Semiconductor-mediated photocatalysed degradation of two selected azo dye derivatives, amaranth and bismarck brown in aqueous suspension

M. Abu Tariq, M. Faisal, M. Muneer*

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

Abstract

Semiconductor-mediated photocatalysed degradation of two selected azo dye derivatives such as amaranth (**1**) and bismarck brown (**2**) has been investigated in aqueous suspension by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time. The degradation was studied under different conditions such as types of TiO_2, pH, substrate concentration, catalyst concentration, and in the presence of electron acceptors such as hydrogen peroxide (H_2O_2), potassium bromate ($KBrO_3$) and ammonium persulphate ($(NH_4)_2S_2O_8$) besides air. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 showed comparatively highest photocatalytic activity. The dye derivative, bismarck brown (**2**) was found to degrade faster than amaranth dye (**1**).
© 2005 Elsevier B.V. All rights reserved.

Keywords: Photocatalysis; Amaranth; Bismarck brown; Titanium dioxide

1. Introduction

Until 1850, color was obtained from natural resources. Perkin in 1856, synthesized first dye. Since then a large number of dyes are synthesized and used in food, textiles and other industries for different purposes. Most of the synthetic dyes are azo dyes and are suspected to be carcinogenic [1]. From the beginning of the 19th century amaranth (**1**) (Fig. 1) had been used as a food dye. However, in 70s, Russian studies showed the carcinogenecity of amaranth (**1**) [2]. On the other hand, the dye was still used in most of the European countries, as textile dyes for wool and silk as well as in food and photography [3]. Whereas, bismarck brown (**2**) (Fig. 2) also an azo dye is used in most of the countries as biological stains, it is also used as hair dye, leather and textile dye [4–5].

The release of colored wastewaters in ecosystem from various sources such as industrial effluents, agricultural runoff and chemical spills is a dramatic source of esthetic pollution, eutrophication, and perturbations in aquatic life. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to the societies and regulation authorities around the world [6].

The control of these dye pollutants in water is an important measure in environmental protection. Physical methods, such as adsorption [7], biological methods (biodegradation) [8] and chemical methods like chlorination and ozonation [9] are frequently used. Among these processes proposed, biodegradation has received the greatest attention. However, many organic chemicals, especially those that are toxic or refractory, are not amendable to microbial degradation. Recently considerable attention has been focussed on the use of semiconductor as a means to oxidize toxic organic chemicals [10]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [11–12]. Briefly, when a semiconductor such
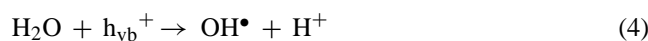
* Corresponding author. Tel.: +91 571 2703515; fax: +91 571 2702758.
 E-mail addresses: cht12mm@amu.ac.in, readermuneer@yahoo.co.in
(M. Muneer).
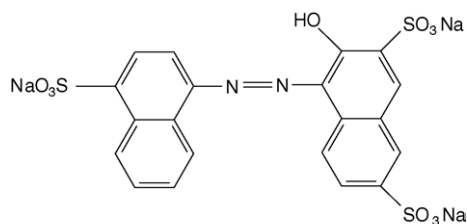
Amaranth (1)

Fig. 1.

as TiO_2 absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e_{cb}^-) leaving behind an electron vacancy or "hole" in the valence band (h_{vb}^+). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}^+ may react with surface-bound H_2O or OH^- to produce the hydroxyl radical and e_{cb}^- is picked up by oxygen to generate superoxide radical anion $O_2^{\bullet-}$ as indicated in the following Eqs. (1)–(4).

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \tag{1}$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \tag{2}$$

$$O_2^{\bullet-} + H_2O \rightarrow OH^\bullet + OH^- + O_2 + HO_2^- \tag{3}$$

$$H_2O + h_{vb}^+ \rightarrow OH^\bullet + H^+ \tag{4}$$

It has been suggested that the hydroxyl radicals $OH^\bullet$ and superoxide radical anions $O_2^{\bullet-}$ are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye. Alternatively, direct absorption of light by the dye, can lead to charge injection from the excited state of the dye to the conduction band of the semiconductor as summarized in the following Eqs. (5) and (6);

$$Dye_{ads} + h\nu \rightarrow Dye_{ads*} \tag{5}$$

$$Dye_{ads*} + TiO_2 \rightarrow Dye_{ads^+} + TiO_2 (e^-) \tag{6}$$
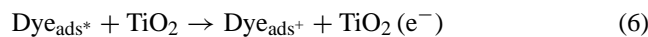
Photocatalytic degradation of amaranth (1) has been reported recently in the presence of TiO_2 [13]. No major effort has been made to study a detailed degradation kinetics that is essential from application point of view. Therefore, we have studied the photocatalytic degradation of two selected azo dye derivatives, amaranth (1) and bismarck brown (2)
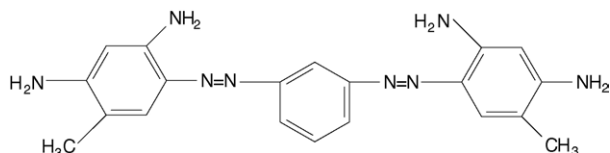
Bismarck brown (2)

Fig. 2.

in aqueous suspensions of TiO_2 under a variety of condition such as types of TiO_2, pH, substrate concentration, catalyst concentration and in the presence of electron acceptors.

2. Experimental methods

2.1. Reagent and chemicals

Amaranth (1) (70%) and bismarck brown (2) (40%) were obtained from Loba Chemie Pvt. Ltd., Mumbai, India and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide Degussa P25 was used in most of the experiments, whereas, other catalyst types, namely, Hombikat UV100 (Sachtleben Chemie GmbH) and PC500 (Millennium Inorganics) were used for comparative studies. Degussa P25 contains 80% anatase and 20% rutile with a specific BET surface area of $50 \, m^2 \, g^{-1}$ and a primary particle size of 20 nm [14]. Hombikat UV100 consists of 100% pure anatase with a specific BET surface area of $250 \, m^2 \, g^{-1}$ and a primary particle size of 5 nm [15]. The photocatalyst PC 500 has a BET-surface area of $287 \, m^2 \, g^{-1}$ with 100% anatase and primary particle size of 5–10 nm [16]. The other chemicals used in this study such as NaOH, HNO_3, H_2O_2, $(NH_4)_2S_2O_8$ and $KBrO_3$ were obtained from Merck.

2.2. Procedure

Solutions of dye derivatives amaranth (1) and bismarck brown (2) of the desired concentration were prepared in double distilled water. An immersion photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of air was used.

For irradiation experiment, $150 \, cm^3$ solution was taken into the photoreactor and required amount of photocatalyst was added and the solution was stirred and bubbled with air for at least 10 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 pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or NaOH. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with air throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury vapour lamp (Philips), the power of lamp in radiant flux is $9375 \, \mu W \, cm^{-2}$. Samples ($6 \, cm^3$) were withdrawn before and at regular intervals during the irradiation. They were centrifuged before analysis.

2.3. Analysis

The decolorization of the dye derivatives was monitored by using UV–vis spectrophotometer (Shimadzu 1601). The

concentration of the dye derivative (**1**) and (**2**) were calculated by calibration curve obtained from the absorbance of the dye derivatives (**1**) ($\lambda_{max} = 524$ nm) and (**2**) ($\lambda_{max} = 463$ nm) at different concentrations. It was calculated in terms of mol L^{-1} min^{-1}.

3. Results and discussion

3.1. Photocatalysis of TiO$_2$ suspensions containing dye derivatives

Irradiation of an aqueous solution of dye derivatives (**1**) and (**2**) in the presence of TiO$_2$ with a 125 W medium pressure mercury lamp leads to change in concentration as a function of time. Fig. 3 shows the change in concentration as a function of irradiation time of an aqueous suspensions amaranth (**1**), 0.4 mM and bismarck brown (**2**), 0.5 mM containing 1 g L^{-1} of TiO$_2$ in the presence of air. The concentration was found to decrease with increase in irradiation time and nearly total decomposition was observed within 75 min of irradiation for amaranth (**1**) and 40 min for bismarck brown (**2**). Control experiments were carried in both cases employing UV-irradiated blank solutions. There was no observable loss of the dye, when the irradiation was carried out in the absence of TiO$_2$ as shown in Fig. 3. The zero irradiation time were obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

The degradation curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics, i.e., the initial slope obtained by the linear regression from the plot of the natural logarithm of the dye as a function of time. Table 1 shows the resulting first order rate constants for oxidation of the two substrates by the different oxidation systems (such as TiO$_2$/UV Light and TiO$_2$/Sunlight). The resulting rate constants has been used in all the subsequent

Table 1
The pseudo-first order rate constants (k) for oxidation of the two derivatives (**1**) and (**2**) by the different oxidation systems UV Light/TiO$_2$ and Sunlight/TiO$_2$

Dye derivatives	Rate constants (k)	
	UV light/TiO$_2$	Sunlight/TiO$_2$
Amaranth (**1**)	6.41×10^{-3}	3.24×10^{-3}
Bismarck brown (**2**)	1.89×10^{-2}	9.65×10^{-3}

plots to calculate the degradation rate for the decomposition of the compounds using expression given below,

$$\frac{-d[C]}{dt} = kc^n \tag{7}$$

C: concentration, *k*: rate constant, *c*: concentration of the pollutant, *n*: order of reaction.

3.2. Comparison of different photocatalysts and catalyst concentration

In view of the advantages of titanium dioxide in the heterogeneous photocatalysis, we have tested the photocatalytic activity of three different commercially available TiO$_2$ types (namely Degussa P25, Hombikat UV100 and PC500) on the degradation of dye derivatives. The reactions were carried out at initial pH 5.68 for (**1**) and 3.25 for dye derivative (**2**). The degradation rate for the decomposition of the dye derivatives (**1**) and (**2**) in the presence of different types of TiO$_2$ at different catalyst concentrations is shown in Figs. 4 and 5, respectively. It has been observed that the photocatalyst Degussa P25 has been found to be better for the degradation of both dye derivatives at all catalyst concentrations tested. In case of dye derivative (**1**), the photocatalytic activity of Degussa P25 has been found to increase with the increase in catalyst concentration from 0.5 to 4 g L^{-1} and levels off at higher catalyst
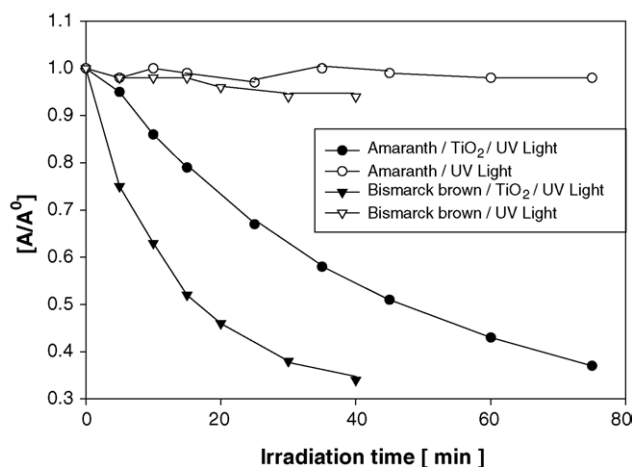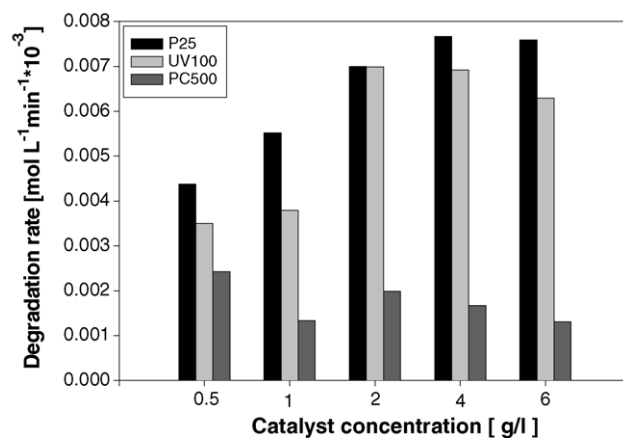
Fig. 3. Change in absorbance as a function of irradiation time for air saturated aqueous suspension of TiO$_2$ (1 g L^{-1}) containing amaranth (**1**, 0.4 mM) and bismarck brown (**2**, 0.5 mM). Light source: 'Phillips' 125 W medium pressure mercury lamp. Irradiation time: 75 min (**1**) and 40 min (**2**).

Fig. 4. Comparison of degradation rate for the decomposition of amaranth (**1**) in the presence of different types of photocatalyst at different catalyst concentrations. Experimental conditions: $V = 150$ mL, Degussa P25, Sachtleben Hombikat UV 100, PC 500 (0.5, 1, 2, 4 and 6 g L^{-1}), immersion photochemical reactor, 125 W medium pressure Hg lamp, continuous air purging and stirring, irradiation time = 75 min.
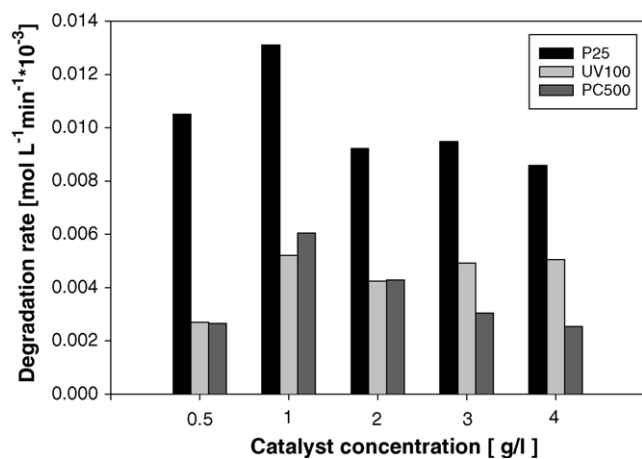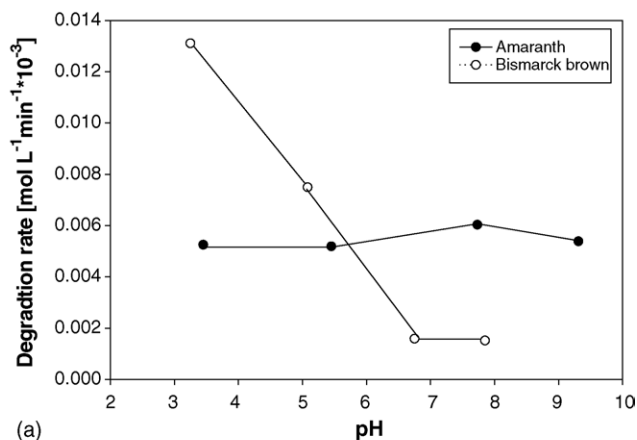
Fig. 5. Comparison of degradation rate for the decomposition of bismarck brown (**2**) in the presence of different types of photocatalyst at different catalyst concentrations. Experimental conditions: $V = 150$ mL, Degussa P25, Sachtleben Hombikat UV 100, PC 500 (0.5, 1, 2, 3 and 4 g L^{-1}), irradiation time = 40 min.

concentration. On the other hand it is interesting to note that the activity of Hombikat UV100 increase with the increase in catalyst concentration from 0.5 to 2 g L^{-1} and slight increase efficiency was observed at higher concentrations. In the case of dye derivative (**2**), the degradation for the decomposition of dye has been found to increase with increase in catalyst concentration of Degussa P25 from 0.5 to 1 g L^{-1}, decrease and more or less same efficiency was observed at catalyst concentration from 2 to 4 g L^{-1}. A similar trend was observed when the photocatalyst Hombikat UV100 and PC500 were used for the degradation of the dye derivatives. The reason for better photocatalytic activity of Degussa P25 could be attributed to the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating the electron hole pairs. The electron transfer, from the rutile c_B (conduction band) to electron traps in anatase phase, takes place. Recombination thus inhibited, allowing the hole to move to the surface of particle and react [17].

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, in some cases 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 traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration [(TiO$_2$)$_{OPT}$] has to be found, in order to avoid excess catalyst and ensure total absorption of efficient photons.
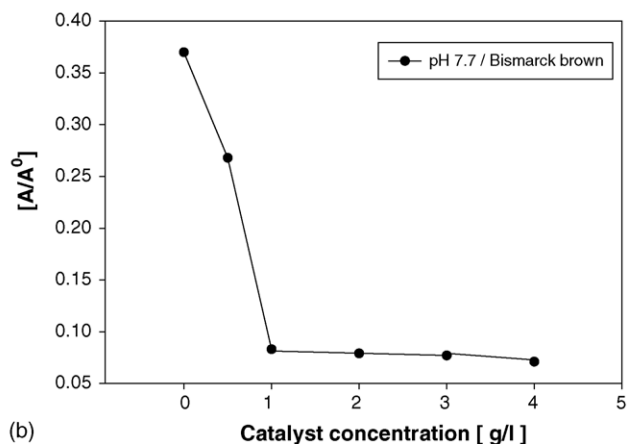
Fig. 6. (a) Comparision of degradation rate of amaranth (**1**) and bismarck brown (**2**) as a function of pH. Experimental conditions: $V = 150$ mL, Degussa P25, pH of dye (**1**) (3.45, 5.45, 7.73 and 9.31) and of dye (**2**) (3.25, 5.08, 6.75 and 7.85), irradiation time dye (**1**) = 75 min and dye (**2**) = 40 min. (b) Change in concentration as a function of different concentration of TiO$_2$ (0.5, 1, 2, 3 and 4 g L^{-1}) at pH 7.7 for bismarck brown (**2**), stirring for 24 h in dark, showing adsorption of the dye on the surface of the photocatalyst.

3.3. pH effect

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 formed. Therefore, the degradation of both dye derivatives was studied at different pH range from 3 to 10. The degradation rate for the decomposition of dye derivatives (**1**) and (**2**) as a function of reaction pH is shown in Fig. 6(a). The degradation rate for the dye derivative (**1**) has been found to be more or less same in the pH range studied within the experimental limits. However, in case of (**2**) the rate decreases with the increase in reaction pH and highest efficiency was observed at pH 3.25.

The adsorption of the dye derivatives (**1**) and (**2**) on the surface of photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h at different pH such as 3.45, 5.45, 7.73, 9.31 for dye (**1**) and at 3.25, 5.08, 6.75, 7.85 for dye (**2**). Analysis of the samples after centrifugation indicates

Table 2
Absorbance intensity observed at different pH for dye derivative bismarck brown (**2**) by stirring the aqueous solution in the dark for 24 h

Dye derivative	pH	Absorbance (Abs.)
Bismarck brown (**2**)	3.25	1.696
	5.14	0.595
	6.64	0.125
	7.67	0.111

no observable loss of the dye derivative (**1**), at any pH. However, in case of dye derivative (**2**), some considerable loss of the compound is observed at different pH studied as shown in Table 2. Interestingly, it has been observed that the dye derivative (**2**) strongly adsorbs on the surface of the photocatalyst at pH 7.7 as shown by the change in absorption intensity as a function of catalyst concentration in Fig. 6(b). The lowest degradation efficiency was observed at the pH where maximum adsorption takes place (Fig. 6(a)), this may be due to the fact that the absorption intensity decreases from 1.6 to 0.1 (463 nm, at the start of irradiation) and a new absorption maxima appears at 367 nm. The additional absorption maxima at this wavelength indicates that the molecule undergoes structural changes at this pH. Another reason for lower degradation efficiency at high pH value could also be attributed on the basis of the fact that the excitation of TiO_2 gets minimized due to high adsorption of the dye at the surface of TiO_2.

The interpretation of pH effect on the photocatalytic process is very difficult because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions respectively, as shown in following equations,

$$TiOH + H^+ \rightarrow TiOH_2^+$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O.$$
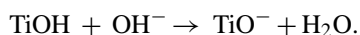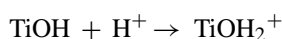
The point of zero charge (pzc) of the TiO_2 (Degussa P25) is widely reported at pH ~ 6 [18]. Thus, the TiO_2 surface will remain positively charged in acidic medium (pH < 6.25) and negatively charged in alkaline medium (pH > 6.25). The better efficiency for the degradation of compounds at lower pH may be due to the fact that the lone pairs of electrons present on the nitrogen atoms of amino groups can be protonated and deprotonated under acidic and basic conditions. Apparently the photocatalytic oxidation seems to be favored in the structural orientation of the molecule, when it is protonated under lower pH values. In a recent study by Guillard et al. [19] and Aguedach et al. [20], it has been shown that the azo dye derivatives such as reactive black 5, reactive yellow 145 and orange G undergo slow degradation at high pH values. The author proposed that the formation of $OH^\bullet$ by reaction between OH^- and H^+, at basic pH, was not at the origin of the increase of the photocatalytic efficiency of the other dyes.
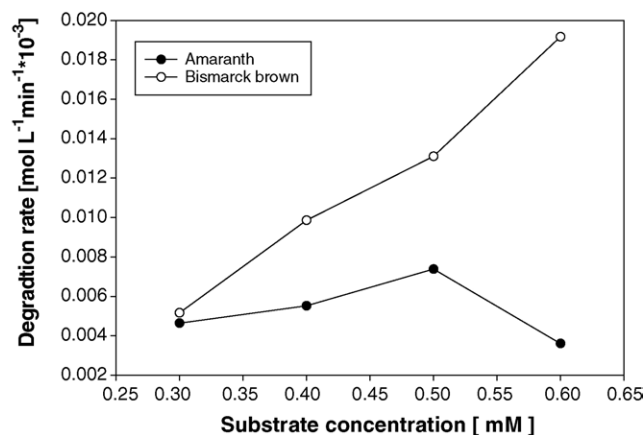

Fig. 7. Comparison of degradation rate of amaranth (**1**) and bismarck brown (**2**) as a function of substrate concentration. Experimental conditions: $V = 150$ mL, Degussa P25, substrate concentration of dye (**1**) and (**2**) (0.3, 0.4, 0.5 and 0.6 mM), irradiation time dye (**1**) = 75 min and dye (**2**) = 40 min.

3.4. Effect of substrate concentration

It is important both from mechanistic and application points of view to study the dependence of on the substrate concentrations photocatalytic reaction rate. Hence, the influence of substrate concentration of both the dye derivatives (**1**) and (**2**) was studied in the range varying from 0.3 to 0.6 mM. The degradation rate for the decomposition of the dye derivatives (**1**) and (**2**) as a function of substrate concentration is shown in Fig. 7. It is interesting to note that the rate for the decomposition of dye derivative (**1**) increases with the increase in substrate concentration from 0.3 to 0.5 mM and a further increase in substrate concentration lead to the decrease in the degradation rate. In contrast, in case of dye derivative (**2**) the rate was found to increase with increase in substrate concentration from 0.3 to 0.6 mM. The decrease in the degradation rate of dye derivative (**1**) at high concentration is may be due to the fact that as the initial concentrations of the dye increases, the color of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generations of relative amount of $OH^\bullet$ and $O_2^{\bullet-}$ on the surface of the catalyst do not increase as the intensity of light, illumination time and concentration of the catalyst are constant. Conversely, their concentrations will decrease with 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, for a given mass of TiO_2, the degradation efficiency of the dye decreases as the dye concentration increases.

3.5. Effect of electron acceptors

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
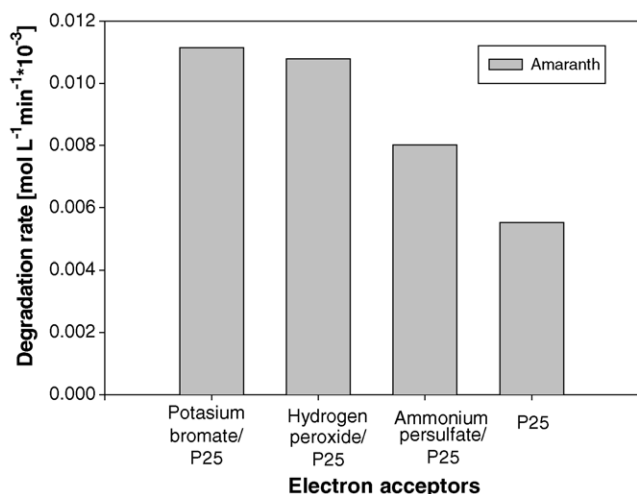
Fig. 8. Comparison of degradation rate in the presence of different electron acceptors for the photocatalytic degradation of amaranth (**1**). Experimental conditions: $V = 150$ mL, Degussa P25, potassium bromate, ammonium persulfate and hydrogen peroxide, irradiation time dye (**1**) = 75 min.

efficient and thus represent the major energy-wasting step thereby 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 additives to enhance the degradation rate may often be justified. In this connection, we have studied the effect of electron acceptors such as hydrogen peroxide, bromate and persulphate ions on the
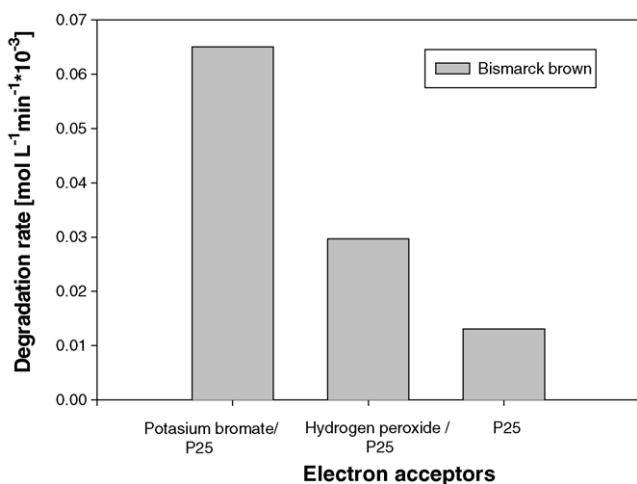

Fig. 9. Comparison of degradation rate in the presence of different electron acceptors for the photocatalytic degradation of bismarck brown (**2**). Experimental conditions: $V = 150$ mL, Degussa P25, potassium bromate and hydrogen peroxide, irradiation time dye (**2**) = 40 min.
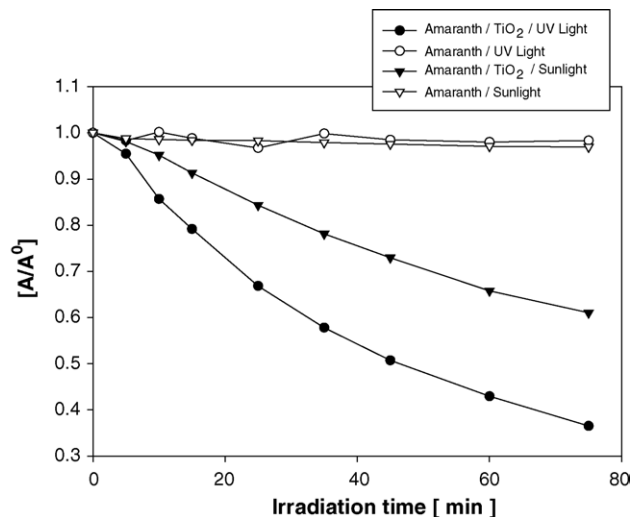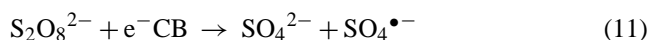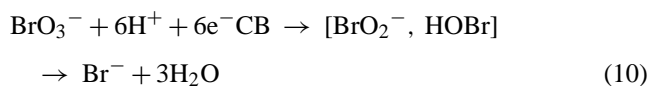

Fig. 10. Comparison of change in concentration as a function of irradiation time for the dye derivative (**1**) under sunlight and UV light source in the presence and absence of TiO$_2$. Irradiation time: 75 min.

photocatalytic degradation of the model compounds under investigation. These acceptors are known to generate reactive species according to the following Eqs. (8)–(12);

$$H_2O_2 + e^-CB \rightarrow OH^\bullet + OH^- \tag{8}$$

$$BrO_3^- + 2H^+ + e^-CB \rightarrow BrO_2^\bullet + H_2O \tag{9}$$

$$BrO_3^- + 6H^+ + 6e^-CB \rightarrow [BrO_2^-, HOBr]$$
$$\rightarrow Br^- + 3H_2O \tag{10}$$

$$S_2O_8^{2-} + e^-CB \rightarrow SO_4^{2-} + SO_4^{\bullet-} \tag{11}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^\bullet + H^+ \tag{12}$$

The respective one-electron reduction potentials of different species are: E (O$_2$/O$_2^{\bullet-}$) = -155 mV, E (H$_2$O$_2$/HO$^\bullet$) =
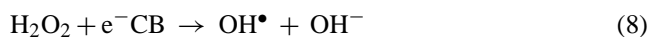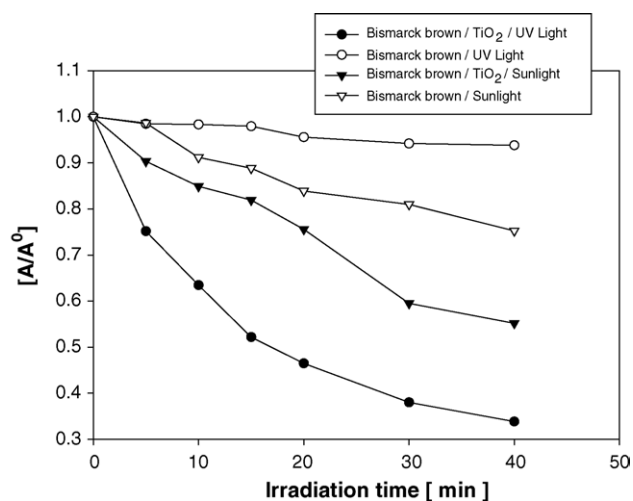

Fig. 11. Comparison of change in concentration as a function of irradiation time for the dye derivative (**2**) under sunlight and UV light source in the presence and absence of TiO$_2$. Irradiation time: 40 min.

800 mV, E (BrO$_3^-$/BrO$_2^\bullet$) = 1150 mV, and E (S$_2$O$_8^{2-}$/ SO$_4^{-\bullet}$) = 1100 mV [21]. From thermodynamic point of view all employed electron acceptors should therefore be more efficient than air. Figs. 8 and 9 show the degradation rate for the decomposition of amaranth (**1**) and bismarck brown (**2**) in the presence of different electron acceptors, TiO$_2$ and air. In case of dye derivative (**1**) all the additives were found to enhance the degradation rates. However, in case of dye (**2**) all the additives such as potassium bromate and hydrogen peroxide showed beneficial effect on the degradation rate. In contrast, in the presence of ammonium per sulphate the dye (**2**) was found to coagulate on the surface of the semiconductor, which lead to decrease in absorption intensity. The presence of oxidants reduces the time interval from 40 to 20 min for complete decolourization of dye derivative (**2**). There was no observable loss of the compound when irradiations were carried out using KBrO$_3$ in the absence of TiO$_2$ particle.

3.6. Photocatalysis of TiO$_2$ suspensions containing dye derivatives amaranth (**1**) and bismarck brown (**2**) under sunlight

Wastewater treatments based on these processes, using sunlight is preferred from the application point of view. Hence, the aqueous suspensions of TiO$_2$ containing dye derivatives (**1**) and (**2**) were exposed to solar radiation. Figs. 10 and 11 show the change in concentration as a function of irradiation time on illumination of an aqueous suspension of dye derivatives (**1**) and (**2**) in the presence and absence of TiO$_2$ (Degussa P25, 1 g L^{-1}) under sunlight and UV light source. It was found that the degradation of the model compounds proceeds much more rapidly in the presence of UV light source as compared to sunlight. Blank experiments were carried out under sunlight in the absence of TiO$_2$ where some observable loss of both the dye derivatives was observed.

4. Conclusion

TiO$_2$ can efficiently catalyze the decomposition of dye derivatives (**1**) and (**2**) in the presence of UV-light and air. Dye derivative (**2**) was found to degrade more efficiently as compared to the dye (**1**). Degussa P25 showed superior photocatalytic activity as compared with other TiO$_2$ types. In case of dye derivative (**1**), reaction pH shows a little effect on degradation rate, highest efficiency was observed at pH 7.73. Whereas, in the case of dye derivative (**2**) degradation rate decreases with increase in reaction pH and highest efficiency was observed at pH 3.25. The most appropriate concentration for the maximum degradation rate was 0.5 mM and a further increase in substrate concentration decreases the degradation rate of amaranth (**1**). However, dye derivative (**2**) have a better degradation rate from lower substrate concentration to higher substrate concentration. In case of both dye derivatives (**1**)

and (**2**) presence of electron acceptors enhances the degradation rates. The adsorption study of dye derivatives amaranth (**1**) and bismarck brown (**2**) on the surface of the photocatalyst indicate some observable loss of compound in case of bismarck brown (**2**), whereas, amaranth (**1**) shows negligible adsorption on the photocatalyst surface. It can be observed that the adsorption of dye derivative (**2**) on the surface of photocatalyst is better and hence degrades more efficiently as compared to dye derivative (**1**).

References

[1] M.A. Brown, S.C. De Vito, Predicting azo dye toxicity, Crit. Rev. Environ. Sci. Technol. 23 (1993) 249.

[2] M. Perez-Urquiza, J.L. Beltran, Determination of dyes in foodstuffs by capillary zone electrophoresis, J. Chromatogr. A 898 (2000) 271.

[3] M. Capon, V. Courilleau, C. Valette, E.N.S. Cachan, Chimie des Couleurs et Des Odeurs, Cultures et Techniques, Nantes, France, 1993.

[4] M.W. Girolami, R.W. Rousseau, Effects of Bismarck brown R on the growth rates of large and small potassium alum crystals, J. Cryst. Growth 71 (Issue 1, Jan–Feb) (1985) 220.

[5] J.M. Vazquez, E. Martinez, J. Roca, P. Coy, S. Ruiz, Use of triple stain technique for simultaneous assessment of vitality and acrosomal status in boar spermatozoa, Theriogenology 38 (Issue 5) (1992) 843.

[6] R.M. Dowd, M.P. Anderson, M.L. Johnson, Proceedings of the Second National Outdoor Action Conference on Aquifier 1365–1379.

[7] I. Safarik, K. Nymburska, M. Safarikova, Adsorption of water-soluble organic dyes on magnetic charcoal, J. Chem. Tech. Biotechnol. 69 (1997) 1.

[8] J.J. Roxon, A.J. Ryan, S.E. Wright, Reduction of water-soluble azo dyes by intestinal bacteria, Food Cosmet Toxicol. 5 (1967) 367.

[9] Y.M. Slokar, A.M. Le Marechal, Methods of decoloration of textile wastewaters, Dyes Pigments 37 (1998) 335.

[10] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air, National Renewal Energy Laboratory, USA, 2001.

[11] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic contaminants: Mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178.

[12] R.W. Mathews, S.R. McEvoy, Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide, J. Photochem. Photobiol. A: Chem. 64 (1992) 231.

[13] M. Karkmaz, E. Puzenat, C. Guillard, J.M. Hermann, Photocatalytic degradation of the alimentary azo dye amaranth Mineralization of the azo group to nitrogen, Appl. Catal. B: Environ. 51 (2004) 183.

[14] R.I. Bickley, T.G. Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, A Spectral investigation of titanium dioxide photocatalysts, J. Solid State Chem. 92 (1992) 178.

[15] M. Lindner, D.W. Bahnemann, B. Hirthe, W.D. Griebler, Solar water detoxification: Novel TiO$_2$ powders as highly active photocatalysts, J. Sol. Energy Eng. 119 (1997) 120.

[16] S. Rauer, Untersunchung von kommerziell erhaltlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivtat, Diplomarbeit,

fachhochschule Hannover, Fachbereich Maschinenbau Vertiefung Umwelt-und Verfahrenstechnil, Hannover, Germany, 1998.

[17] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO$_2$ using EPR, J. Phys. Chem. B. 107 (2003) 4545.

[18] J. Augustynski, Structural Bonding, Springer, Berlin, New York, 1988, p. 69, chapter 1.

[19] C. Guillard, H. Lanchheb, A. Houas, M. Ksibi, E. Elaloui, J.M. Herrmann, Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO$_2$ comparison of the efficiency of powder and supported TiO$_2$, J. Photochem. Photobiol. A: Chem. 158 (2003) 27.

[20] A. Aguedach, S. Brosillon, J. Morvan, E.K. Lhadi, Photocatalytic degradation of azo dyes reactive black 5 and reactive yellow 145 in water over a newly deposited titanium dioxide, App. Catal. B: Environ. 57 (2005) 55.

[21] P. Wardman, Reduction potential of one-electron couples involving free radicals in aqueous solution, J. Phys. Chem. Ref. Data 18 (1989) 1637.