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Semiconductor mediated photocatalysed degradation of an anthraquinone dye, Remazol Brilliant Blue R under sunlight and artificial light source

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Abstract

Semiconductor mediated photocatalysed degradation of an anthraquinone dye Remazol Brilliant Blue R under sunlight and artificial light source has been investigated in aqueous suspensions of titanium dioxide by monitoring the change in absorption intensity as a function of irradiation time under a variety of conditions. The degradation kinetics were studied under different conditions such as pH, catalyst concentration, substrate concentration, different types of TiO_2 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 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 under UV light, whereas Hombikat UV100 was better under sunlight as compared with other photocatalysts. The degradation products were analysed by GC–MS technique and probable pathways for the formation of products are proposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Photocatalysis; Anthraquinone dye; Remazol Brilliant Blue R; Titanium dioxide

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1. Introduction

Colour removal from textile wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but often due to their visibility in receiving waters. Recent studies indicate that approximately 12% of synthetic dyes is lost during manufacturing and processing operations and that 20% of the resultant colour enter the environment through effluents from industrial wastewater treatment plants [1]. Colour in dye-house effluents has often been associated with the application of dyestuffs, during which up to 50% of the dyes may be lost to the effluent [2], which poses a major problem for the industry as well as a threat to the environment [3–7]. Decoulourization of dye effluents has therefore acquired increasing attention. Decoulourization of dye effluent by bisulfite-catalysed borohydride reduction has been reported earlier [8]. During the past two decades, photocatalytic process involving TiO_2 semiconductor particles under UV light illumination have been

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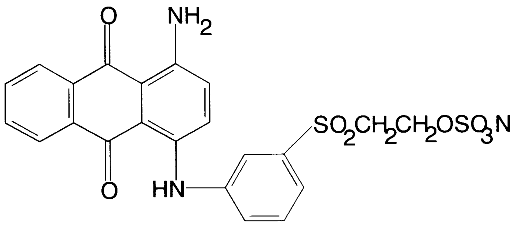
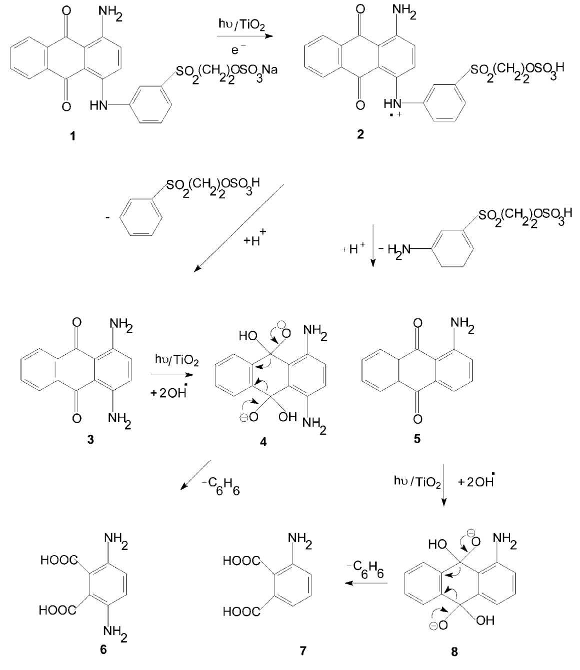
shown to be potentially advantageous and useful in the treatment of wastewater pollutants. Earlier studies [9–12] have shown that a wide range of organic substrates such as alkanes, alkenes, aromatics, surfactants and pesticides, can be completely photomineralized in the presence of TiO_2 and oxygen.

There are several studies related to the use of semiconductors in the photomineralization of photostable dyes [13–29]. Photoexcitation of semiconductor leads to the formation of electron hole pair, which can eventually bring about redox reaction from organic substrates, dissolve in water. Alternatively, direct absorption of light by the dye, adsorbed on the semiconductor surfaces can lead to charge injection from the excited state of the dye to the conduction band of semiconductor. There are several classes of dyes, which do not favour donation from the excited states, such as anthraquinone dyes, which are widely used as textile dyes. Since these dye derivatives are becoming a class of concerning water pollutant and are accumulating in the environment, there is a strong need to determine the optimal conditions for rapid degradation of the dye. For practical application of wastewater treatment based on these processes the utilization of most environmentally and abundant energy source such as sunlight would be preferred.

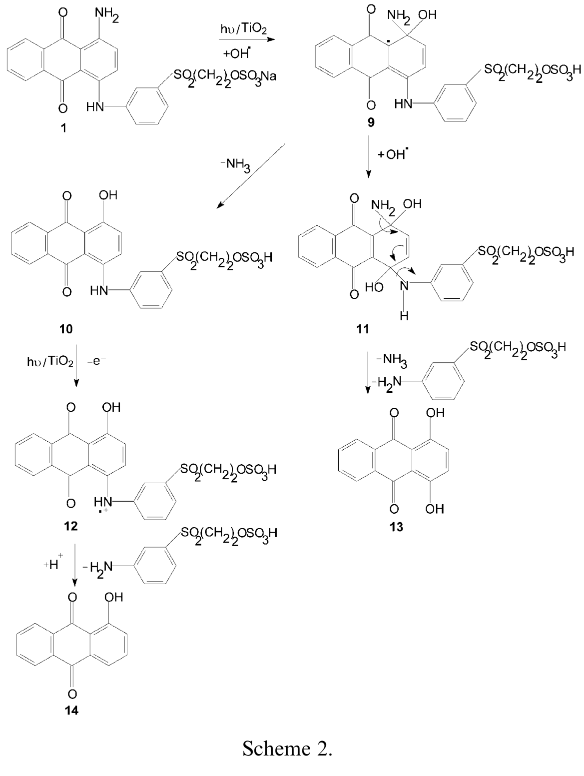
With this view we have undertaken a detailed study on the photodegradation of the anthraquinone dye, Remazol Brilliant Blue R (**1**) sensitized by TiO_2 in aqueous solution under sunlight and artificial light source examining various reaction parameters, e.g. reaction pH, substrate and catalyst concentration, type of photocatalyst and addition of several electron acceptors.



(1)



Scheme 1.



Scheme 2.

2. Experimental

2.1. Reagent and chemicals

Remazol Brilliant Blue R was obtained from Aldrich and used without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, P25 (Degussa AG) and Hombikat UV100 (Sachtleben chemie GmbH) were used in most of the experiments, another catalyst powder namely PC500 (Millenium Inorganic Chemicals) was used for comparative studies. 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 [30]. Hombikat UV100 consists of 100% anatase with a specific BET-surface area >250 $m^2\ g^{-1}$ and primary particle size of 5 nm [31]. 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 [32]. The other chemicals used in this study such as NaOH, HNO_3, $(NH_4)_2S_2O_8$, H_2O_2 and $KBrO_3$ were obtained from Merck.

2.2. Procedure

For experiments under UV light, stock solutions of the dye with desired concentration were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass was used in this study. For irradiation experiment 250 ml of the desired solution was filled into the reactor and the required amount of photocatalyst was added and the solution was stirred 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 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 for analysis.

The sunlight experiments were carried out between 9.00 a.m. to 2.30 p.m. during the months of November (winter season) at Aligarh City which is about 140 km from New Delhi. Reactions were carried out in round-bottom flasks (250 ml) made of Pyrex glass. The solution (250 ml) of the desired concentration of the model compound containing the required amount of photocatalyst was taken and stirred for 30 min in the dark in the presence of oxygen for equilibration. The solution was then placed on a flat platform with continuous stirring and purging of molecular oxygen. Samples (10 ml) were collected before and at regular intervals during the illumination for analysis.

2.3. Analysis

The degradation was monitored by measuring the absorbance on a Systronics UV–vis spectrophotometer (model 118). The absorbance of the dye was followed at 592 nm wavelength. For each experiment the degradation rate of the model pollutant was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of the absorbance of the dye as a function of irradiation time, i.e. first-order degradation kinetics. It was calculated in terms of $[ML^{-1}\ min^{-1}]$.

For characterization of intermediate products, aqueous solutions (250 ml) of the compound containing (P25, 1 gl^{-1}) was taken in the immersion well photochemical reactor. The mixture was irradiated with a 125 W medium pressure mercury lamp for 1 h 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 injection volume 0.5 μl with helium as a carrier gas was used.

3. Results

3.1. Photolysis of TiO_2 suspensions containing Remazol Brilliant Blue R

Fig. 1 shows the change in absorption intensity at 592 nm on irradiation of an aqueous solution of Remazol Brilliant Blue R (**1**, 0.25 mM) in the absence and presence of the photocatalyst (TiO_2, 1 g l^{-1}) under oxygen, by the 'Pyrex' filtered output of a 125 W medium pressure mercury lamp under UV light and sunlight source. There was no observable loss of the dye, when the irradiation was carried out in the absence of TiO_2 as shown in the figure. It has been observed that 79% degradation of the pollutant takes place in the presence of UV light whereas only 53% degradation was observed under sunlight source after 90 min of illumination. It is clear from the figure that the degradation of the dye is much faster in the presence of UV light as compared to sunlight source. Both degradation curves can be fitted reasonably well by an exponential decay curve suggesting first-order kinetics. The degradation rate was calculated using following equation,

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

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

Control experiments were carried out in all cases, employing unirradiated blank solutions. It has been found that there was no observable loss of the dye due to adsorption on the TiO_2 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

Titanium dioxide has become the semiconductor with the highest photocatalytic activity, being non-toxic, stable in aqueous solution and relatively inexpensive too. Several reviews have been made, regarding the mechanistic and kinetic question as well as the influence of experimental parameters. It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation techniques [33]. Anpo and coworkers [34–38] synthesized several modified photocatalyst with an aim to enhance the photocatalytic efficiency of the pollutant under visible light. The aim of the present study was to determine the best photocatalyst among different TiO_2

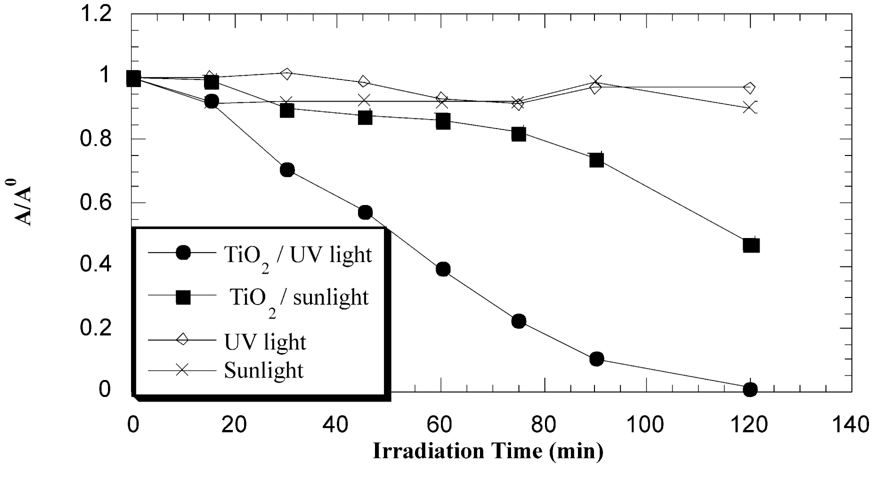


Fig. 1. Change in intensity at 592 nm vs irradiation time in the presence and absence of the photocatalyst. Experimental conditions: (a) UV light: dye concentration (0.25 mM), V = 250 ml, photocatalyst: Degussa P25 (1 gl^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 2 h. (b) Sunlight: dye concentration (0.25 mM), V = 250 ml, round-bottom flask (250 ml), photocatalyst: Hombikat UV100 (1 gl^{-1}), cont. O_2 purging and stirring, irradiation time = 2 h.

material and find further means to accelerate the efficiency of the photocatalytic process.

The degradation of **1** was tested with three different commercially available photocatalysts, namely Degussa P25, Hombikat UV100 and PC500. Fig. 2 shows the degradation rate for the decomposition of the dye in the presence of different photocatalyst under sunlight as well as UV light source. It has been observed that the degradation of dye under UV light proceeds much more rapidly in the presence of P25, whereas Hombikat UV100 was slightly better under sunlight as compared with other catalysts.

In all following experiments, Degussa P25 was used for the UV light experiment whereas Hombikat UV100 was used as photocatalyst under

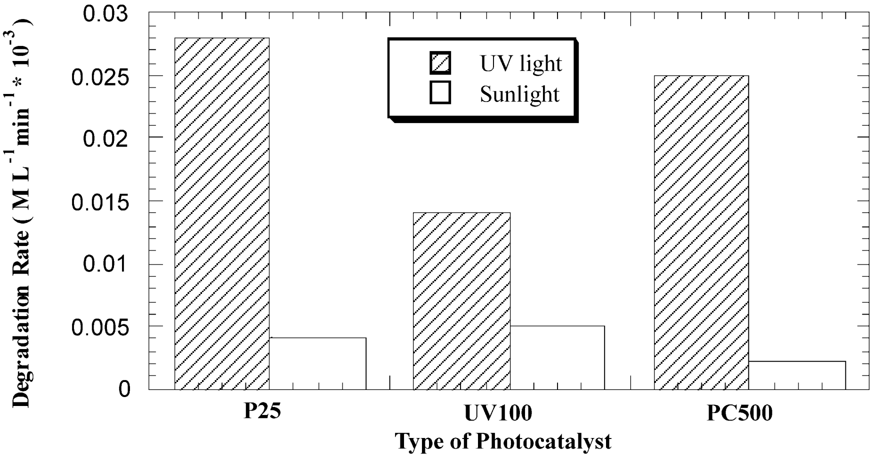


Fig. 2. Comparison of degradation rate for the decomposition of Remazol Brilliant Blue R under different photocatalysts: experimental conditions: (a) UV light: dye concentration (0.25 mM), V = 250 ml, photocatalysts: Degussa P25 (1 gl^{-1}), Sachtleben Hombikat UV 100 (1 gl^{-1}), PC 500 (1 gl^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging, irradiation time = 2 h. (b) Sunlight: dye concentration (0.25 mM), V = 250 ml, round-bottom flask (250 ml), photocatalysts: Degussa P25 (1 gl^{-1}), Sachtleben Hombikat UV 100 (1 gl^{-1}), PC 500 (1 gl^{-1}), cont. O_2 purging and stirring, irradiation time = 2 h.

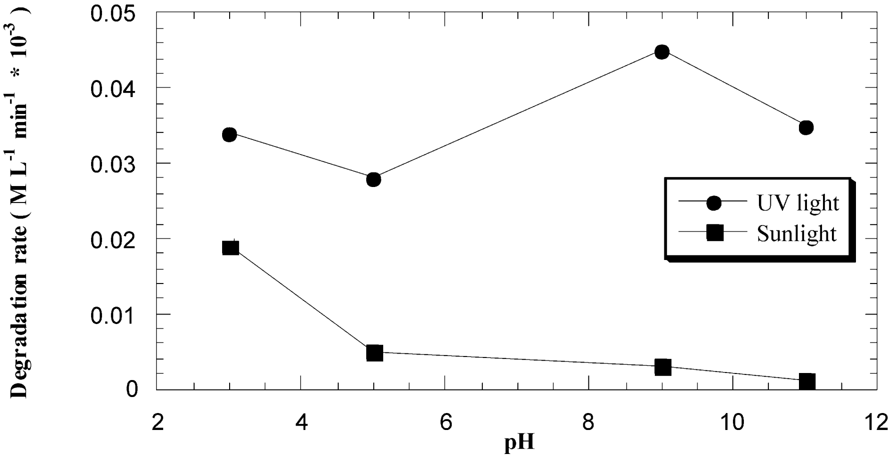


Fig. 3. Influence of pH on the degradation rate for the decomposition of Remazol Brilliant Blue R: experimental conditions: (a) UV light: dye concentration (0.25 mM), V = 250 ml, photocatalyst: Degussa P25 (1 gl^{-1}), reaction pH: 3, 5.2, 9 and 11, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 2 h. (b) Sunlight: dye concentration (0.25 mM), V = 250 ml, round-bottom flask (250 ml), photocatalyst: Hombikat UV100 (1 gl^{-1}), reaction pH 3, 5.2, 9 and 11, cont. O_2 purging and stirring, irradiation time = 2 h.

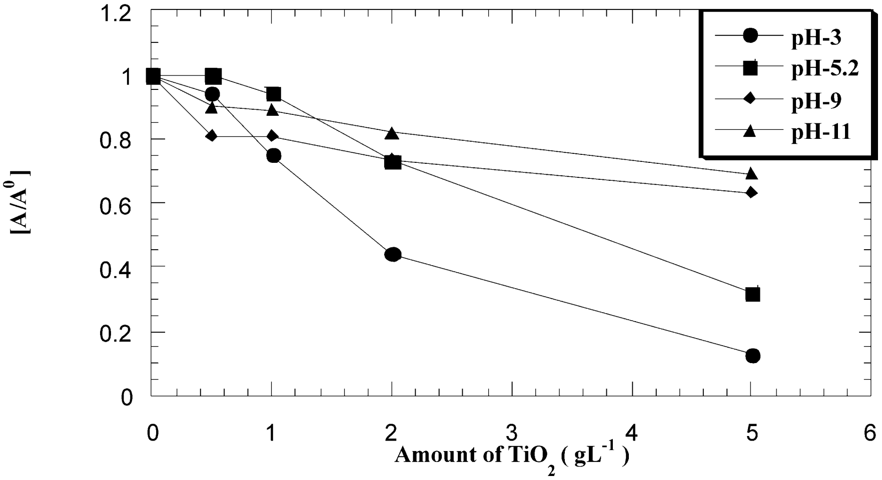


Fig. 4. Change in absorbance at 592 nm vs amount of TiO_2 at different pH, showing the adsorption of Remazol Brilliant Blue R in the dark. Experimental conditions: dye concentration (0.25 mM), V = 250 ml, photocatalyst: Degussa P25 (1 gl^{-1}), stirring in the dark for 24 h.

sunlight experiments, since this material exhibited the highest overall activity for the degradation of the pollutant under investigation.

3.3. pH effect

Employing Degussa P25 and UV100 as photocataysts the degradation of the dye was studied in pH range between 3 and 11 under UV light and sunlight source. The degradation rate for the decomposition of the dye as a function of reaction pH is shown in Fig. 3. It is pertinent to mention here that the pH of the solution was adjusted before irradiation and it is not maintained throughout the reaction. A decrease in the pH of the reaction mixture was observed at the end of illumination. It has been observed that under sunlight the highest efficiency for the degradation of the dye was observed at pH 3, which slowly decreases with the increase in pH of the reaction mixture. On the other hand, when the reaction was carried out under UV light, higher efficiency was observed at pH 9, whereas the efficiency for the degradation of the dye at pH 3, 5.2 and 11 was similar within the experimental error limits.

The adsorption study of the dye was investigated by stirring the aqueous solution in the dark for 24 h, containing varying amount of TiO_2 such as 0, 0.5, 1, 2 and 5 g l^{-1} at pH 3, 5.2, 9 and 11. The change in absorption intensity as a function of catalyst concentration at varying pH (Fig. 4) indicates that appreciable adsorption of the dye on the surface of the photocatalyst takes place at pH 3 and 5.2.

3.4. Effect of substrate concentration

It is important both from a mechanistic and from an application point of view to study the dependence of photocatalytic reaction rate on the substrate concentration. Hence the effect of substrate concentration on the degradation of the dye was studied at different concentrations such as 0.12, 0.25, 0.35 and 0.5 mM. Fig. 5 shows the degradation rate for decomposition of the dye as a function of substrate concentration employing Degussa P25 and UV100 under UV light and sunlight sources, respectively. It is interesting to note that the degradation rate under UV light source increases with the increase in substrate concentration from 0.12 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. On the other hand, when the reaction was carried out under sunlight highest efficiency was observed at 0.12 mM, which slowly decreases with the increase in substrate concentration.

3.5. Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of Remazol Brilliant Blue R has been investigated employing different concentrations of Degussa P25 with UV light and UV100 under sunlight varying from 0.5 to 5 g l^{-1}. As expected, the degradation rate for the decomposition of the anthraquinone dye **1**, both light sources have been found to increase with the increase in catalyst concentration as shown in

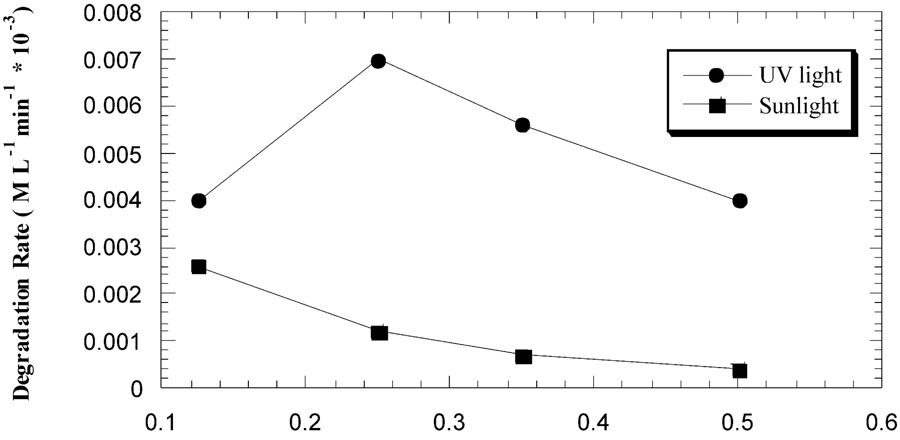


Fig. 5. Influence of substrate concentration on the degradation rate for the decomposition of Remazol Brilliant Blue R: experimental conditions: (a) UV light: substrate concentrations (0.12, 0.25, 0.35 and 0.5 mM), V = 250 ml, photocatalyst: Degussa P25 (1 gl^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 2 h. (b) Sunlight: substrate concentrations (0.12, 0.25, 0.35 and 0.5 mM), V = 250 ml, round bottom flask (250 ml), photocatalyst: Hombikat UV100 (1 gl^{-1}), cont. O_2 purging and stirring, irradiation time = 2 h.

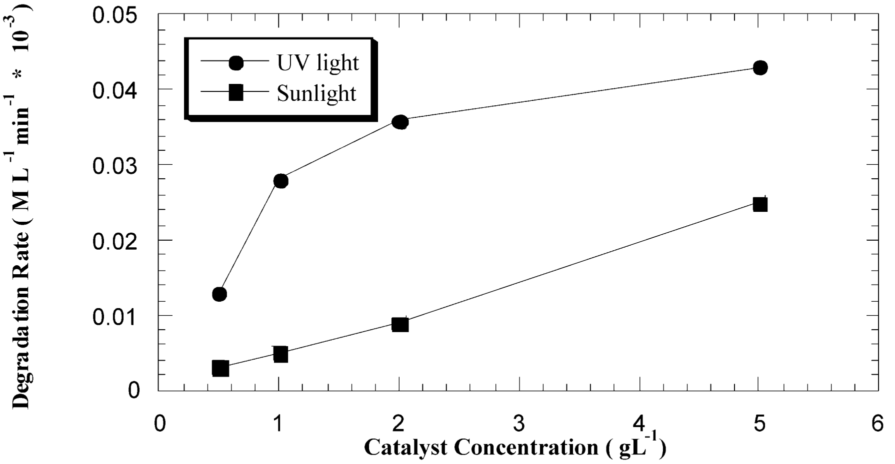


Fig. 6. Influence of catalyst concentration on the degradation rate for the decomposition of Remazol Brilliant Blue R: experimental conditions: (a) UV light: dye concentration (0.25 mM), V = 250 ml, photocatalyst concentrations (P25: 0.5, 1, 2 and 5 gl^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging, irradiation time = 2 h. (b) Sunlight: dye concentration (0.25 mM), V = 250 ml, round-bottom flask (250 ml), photocatalyst concentrations (UV100: 0.5, 1, 2 and 5 gl^{-1}), cont. O_2 purging and stirring, irradiation time = 2 h.

Fig. 6, which is the characteristic of the heterogeneous photocatalysis.

3.6. Effect of electron acceptors

Since hydroxyl radicals appear to play an important role in the photocatalysis, electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the (e^-/h^+) pair recombination. The degradation rates for the decomposition of **1** both under UV light and sunlight sources, in the presence of various electron acceptors are shown in Fig. 7. All the additives showed a benificial effect on the degradation of the dye under sunlight, whereas under UV light bromate ions has been found to enhance the degradation rate of the pollutant remarkably as shown in the figure.

3.7. Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye in the aqueous suspensions of titanium dioxide through GC–MS analysis. The GC–MS analysis of the irradiated mixture showed the formation of five products (**14**, **6**, **7**, **5**, and **13**) appearing at retention times (t_R) 9.23, 9.28, 9.70, 11.13 and 11.19 min, respectively. The products were identified based on their molecular ion and mass spectrometric fragmentation peaks, which are given below:

Compound **5**: 223 (M^+), 205, 167, 149, 132, 121, 104, 76, 57.
Compound **6**: 197 (M^{+1}),183, 169, 155, 141, 127, 112, 113, 99, 84, 71, 57.
Compound **7**: 183 (M^+), 168, 154, 140, 126, 113, 103, 97, 85, 71, 57.
Compound **13**: 240 (M^+),197, 183, 168, 154, 141, 127, 113, 99, 85, 71, 57.
Compound **14**: 224 (M^+), 196, 179, 175, 154, 141, 126, 113, 85, 71, 56.

4. Discussion

The photocatalysed degradation of various organic systems employing irradiated TiO_2 is well documented in the literature [9]. The initial step in

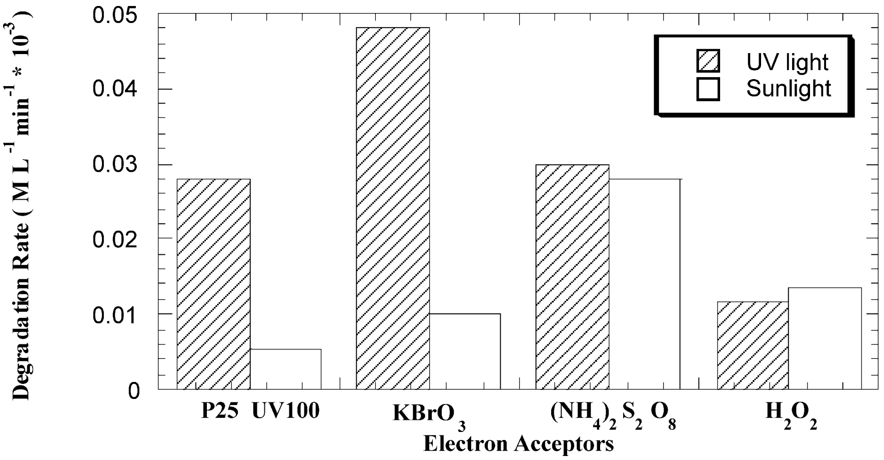


Fig. 7. Photocatalytic degradation rate for the decomposition of Remazol Brilliant Blue R in the presence of different electron acceptors: Experimental conditions: (a) UV light: dye concentration (0.25 mM), V = 250 ml, photocatalyst: Degussa P25 (1 gl^{-1}), electron acceptors: $KBrO_3$ (5 mM), H_2O_2 (10 mM), $(NH_4)_2S_2O_8$ (5 mM), immersion well photoreactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 2 h. (b) Sunlight: dye concentration (0.25 mM), V = 250 ml, round-bottom flask (250 ml), photocatalyst: Hombikat UV100 (1 gl^{-1}), electron acceptors: $KBrO_3$ (5 mM), H_2O_2 (10 mM), $(NH_4)_2S_2O_8$ (5 mM), cont. O_2 purging and stirring, irradiation time = 2 h.

the TiO_2 mediated photocatalysed degradation is proposed to involve the generation of (e^-/h^+) pair leading to the formation of hydroxyl radical and superoxide radical anion [Eqs. (1)–(3)];

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

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

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

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. In the present case both mechanisms can be operating in oxygen saturated solution.

The results on the photodegradation of the model compound using different kinds of TiO_2 photocatalyst with different bulk and surface properties, i.e., BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface, are apparently responsible for the photocatalytic activity, since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs. Martin et al. [39] have shown 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. Assuming that adsorption/desorption of the substrate and reaction intermediates is relatively slow in comparison to the formation of electron/hole pair, one would expect higher degradation rates when a photocatalyst such as Degussa P25 is used which generates longer lifetime of the photogenerated (e^-/h^+) pairs. Thus higher concentration of electrons and holes are available for suitable reactants to initiate the photocatalytic reaction. For Sachtleben Hombikat UV100 one would expect high efficiencies when the adsorption/desorption of the substrate and reaction intermediates is relatively fast and recombination of electron and holes is prevented by the reaction of electrons with suitable donor (pollutant molecule), respectively. It is interesting to note that the photocatalyst P25 showed better efficiency when the irradiation was carried out under UV light source, whereas, the photocatalyst Hombikat UV100 was found to be better for the decomposition of the dye under sunlight source. Hence it is difficult to differentiate between the two mechanisms.

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 this study it has been shown that the degradation rate for the model compounds under investigation is strongly influenced by the reaction pH. It has been observed that under sunlight highest efficiency for the degradation of the dye was observed at pH 3, which slowly decrease with the increase in pH of the reaction mixture. On the other hand, when the reaction was carried out under UV light higher efficiency was observed at pH 9, whereas the efficiency for the degradation of the dye at pH 3, 5.2 and 11 was similar within the experimental error limits.

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 [40]. Due to the low p*K*a value of the sulfonic acid group, **1** will be fully in the anionic form within the pH range studied. With increasing pH, the negative charges on TiO_2 are expected to repel the dye and a decrease in efficiency of photodegradation with increasing pH is expected. The results are in agreement with the assumption when the reaction was carried out under sunlight. In contrast, a completely different behavior was observed when the reaction was carried out under UV light source.

The effect of substrate concentration on the degradation rate for the degradation of **1** (Fig. 5) has been 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 photomineralisation of organic substrates with irradiated TiO_2 follows the Langmuir–Hinshelwood (L–H) law for the four possible situations, i.e., (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 of the dye under sunlight are in agreement with the assumption of the L–H model. On the other hand, under UV light source the degradation rate for the decomposition of the dye increases with the increase in the substrate concentration from 0.125 to 0.25 mM. A further increase in substrate concentration leads to decrease in the degradation rate under UV light. 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 $^{\bullet}OH$ and $O_2^{\bullet -}$ on the surface of the catalyst do not increase as the intensity of light and illumination time are constant. Conversely, their concentration 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 molecule. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

One practical problem in using TiO_2 as a photcatalyst is the undesired electron/hole recombination, which, in the absence of a proper electron acceptor or donor, is extremely efficient and thus represents the major energy-wasting step, hence 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 redicals 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 wastewaters, 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, bromate and persulphate ions on the photocatalytic degradation of the model compound under investigation. These acceptors are known to generate hydroxyl radicals according to the following Eqs. (4)–(8);

$$H_2O_2 + e_{CB}^- \rightarrow O^{\bullet}H + OH^- \tag{4}$$

$$BrO_3^- + 2H^+ + e_{CB}^- \rightarrow BrO^{\bullet}{}_2 + H_2O \tag{5}$$

$$\begin{aligned} BrO_3^- + 6H^+ + 6e_{CB}^- &\rightarrow \left[BrO_2^-,\ HOBr\right] \\ &\rightarrow Br^- + 3H_2O \end{aligned} \tag{6}$$

$$S_2O_8^{2-} + e_{cb}^- \rightarrow SO_4^{2-} + SO_4^- \tag{7}$$

$$SO_4^{\bullet}{-} + H_2O \rightarrow SO_4^{2-} + \overset{\bullet}{O}H + H^+ \tag{8}$$

As expected, all the additives showed a beneficial effect on the photocatalytic degradation of **1** under sunlight, as shown in Fig. 7. On the other hand, in the case of UV light experiments, bromate ions have been found to enhance the efficiency for the degradation of the dye markedly. The effective electron acceptor ability of $KBrO_3$ has been observed in number of studies before [41–43]. The reason can be attributed to the number of electrons it reacts as shown in Eq. (6).

The photocatalyzed degradation of the dye has been found to yield several intermediate products out of which five products have been identified based on their molecular ion and mass spectrometric fragmentation peaks. A plausible mechanism for the formation of different 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 cation **2**, which may undergo loss of aminophenyl moiety followed by abstraction of a proton leading to the formation of the observed product **5**. This product undergoes addition of hydroxyl radical followed by ring cleavage leading to the formation the observed product **7**. The dicarboxylic acid derivative **6** may be arising through a similar pathway as shown in the scheme.

The formation of mono and dihydroxy derivatives **14** and **13** could be understood in terms of the pathways shown in Scheme 2. The dye derivative **1**, upon the addition of a hydroxyl radical, may lead to the formation of the radical species **9** which may undergo loss of ammonia followed by an electron transfer to give the radical cation **12**. This intermediate may undergo loss of aminophenyl group followed by abstraction of a proton to give the monohydroxy derivative **14**. The formation of dihydroxy derivative **13** may similarly be formed through the addition of a hydroxyl radical to the redical derivative **9** with subsequent loss of ammonia and aminophenyl moiety.

5. Conclusion

TiO_2 can efficiently photocatalyse the textiles dye derivative such as Remazol Brilliant Blue R using artificial and sunlight radiation sources. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a 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 analysis of the intermediate products formed during the photodegradation process could be a useful source of information on the degradation pathways.

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