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Heterogeneous photocatalytic degradation of an anthraquinone and a triphenylmethane dye derivative in aqueous suspensions of semiconductor

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Abstract

The photochemical reactions of two selected dye derivatives, such as acid blue 45 (**1**) and xylenol orange (**2**) have been investigated in aqueous suspensions of titanium dioxide (TiO_2) under a variety of conditions. The reactions were studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time. The dye derivatives under investigation were found to degrade during irradiation in the presence of TiO_2 and oxygen. The degradation of the dye derivatives was studied under different conditions such as different types of TiO_2, reaction pH, catalyst concentration, substrate concentration, and in the presence of electron acceptors like hydrogen peroxide and potassium bromate, besides oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The degradation of dyes was also investigated under sunlight and the efficiency of degradation was compared with that of the artificial light source. The photocatalyst Hombikat UV100 was found to be more efficient for the degradation of acid blue 45 (**1**). However, Degussa P25 showed better photocatalytic activity in case of xylenol orange (**2**).

Keywords: Photocatalysis; Textile dye; Acid blue 45; Xylenol orange; Titanium dioxide; Semiconductor

1. Introduction

Environment is the representative of physical components of the earth wherein man is the important factor influencing this environment. Among the different physical components water is the most essential component of life. Total amount of water existing in the earth in the form of ground water, surface water, etc. is 1.4×10^9 km^3 approximately [1]. Mankind is constantly using this amount of water for different purposes including commercial and domestic uses. Due to natural calamities or by some anthropogenic activities like inordinate population growth, fast industrialization, rapid urbanization and modified agricultural operations, environmental pollution occurs, which has adverse effects on all forms of life. As water is one of the fundamental requirements of life, addition of any natural or artificial foreign matter from various sources such as industrial effluents, agricultural runoff and chemical spills contaminates the water [2]. These effluents include several non-biodegradable, toxic organic substances like pesticides, herbicides, dyes, etc. These substances are highly toxic, stable to natural decomposition and are persistent to the environment. Of all these organic substances, dyes pose a great threat to the environment [3]. Recent studies indicate that during manufacturing and processing operations substantial amount of dyestuff is lost and resultant color enters the environment through effluents from industrial wastewater treatment plants [4]. Decomposition of dye effluents has therefore acquired increasing attention.

Earlier studies [5] have shown that a wide range of organic substrates can be completely photomineralized in the presence

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of TiO_2 and oxygen. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in literature [6,7]. Briefly, when a semiconductor such 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)−(3):

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \tag{1}$$

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

$$H_2O + h^+_{vb} \rightarrow OH^{\bullet} + H^+ \tag{3}$$

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 equations:

$$Dye_{ads} + h\nu \rightarrow dye_{ads}* \tag{4}$$

$$Dye_{ads}* + TiO_2 \rightarrow dye^{+\bullet}_{ads} + TiO_2(e^-) \tag{5}$$

It has been shown earlier that the heterogeneous photocatalytic oxidation processes can be used for removing coloring material from dye effluent in the presence of light [5,8−10] and the photocatalytic degradation of an anthraquinone dye [11−15] and a triphenylmethane dye has been reported [16−19].

The dye derivatives, acid blue 45 (**1**) and xylenol orange (**2**) have been extensively used in textile industry, leather dyeing, paper printing, photography and as a biological stain. Photocatalytic degradation of xylenol orange (**2**) has been reported recently in the presence of TiO_2[13,14]. However, no major effort has been made to study detailed degradation kinetics of dye derivatives **1** and **2** that is essential from application point of view. With this view, we have studied the degradation of two selected dye derivatives such as acid blue 45 (**1**) and xylenol orange (**2**) as shown in Chart 1, in aqueous suspensions of TiO_2 under a variety of conditions.

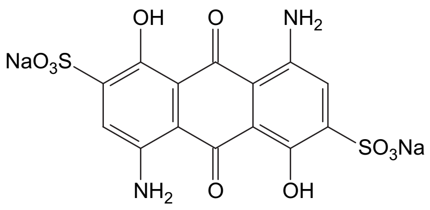
2. Experimental methods

2.1. Reagent and chemicals

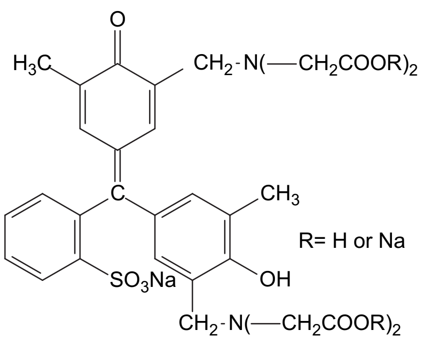
The dye derivatives, acid blue 45 (**1**, 50%) was obtained from Sigma−Aldrich, India, whereas xylenol orange (**2**, 90%) was obtained from Central Drug House (P) Ltd. New Delhi, India. These compounds were used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, Degussa P25 (Degussa AG) was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben Chemie GmbH) and PC500 (Millennium inorganic chemicals) were used for comparative study. Degussa P25 consists of 75% anatase and 25% rutile with a specific BET-surface area of 50 $m^2\,g^{-1}$ and primary particle size of 20 nm [20]. Hombikat UV100 consists of 100% anatase with a specific BET-surface area of >250 $m^2\,g^{-1}$ and primary particle size of 5 nm [21]. The photocatalyst PC500 has a BET-surface area of 287 $m^2\,g^{-1}$ with 100% anatase and primary particle size of 5−10 nm [22]. The other chemicals used in this study such as NaOH, HNO_3, H_2O_2 and $KBrO_3$ were obtained from Merck.

2.2. Procedure

Stock solutions of the dye derivative containing desired concentration were prepared in double distilled water. An immersion well 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 mL aqueous solution of the dye of desired concentration was taken in the photoreactor and required amount of photocatalyst was added and the solution was



acid blue 45 (1)



xylenol orange (2)

Chart 1.

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 bubbling throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips), the power of lamp in radiant flux was 9375 mW cm^{-2}. Samples (6 mL) were collected before and at regular intervals during irradiation. They were centrifuged before analysis.

The sunlight experiments were carried out in order to compare the degradation efficiency of the compound under investigation with that of artificial light. Reactions were carried out in the same photochemical reaction vessel where irradiation was carried out with the artificial light source. Aqueous solution (150 mL) of desired concentration of the model compound containing required amount of photocatalyst was taken and stirred for 10 min in the dark and the solution was then placed on flat platform under sunlight with continuous stirring and purging of air. Samples (6 mL) were collected before and at regular intervals during illumination and analyzed after centrifugation.

2.3. Analysis

The photocatalytic degradation of the dye derivatives was monitored using UV spectroscopic analysis technique (Shimadzu UV−vis 1601). The double beam spectrophotometer has an in-built tungsten and deuterium lamps, which provide the measurement of optical density (OD) in the range 200−1100 nm (near-UV and visible regions). The samples were analyzed using quartz cuvette, as it has zero absorption in the above wavelength regions.

The concentrations of dye derivatives were calculated by standard calibration curve obtained from the absorbance of the dye derivatives at different concentrations. The change in absorbance of the dye derivatives **1** and **2** was followed at their λ_{max} as a function of irradiation time.

3. Results and discussion

3.1. Photocatalysis of aqueous suspensions of dye derivatives (*1* and *2*) in the presence of TiO_2

Irradiation of an aqueous suspension of the dye derivatives **1** and **2** in the presence of TiO_2 with a Pyrex filtered output of a 125 W medium pressure mercury lamp with constant bubbling of air leads to change in absorption intensity as a function of irradiation time. This absorption intensity is used to calculate the concentration using the standard calibration curve which in turn is used to calculate the rate constant.

Fig. 1 shows the change in concentration as a function of time on irradiation of an aqueous suspension of dye derivatives, **1** and **2** in the presence and absence of the photocatalyst. It could be seen from the figure that 51% and 73% degradation of the compound takes place in the presence of photocatalyst whereas in the absence of photocatalyst no observable loss of the dye could be seen.

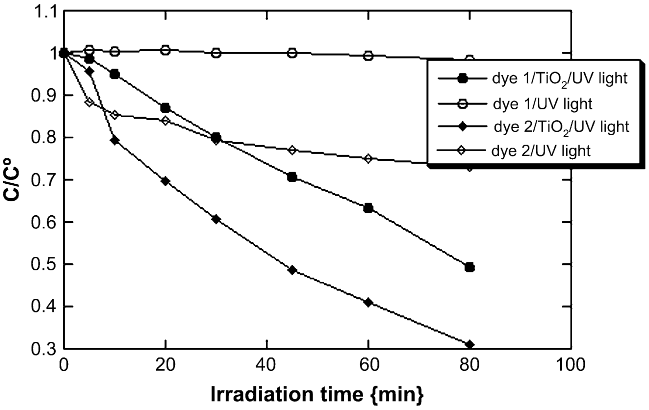


Fig. 1. Comparison of change in concentration as a function of irradiation time for an aqueous suspension of acid blue 45 (**1**) and xylenol orange (**2**) in the presence and absence of photocatalyst under UV light source. Experimental conditions: (a) dye concentration: (0.4 mM for **1**) and (0.3 mM for **2**), photocatalyst: TiO_2 (Hombikat UV100, 1 g L^{-1} for **1**), (Degussa P25, 1 g L^{-1} for **2**), $V = 150$ mL, immersion well photoreactor, 125 W medium pressure Hg lamp, continuous air purging and stirring, irradiation time = 80 min.

The curve for the change in substrate concentration as a function of irradiation time for the degradation of the dye derivatives **1** and **2** as shown in Fig. 1 can be fitted reasonably well by exponential decay curve suggesting the first order kinetics. In contrast, the curve showing the change in concentration vs. irradiation time for the photocatalytic degradation of the dye derivative can reasonably be fitted by the exponential decay curve suggesting the zero order kinetics. For the sake of the uniformity we have considered this curve also as a first order kinetics. For each experiment, the degradation rate constant of the dye derivatives was calculated from the plot of the natural logarithm of the concentration of the dye derivatives as a function of irradiation time. The degradation rate for the decomposition of the dye derivatives was calculated using formula given below:

$$-\mathrm{d}[C]/\mathrm{d}t = kc^n \qquad (6)$$

where C = concentration of the pollutant, k = rate constant, and n = order of reaction.

The degradation rate for the decomposition of the dye derivatives for the first order reaction was calculated in terms of mol L^{-1} min^{-1}.

Control experiments were carried by irradiating aqueous solution of the dye in the absence of photocatalyst, where no observable loss of the dye derivatives was observed. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.2. Comparison of different photocatalysts and catalyst concentration

We have tested the photocatalytic activity of three different commercially available TiO_2 powders (namely Degussa P25, Hombikat UV100, and Millennium Inorganic PC500) employing various catalyst concentrations on the degradation kinetics of the dye derivatives under investigation. The degradation rate obtained for the decomposition of dye derivatives **1** and **2**, in the presence of different types of TiO_2 powders is shown in Figs. 2 and 3, respectively. It has been observed that the degradation of dye derivative **2** under investigation proceeds much more rapidly in the presence of Degussa P25. However, in case of dye derivative **1**, Hombikat UV100 shows better photocatalytic activity as compared to other TiO_2 samples. As expected, the degradation rate was found to increase with the increase in catalyst concentration, which is the characteristic of heterogeneous photocatalysis.

Earlier study [23] has shown that Degussa P25 owes its high photoreactivity due to slow recombination between electron and holes whereas Sachtleben Hombikat UV100 has a high photoreactivity due to fast interfacial electron transfer rate. Since the photocatalyst Degussa P25 was found to be more efficient photocatalyst for degradation of dye derivative **2**, it indicates that the rate-limiting step is the lifetime of electron–hole pairs, whereas in case of dye derivative **1**, it could be proceeded via interfacial electron transfer.

Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds [24–26]. On the other hand Lindner et al. [27] showed that Hombikat UV100 was almost four times more effective than Degussa P25 when dichloroacetic acid was used as the model pollutant. Also Hombikat UV100 was found to be better for the degradation of benzidine, 1,2-diphenyl hydrazine [28] and remazol briliant blue R [15] as shown in a recent study. These results indicate that the activity of the photocatalyst also depends on the type of the model pollutant.

The reason for the 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 electron–hole pairs. The electron transfer, from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react [29]. The reason for better photocatalytic activity of Hombikat UV100 could be attributed to the fact that the specific BET-surface area and particle size are more as compared to other photocatalysts [30].

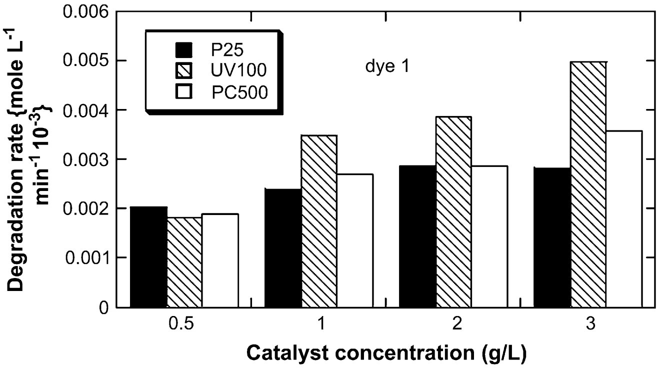


Fig. 2. Comparison of degradation rate for decomposition of acid blue 45 (**1**) in the presence of different types of photocatalyst at different catalyst concentrations. Experimental conditions: dye concentration: 0.4 mM, $V = 150$ mL, photocatalyst: TiO_2 (Degussa P25, Hombikat UV100 and PC500 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 80 min.

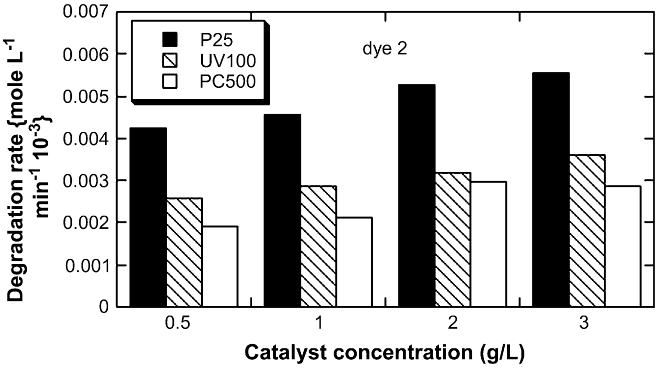


Fig. 3. Comparison of degradation rate for decomposition of xylenol orange (**2**) in the presence of different types of photocatalyst at different catalyst concentrations. Experimental conditions: dye concentration: 0.3 mM, $V = 150$ mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (0.5, 1, 2 and 3 g L^{-1}), irradiation time = 80 min.

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 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., 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 insure total absorption of efficient photons. Our results on the effect of catalyst concentration on the degradation rate for the decomposition of dye derivatives under investigation are in agreement with numerous studies reported in literature [24–26,31].

In all following experiments, Degussa P25 was used as the photocatalyst for the degradation of **2** and Hombikat UV100 for dye derivative **1**, since these materials exhibited the highest overall activity for the degradation of dyes under investigation.

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 it forms. Employing Hombikat UV100 as photocatalyst for the decomposition of **1** in aqueous suspensions of TiO_2 was studied in the pH range between 3.0 and 10.3. Fig. 4 shows the degradation rate for the

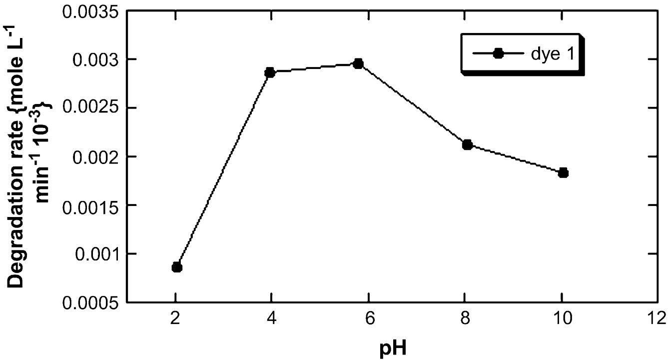


Fig. 4. Influence of pH on the degradation rate for the decomposition of acid blue 45 (**1**). Experimental conditions: 0.4 mM, $V = 150$ mL, photocatalyst TiO_2 (Hombikat UV100, 1 g L^{-1}), reaction pH (2.05, 3.98, 5.8, 8.05 and 10.05), irradiation time = 80 min.

decomposition of the dye derivative, **1** as a function of reaction pH. It has been observed that dye derivative, **2** undergoes color change at different pH values, which results in shift of λ_{max} at different pH range studied. Therefore the degradation of this dye could not be studied as a function of pH.

The adsorption of the dye derivative, **1** on the surface of photocatalyst was investigated by stirring the aqueous solution of dye in the dark for 24 h at different pH values. Analysis of the samples after centrifugation indicates some observable loss of compound **1** at different pH values (1, 1.98, 4.11, 6.28, 8.15 and 10.05).

The degradation rate for the dye derivative **1** was found to increase with increase in pH and highest efficiency was obtained at pH 5.8 and further increase in pH leads to decrease in degradation rate. In this study it has been shown that the degradation rate for the decomposition of the dye derivatives under investigation is highly influenced by the reaction pH.

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:

$$TiOH + H^+ \rightarrow TiOH_2^+ \quad (7)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \quad (8)$$

The point of zero charge (pzc) of TiO_2 (Degussa P25) is widely reported at pH ~ 6.25 [32]. Thus, the TiO_2 surface will remain positively charged in acidic medium ($pH < 6.25$) and negatively charged in alkaline medium ($pH > 6.25$).

A similar result has been reported earlier in the photocatalytic degradation of a number of dyes [12,33].

3.4. Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of initial substrate concentration on the degradation kinetics of the pollutant. Effect of substrate concentration on the degradation of the dye derivatives, **1** and **2** was studied at different concentrations varying from 0.3 to 0.6 mM. The degradation rate for the decomposition of dye derivatives, **1** and **2** as a function of substrate concentration is shown in Figs. 5 and 6, respectively.

It is interesting to note that the degradation rate for the decomposition of dye derivative **1** decreases with the increase in substrate concentration and highest efficiency was obtained at 0.3 mM. On the other hand, in the case of compound **2**, the rate has been found to increase with the increase in substrate concentration from 0.3 to 0.5 mM. A further increase in substrate concentration leads to decrease in the degradation rate.

The decrease in degradation rate with increase in substrate concentration 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 generation of relative amount of $OH^{\bullet}$ and $O_2^{-\bullet}$ on the surface of the catalyst do not increase as the intensity of light, irradiation time and catalyst concentration 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, 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 efficient and represents 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: (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. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified. With this view, we have studied the effect of electron acceptors such as potassium bromate and hydrogen peroxide in the presence of TiO_2 and air on the degradation of dyes under investigation.

The degradation rate for the decomposition of the dye derivatives, **1** and **2** in the presence of hydrogen peroxide and potassium bromate is shown in Fig. 7.

The additives, potassium bromate shows better degradation rate for the decomposition of dye derivative **2**. Whereas, in the case of **1**, the additive H_2O_2 showed a pronounced effect for the decomposition of the compound as illustrated in Fig. 7.

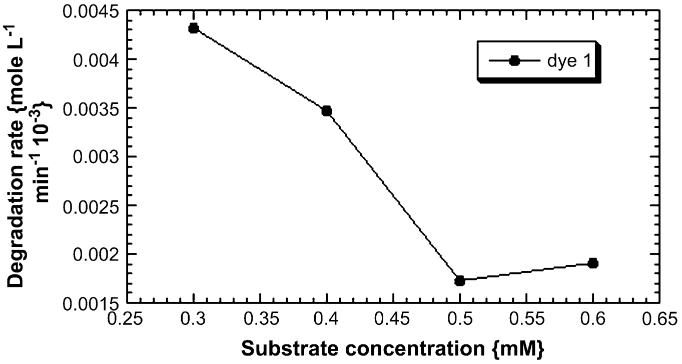


Fig. 5. Influence of substrate concentration on the degradation rate for the decomposition of acid blue 45 (**1**). Experimental conditions: substrate concentrations: (0.3, 0.4, 0.5 and 0.6 mM), $V = 150$ mL, photocatalyst: TiO_2 (Hombikat UV100, 1 g L^{-1}), irradiation time = 80 min.

The electron acceptors such as hydrogen peroxide and potassium bromate are known to generate hydroxyl radicals by the mechanisms shown in Eqs. (9)–(11):

$$H_2O_2 + e^-_{cb} \rightarrow OH^{\bullet} + OH^- \quad (9)$$

$$BrO_3^- + 2H^+ + e^-_{cb} \rightarrow BrO_2^{\bullet} + H_2O \quad (10)$$

$$BrO_3^- + 6H^+ + 6e^-_{cb} \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \quad (11)$$

The respective one-electron reduction potentials of different species are E ($O_2/O_2^{-\bullet}$) = −155 mV, E ($H_2O_2/OH^{\bullet}$) = 800 mV and E ($BrO_3^-/BrO_2^{\bullet}$) = 1150 mV [34], From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen.

The effective electron acceptor ability of $KBrO_3$ has been observed in number of studies before [25,26,35]. The reason can be attributed to the maximum number of electrons it reacts as shown in Eqs. (10) and (11). Another possible explanation might be a change in the reaction mechanism of the photocatalytic degradation. Since the reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing agents, e.g. $BrO_2^-$and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Linder has proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions considering direct oxidation of the substrate by bromate ions [36]. A similar mechanism might also be operative in the model compound **2** under investigation.

It is important to note that dye derivative **1** is an anthraquinone dye, which acts as electron acceptor rather than electron donor, and in this case H_2O_2 has been found to be more efficient additive. The effect of H_2O_2 has been investigated in numerous studies and it was observed that it increases the photodegradation rates of organic pollutants [37,38]. The enhancement of the degradation rate of dye derivative **1** on addition of H_2O_2 can be rationalized in terms of several reasons. Firstly, it increase 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 ($OH^- + h^+ \rightarrow OH^{\bullet}$). Secondly, H_2O_2 may split photolytically to produce $OH^{\bullet}$ radicals directly, as cited in studies of homogeneous photo-oxidation using UV/ ($H_2O_2 + O_2$) [39]. Thirdly, the solution phase may at times

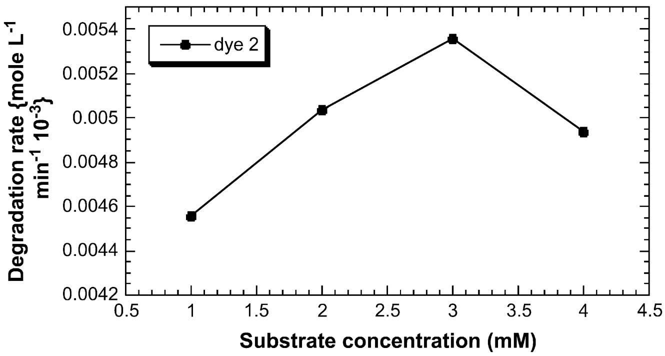


Fig. 6. Influence of substrate concentration on the degradation rate for decomposition of xylenol orange (**2**). Experimental conditions: substrate concentrations: (0.3, 0.4, 0.5, and 0.6 mM), $V = 150$ mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), irradiation time = 80 min.

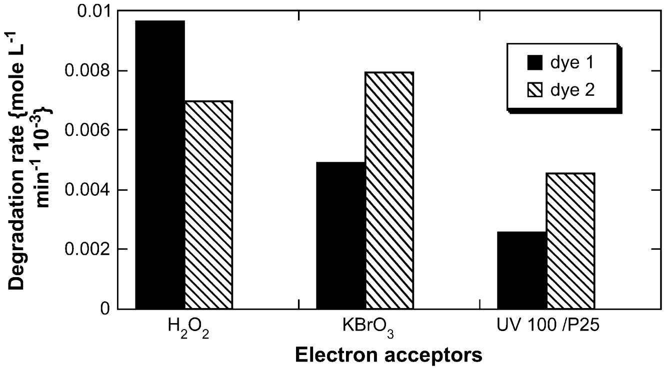


Fig. 7. Comparison of degradation rate for the decomposition of acid blue 45 (**1**) and xylenol orange (**2**) in the presence of hydrogen peroxide and potassium bromate. Experimental conditions: dye concentration: (0.4 mM for **1**) and (0.3 mM for **2**) photocatalyst: TiO_2 (Hombikat UV100, 1 g L^{-1} for **1**, Degussa P25 for **2**) $V = 150$ mL, electron acceptors: $KBrO_3$ (5 mM), H_2O_2 (10 mM), irradiation time = 80 min.

be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer, and peroxide addition thereby increase the rate towards what it would have been had an adequate oxygen supply been provided.

3.6. Photocatalysis of TiO_2 suspension containing dye derivatives under sunlight

For practical applications of wastewater treatment based on these processes, the utilization of sunlight is preferred. Hence the aqueous suspension of TiO_2 containing dye derivatives was exposed to solar radiation. Fig. 8 shows the comparison of change in concentration as a function of irradiation time on illumination of an aqueous suspension of dye derivatives in the absence and presence of TiO_2 under sunlight and UV light source. It was found that the degradation of the model compound **1** proceeds much more rapidly, whereas in the case of **2** the degradation efficiency in the two light sources were found to be more or less same within the experimental limit in the presence of UV light source as compared to sunlight source. Blank experiments were carried out under sunlight in the absence of TiO_2 where no observable loss of the dye derivative takes place as shown in the figure.

4. Conclusion

TiO_2 can efficiently catalyze the photomineralization of dye derivatives **1** and **2** in the presence of light. Dye **1** was found to degrade more efficiently as compared to dye **2**. The photocatalyst Hombikat UV100 showed better photocatalytic activity for the degradation of dye derivative **1**, whereas in the case of dye derivative **2**, Degussa P25 was found to exhibit better photocatalytic activity under investigation. The degradation of dye derivatives were also investigated under sunlight and the efficiency of degradation was compared with that of the artificial light source. The addition of electron acceptors such as potassium bromate and hydrogen peroxide can enhance the decomposition of model system. 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 investigations were conducted at the laboratory scale in order to determine the optimum degradation condition and further studies are required for the practical effluent treatment.

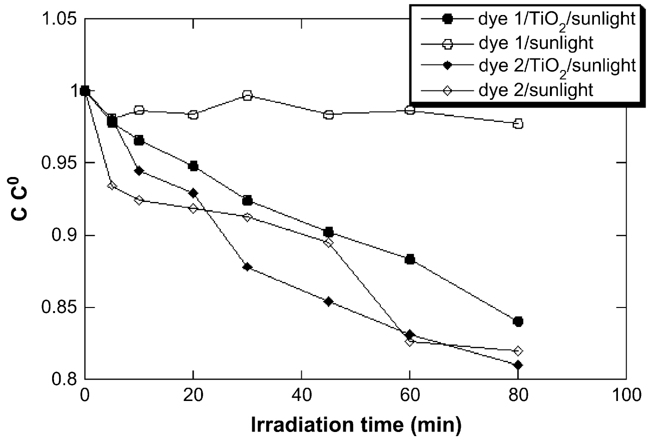


Fig. 8. Comparison of change in concentration as a function of irradiation time for an aqueous suspension of acid blue 45 (**1**) and xylenol orange (**2**) in the presence and absence of photocatalyst under sunlight. Experimental conditions: (a) dye concentration: (0.4 mM for **1**) and (0.3 mM for **2**), photocatalyst: TiO_2 (Hombikat UV100, $1\ g\,L^{-1}$ for **1**), (Degussa P25, $1\ g\,L^{-1}$ for **2**), $V = 150$ mL, immersion well photoreactor, 125 W medium pressure Hg lamp, continuous air purging and stirring, irradiation time = 80 min.

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References

[1] World Resources Institute N.Y.O., 1994–1995; 1994.
[2] Ligrini O, Oliveros E, Braun A. Photochemical processes for water treatment. Chem Rev 1993;93:671–98.
[3] Brown MA, Vito SC. Crit Rev Environ Sci Technol 1993;23:249–324.
[4] Helmes CT, Sigman CC, Fund ZA, Thompson MK, Voeltz MK, Makie M, et al. A study of azo and nitro dyes for the selection of candidates for carcinogen bioassay. J Environ Sci Health A Chem 1984;19:97–231.
[5] Blake DM. Bibliography of work on the photocatalytic removal of hazardous compounds from water and air. USA: National Renewal Energy Laboratory; 2001. p. 40–253.
[6] Turchi CS, Ollis DF. Photocatalytic degradation of organic contaminants: mechanism involving hydroxyl radical attack. J Catal 1990;122:178–85.
[7] Mathews RW, McEvoy SR. Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide. J Photochem Photobiol A Chem 1992;64:231–46.
[8] Gonçalves M Sameiro T, Pinto Elisa MS, Nkeonye Peter, Oliveira-Campos Ana MF. Degradation of C.I. reactive orange 4 and its simulated dye bath wastewater by heterogeneous photocatalysis. Dyes Pigments 2005;64:135–9.
[9] Mozia S, Tomaszewska M, Morawski AW. Photocatalytic degradation of azo dye acid red 18. Desalination 2005;185:449–56.
[10] Liu Chin-Chuan, Hsieh Yung-Hsu, Lai Pao-Fan, Li Chia-Hsin, Kao Chao-Lang. Photodegradation treatment of azo dye wastewater by UV/TiO_2 process. Dyes Pigments 2006;68:191–5.
[11] Lakshmi S, Ranganathan R, Fujita S. J Photochem Photobiol A Chem 1995;88:163.
[12] Muneer M, Philip R, Das S. Potocatalytic degradation of wastewater pollutants. Titanium dioxide mediated oxidation of a textile dye, acid blue 40. Res Chem Intermed 1997;3:233–46.
[13] Saquib M, Muneer M. Photocatalytic degradation of the textile dye, alizarin red S, in aqueous suspension of titanium dioxide. Adv Color Sci Technol 2002;5:71–8.
[14] Saquib M, Muneer M. Photocatalytic degradation of CI acid green 25 and CI acid red 88, in aqueous suspensions of titanium dioxide. Color Technol 2002;118:307–15.
[15] Saquib M, Muneer M. Semiconductor mediated photocatalysed degradation of an anthraquinone dye, remazol brilliant blue R under sunlight and artificial light source. Dyes Pigments 2002;53:237–49.

[16] Gupta AK, Anjali Pal, Sahoo C. Photocatalytic degradation of a mixture of crystal violet (basic violet 3) and methyl red dye in aqueous suspension using Ag^+ doped TiO_2. Dyes Pigments 2006;69:224–32.

[17] Martins AO, Canalli VM, Azevedo CMN, Pires M. Degradation of pararosaniline (C.I. basic red 9 monohydrochloride) dye by ozonation and sonolysis. Dyes Pigments 2006;6:227–34.

[18] Sahoo C, Gupta AK, Anjali Pal. Photocatalytic degradation of crystal violet (C.I. basic violet 3) on silver ion doped TiO_2. Dyes Pigments 2005;66:189–96.

[19] Saquib M, Muneer M. TiO_2 – photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions. Dyes Pigments 2003;56:37–49.

[20] 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.

[21] Lindner M, Bahnemann D, Hirthe B, Griebler WD. Solar water detoxification: novel TiO_2 powders as highly active photocatalysts. J Sol Energy Eng 1997;119:120–5.

[22] Rauer S, Untersunchung von kommerziell erhaltlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivtat, Diplomarbeit, fachhochschule Hannover, Fachbereich Maschinenbau Vertiefung Umwelt-und Verfahrenstechnil, Hannover, Germany; 1998.

[23] Martin ST, Hermann H, Choi W, Hoffmann MR. Time resolved microwave conductivity: part I – TiO_2 photoreactivity and size quantization. J Chem Soc Faraday Trans 1994;90:3315–23.

[24] Muneer M, Theurich J, Bahnemann D. Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate. J Photochem Photobiol A Chem 2001;143:213–9.

[25] Muneer M, Bahnemann D. semiconductor mediated photocatalysed degradation of two selected pesticide terbacil and 2,4,5-tribromoimidazole. Water Sci Technol 2001;144:331–7.

[26] Muneer M, Theurich J, Bahnemann D. Formation of toxic intermediates upon the photocatalytic degradation of the pesticide diuron. Res Chem Intermed 1999;5:667–83.

[27] Lindner M, Bahnemann D, Hirthe B, Griebler WD. Novel TiO_2 powders as highly active photocatalysts. In: Stine WB, Tanaka T, Laridge DE, editors. solar water detoxification; solar engineering. New York: ASME; 1995. p. 339.

[28] Muneer M, Singh HK, Bahnemann D. Semiconductor-mediated photocatalysed degradation of two selected priority organic pollutants, benzidine and 1,2-diphenyl hydrazine, in aqueous suspension. Chemosphere 2002;9:193–203.

[29] Hurum DC, Agrios AG, Gray KA, Rajh T, Thurnauer MC. Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO_2 using EPR. J Phys Chem B 2003;07:4545–9.

[30] Saquib M, Muneer M. Photocatalytic degradation of two selected textile dye derivatives, eosin yellowish and *p*-rosaniline in aqueous suspensions of titanium dioxide. J Environ Sci Health Part A 2003;8:2581–98.

[31] Singh HK, Muneer M, Bahnemann D. Photocatalysed degradation of a herbicide derivative, bromacil, in aqueous suspensions of titanium dioxide. Photochem Photobiol Sci 2003;2:151–6.

[32] Augustynski J. In: Structure and bonding. Berlin, New York: Springer; 1988. p. 69.

[33] Guillard C, Lachheb H, Houas A, Ksibi M, Elaloui E, Herrmann JM. 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 2003;158:27–36.

[34] Wardman P. Reduction potential of one-electron couples involving free radicals in aqueous solution. J Phys Chem Ref Data 1989;8:1637–755.

[35] Nevim S, Arzu H, Gulin K, Cinar Z. Prediction of primary intermediates and the photodegradation kinetics of 3-aminophenol in aqueous TiO_2 suspensions. J Photochem Photobiol A Chem 2001;139:225–32.

[36] Linder M. Ph.D. thesis, Department of chemistry, University of Hannover, Hannover, Germany; 1997.

[37] Wei TY, Wan CC. Kinetics of photocatalytic oxidation of phenol on TiO_2 surface. J Photochem Photobiol A Chem 1992;69:241–9.

[38] Hallamn M. Photodegradation of di-*n*-butyl-*ortho*-phthalate in aqueous solution. J Photochem Photobiol A Chem 1992;66:215–23.

[39] Peyton GR, Glaze WH. Destruction of pollutants in water with ozone in connection with ultraviolet radiation. Environ Sci Technol 1988;22:761–7.