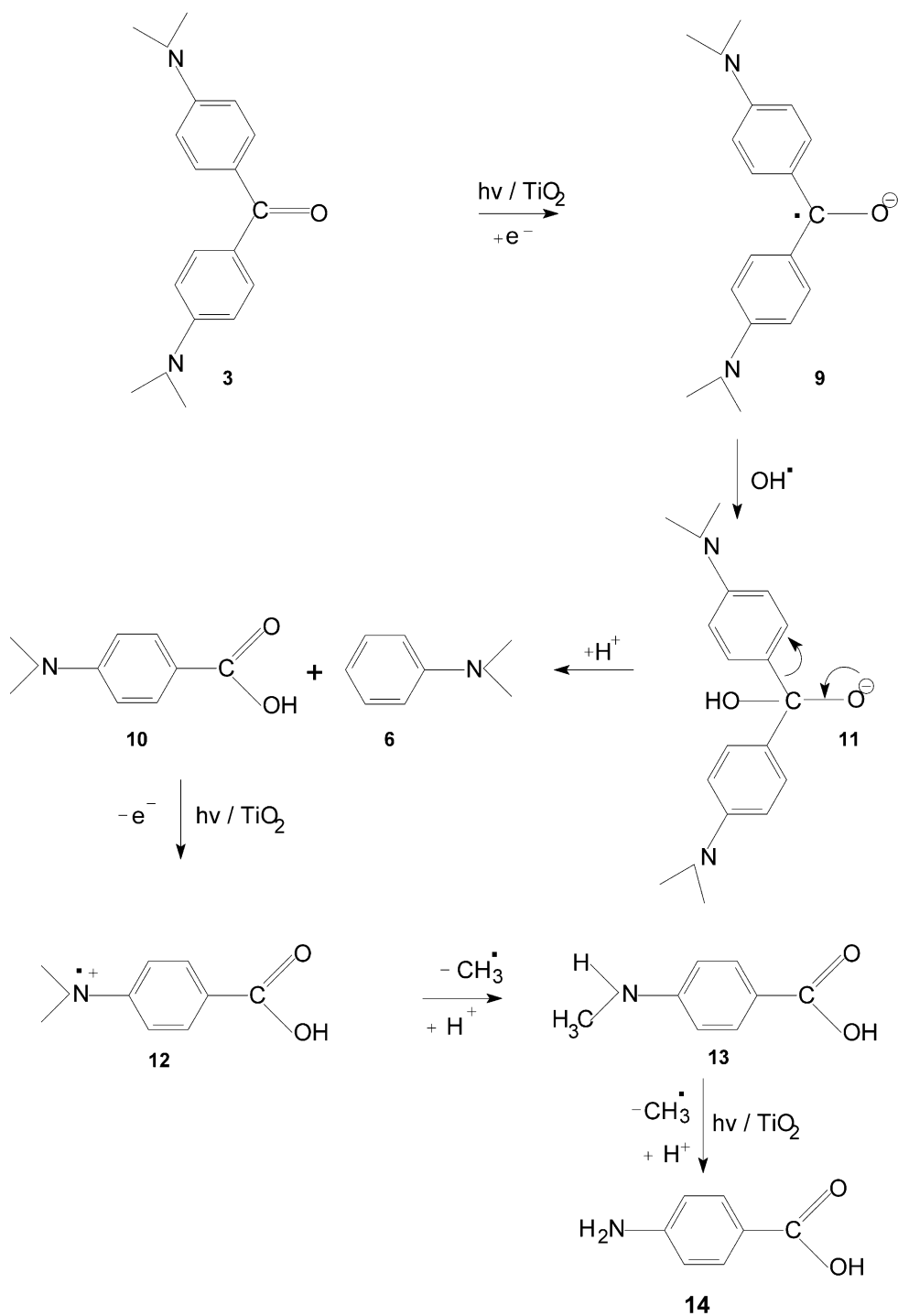
The GC–MS analysis of the irradiated mixture of an aqueous solution gentian violet (**1**) showed the formation of several intermediate products, out of which three products have been identified based on their molecular ion and mass spectrometric fragmentation peaks. A plausible mechanism for the formation of these products involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system is proposed in Schemes 1 and 2, respectively. The model compound **1** upon the transfer of an electron can form the radical species **2**, which may undergo addition of a hydroxyl radical forming **5** which may undergo cleavage either by abstracting a hydroxyl radical to form **4** or by abstracting a proton to form **7** along with the benzophenone derivative **3**. The compound **7** on further transfer of an electron can form the radical cation **6**, which may subsequently undergo loss of



Scheme 1.

methyl group to give the observed product **8** as shown in Scheme 1. The formation of *p*-amino-benzoic acid (**14**) could be understood in terms of the pathways shown in Scheme 2. The benzophenone derivative **3**, upon the transfer of an electron can form the radical anion **9**, which can undergo addition of a hydroxyl radical forming the anionic

species **11**, which upon cleavage can lead to the formation of aniline and benzoic acid derivatives **6** and **10**, respectively. The compound **10** on further transfer of an electron can give rise to radical cation **12**, which may subsequently undergo loss of methyl group to give the observed product **14** as shown in Scheme 2.



Scheme 2.

5. Conclusion

TiO₂ can efficiently photocatalyse the triphenylmethane dye derivative **1** in the presence of light and oxygen. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The best degradation condition depends strongly on the kind of pollutant. The model compound was found to degrade more rapidly in the presence of Degussa P25 as compared to other photocatalyst powders. The persulphate ions can efficiently oxidize the dye in the absence of light. The analysis of the intermediate products formed during the photodegradation process could be a useful source of information on the degradation pathways.

Acknowledgements

Total organic carbon (TOC) analyzer used for the analyses of the samples was a gift equipment from the Alexander von Humboldt Foundation, Germany. Financial support by the Department of Science and Technology (DST), Government Of India, New Delhi and The Third World Academy of Sciences Triesty, Italy is gratefully acknowledged.

References

- [1] Grau P. Textile industry wastewaters treatment. *Water Sci Technol* 1991;24:97–103.
- [2] Pagga U, Bruan D. The degradation of dyestuffs part II: behaviour of dyestuffs in aerobic biodegradation tests. *Chemosphere* 1986;15:479–91.
- [3] Reife A. Dyes environmental chemistry. In: Kirk, editor. *Othmer encyclopedia of chemical technology*, Vol 8. 4th ed. New York: John Wiley & Sons, Inc; 1993. p. 753–84.
- [4] Zollinger H. Chapter 16. In: Eblel HF, Brenzinger CD, editors. *Colour chemistry*, 1st ed. New York: VCH; 1987.
- [5] Searle CE. *Chemical carcinogenesis*. Washington, DC: ACS Monograph, American Chemical Society; 1976.
- [6] Helmes CT, Sigman CC, Fund ZA, Thompson MK, Voeltz MK, Makie M, Klein PE, Lent JB. *J Environ Sci Health A* 1984;19:97.
- [7] Boeninger M. Carcinogenicity and metabolism of azo dyes, especially those derived from benzidine, DHHS (NIOSH), Publication No. 80–119, July 1980.
- [8] Roxon JJ, Ryan AJ, Wright SE. *Food Cosmet Toxicol* 1967;5:367.
- [9] Cook MM, Ulman JA, Israelidis A. Abstracts of Papers, 203 National meeting of the American Chemical Society, San Francisco, 5–10 April, 1992, American Chemical Society, Washington, DC, 1992 and references therein.
- [10] Blake DM. Bibliography of work on the photocatalytic removal of hazardous compounds from water and air. USA: National Renewal Energy Laboratory; 1999.
- [11] Hermann JM. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today* 1999;53:115–29.
- [12] Litter MI. Heterogeneous photocatalysis transition metal ions in photocatalytic systems. *Applied Catalysis B: Environmental* 1999;23:89–114.
- [13] Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. *J Photochem Photobiol C: Photochem Rev* 2000;1:1–21.
- [14] Vinodgopal K, Bedja I, Hotechandani S, Kamat PV. A photocatalytic approach for the reductive decolourization of textile azo dyes in colloidal semiconductor suspensions. *Langmuir* 1994;10:1767–71.
- [15] Vinodgopal K, Kamat PV. Photochemistry of textile azo dyes. Spectral characterization of excited state, reduced and oxidized forms of acid orange 7. *J Photochem Photobiol A: Chem* 1994;83:141–6.
- [16] Ruan S, Wu F, Zhang T, Gao W, Xu B, Zhao M. Surface-state studies of TiO₂ nanoparticles and photocatalytic degradation of methyl orange in aqueous TiO₂ dispersions. *Mater Chem Phys* 2001;69:7–9.
- [17] Takagishi T, Katsuda N. Photodegradation of dyes by spectro-irradiation. *Int Conf Exhib AACTT* 1999:358–66.
- [18] Kunito K, Maeda S, Hongyo S. Photocatalytic degradation of dyes using various reducing agents. *Okayama-ken kogyo Giyutsu Senta* 2000;26:19–21.
- [19] Zamina GM, Zaitsev NK, Krasnyi DV, Karasev AL, Vannikov AV. Photochemical degradation of aqueous solutions of organic dyes under exposure to vacuum ultraviolet radiation. *High Energy Chem* 2000;34:376–9.
- [20] Xu Y, Langford CH. UV or Visible-light-induced degradation of X3B on TiO₂ nanoparticles: the influence of adsorption. *Langmuir* 2001;17:897–902.
- [21] Yang TC-K, Lin-Shu-Yin, Guo W, Chung T-H, Wang S-F, Tsai SHy. In situ studies of the photodegradation of a dye adsorbed on TiO₂ particles by the DRIFTS. *Adsorpt Sci Technol Proc Pac Basin Conf* 2000;2:683–7.
- [22] Hirano K, Suzuki E, Ishikawa A, Moroi T, Shiroishi H, Kaneko M. Sensitization of TiO₂ particles by dyes to achieve hydrogen evolution by visible light. *J Photochem Photobiol A: Chem* 2000;136:157–61.
- [23] Sökmen M, Özkan A. Decolourising textile wastewater with modified titania: the effects of inorganic anions on the photocatalysis. *J Photochem Photobiol A: Chem* 2002;147:77–81.

- [24] Hachem C, Bocquillon F, Zahraa O, Bouchy M. Decolourization of textile industry wastewater by the photocatalytic degradation process. *Dyes and Pigments* 2001;49: 117–25.
- [25] Mills A, Belghazi A, Davies RH, Worsley D, Morris S. A kinetic study of the bleaching of rhodamine 6G photo-sensitised by titanium dioxide. *J Photochem Photobiol A: Chem* 1994;79:131–9.
- [26] Vautier M, Guillard C, Hermann JM. Photocatalytic degradation of dyes in water: case study of indigo and of indigo carmine. *J Catal* 2001;201:46–59.
- [27] Arsalan I, Balcioglu IA, Bahnemann DW. Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UV-A and TiO_2 /UV-A processes. *Dyes and Pigments* 2000;47:207–18.
- [28] Sakthivel S, Neppolian B, Arabindo B, Palanichamy M, Murugesan. ZnO/UV Mediated photocatalytic degradation of acid green 16, a commonly used leather dye. *Indian Journal of Engineering & Material Science* 2000;7:87–93.
- [29] Zhao J, Wu T, Wu K, Oikawa K, Hidaka H, Serpone N. Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/ TiO_2 dispersions under visible light irradiation: evidence for the need of substrate adsorption on TiO_2 particles. *Environ Sci Technol* 1998;32:2394–400.
- [30] Muneer M, Philips R, Das S. Photocatalytic degradation of waste water pollutants. Titanium dioxide-mediated oxidation of a textile dye, acid blue 40. *Res Chem Intermed* 1997;23:233–46.
- [31] Migazawa F. Experimental studies on chemotherapy of candidiasis. *Eisei Shikenjs* 1956;74:341–8.
- [32] Wald ER, Synder MJ, Gutbenlet RL. Group B beta-hemolytic streptococci colonization, acquisition, persistence and effect of umbilical cord treatment with triple dye. *Am J Dis Child* 1977;131:178–80.
- [33] Au W, Parhak S, Collie CJ, Hsu TC. Cytogenetic toxicity of gentian violet and crystal violet on mammalian cells in vitro. *Mutation Res* 1978;58:269–76.
- [34] Chen TC, Day EJ. Gentian violet as possible fungal inhibitor in poultry feed, plate assays on its antifungal activity. *Poultry Sci* 1974;53:1791–9.
- [35] Cross DL, Hughes BL. Safety evaluation of gentian violet for breeder chickens. *Poultry Sci* 1976;55:1179–82.
- [36] Kingsland GV, Anderson J. A study of the feasibility of the use of gentian violet as a fungistat for poultry feed. *Poultry Sci* 1976;55:852–7.
- [37] Littlefield NA, Blackwell BN, Hewitt CC, Gaylor DW. Chronic toxicity and carcinogenicity studies of gentian violet in mice. *Fundam Appl Toxicol* 1985;5:902–12.
- [38] Dacampo R, Moreno SN. The metabolism and mode of action of gentian violet. *Drug Metab Rev* 1990;22:161–78.
- [39] McDonald JJ, Cerniglia CE. Biotransformation of gentian violet to leucogentian violet by human, rat, and chicken intestinal microflora. *Drug Metab Dispos* 1984;12:330–6.
- [40] Azmi W, Sani RK, Banerjee UC. Biodegradation of triphenylmethane dyes. *Enzyme Microb Technol* 1998;22: 185–91.
- [41] Yatome C, Ogawa T, Koza D, Idaka E. Biodegradation of azo and triphenylmethane dyes by *Pseudomonas pseudomallei* 13NA. *J Society Dyers colorist* 1981;97:166–9.
- [42] Kwasniewska K. Biodegradation of gentian violet by red oxidative yeasts. *Bull Environ Contam Toxicol* 1985;34: 323–33.
- [43] Bumpus JA, Brock BJ. Biodegradation of crystal violet by white rot fungus *Phanerochaete chrysosporium*. *Appl Environ Microbiol* 1988;54:1143–50.
- [44] Yatome C, Ogawa T, Matsui M. Degradation of gentian violet by *Bacillus subtilis*. *J Environ Sci Health* 1991;A26: 75–87.
- [45] Yesilada O. Decolourization of gentian violet by fungi. *World J Microbiol Biotech* 1995;11:601–2.
- [46] Rajesh KS, Ravinder SJ, Uttam CB. Reduction of gentian violet to leucogentian violet by *kurthia* sp. and assessment of toxicity. *Advances in Environmental Research* 1999;3: 368–77.
- [47] Bickley RI, Carreno TG, Lees JS, Palmisano L, Tilley RJD. A spectral investigation of titanium dioxide photocatalysts. *J Solid State Chem* 1992;92:178–90.
- [48] Lindner M, Bahnemann DW, Hirthe B, Griebler WD. Solar water detoxification: novel TiO_2 powders as highly active photocatalysts. *J Sol Energy Eng* 1997;119:120–5.
- [49] Rauer S. Untersuchung von kommerziell erhältlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivität, Diplomarbeit, fachhochschule Hannover. Hannover, Germany: Fachbereich Maschinenbau Vertiefung Umwelt-und Verfahrenstechnik; 1998.
- [50] Martin ST, Hermann H, Choi W, Hoffmann MR. Time resolved microwave conductivity part I— TiO_2 photo-reactivity and size quantization. *J Chem Soc Faraday Trans* 1994;90:3315–23.
- [51] Nozik AJ. In: Ollis DF, El-Ekabi H, editors. Photocatalytic purification and treatment of water and air. Amsterdam: Elsevier; 1993. p. 39.
- [52] Weller H. Angew colloidal semiconductor Q-particles: chemistry in the transition region between solid state and molecule. *Chem Int Ed Engl* 1993;41.
- [53] Hiegenderoff H. Untersuchungen zur Bedeutung der Adsorption in der Photokatalyse. Phd thesis, Department of Chemistry, University of Hannover, Hannover, Germany, 1996.
- [54] Peyton GR, Glaze WH. Destruction of pollutant in water with ozone in contamination with ultraviolet radiation. *Environ Sci Technol* 1988;22:761–7.