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Dyes and Pigments 72 (2007) 233–239
DYES and PIGMENTS
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Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania

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Received 11 March 2005; received in revised form 19 June 2005; accepted 31 August 2005
Available online 20 October 2005

Abstract

The photocatalysed degradation of two selected dyes, such as Acridine Orange (**1**) and Ethidium Bromide (**2**) has been investigated in aqueous suspensions of titanium dioxide (TiO_2) under a variety of conditions, which is essential from application point of view. The degradation was monitored by measuring the change in substrate concentration as a function of irradiation time employing UV Spectroscopic analysis technique. The degradation was studied using different parameters such as types of TiO_2, reaction pH, catalyst concentration, substrate concentration and in the presence of different 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, was found to be more efficient for the photocatalytic degradation of dye derivatives **1** and **2**. The dye derivative **1** was found to degrade faster as compared to the dye derivative **2**.

Keywords: Photocatalysis; Acridine Orange; Ethidium Bromide; Titanium dioxide

1. Introduction

Wastewater from chemical laboratories and dye manufacturing industries contains various dyestuffs, which are toxic to microorganisms, aquatic life and human beings. The clean up of these toxic chemicals from water has been a complex problem. Thus several physico-chemical and biological methods have been proposed and are being developed for the destruction of organic contaminants. Among these processes biodegradation has received greatest attention. It is pertinent to mention here that dyestuffs are highly structured organic compounds and are difficult to break down biologically [1–6]. Decolourization of dye effluents has therefore acquired increasing attention.

During the past two decades, photocatalytic degradation involving TiO_2 semiconductor particles under UV light illumination has become a promising technology for the removal of toxic organic and inorganic contaminants from wastewater. TiO_2 is one of the most preferable semiconductors for the photocatalytic process due to its high photosensitivity, non-toxic nature and large band gap. When illuminated with a photon of energy equal to or greater than its band gap width leads to the formation of electron/hole (e^-/h^+) pairs with free electrons produced in the empty 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 [7,8] as indicated in the following Eqs. (1–3):

$$TiO_2 + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (1)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\cdot -} \quad (2)$$

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doi:10.1016/j.dyepig.2005.08.020

$$H_2O + h^+_{VB} \rightarrow OH^{\cdot} + H^+ \quad (3)$$

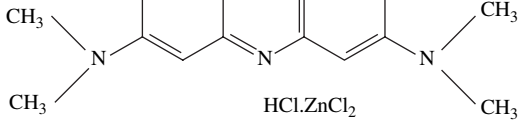
It has been suggested that the hydroxyl radicals ($OH^{\cdot}$) and superoxide radical anions ($O_2^{\cdot -}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye. Alternatively, direct absorption of light by 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:

$$Dye_{ads} + h\nu \rightarrow Dye^*_{ads} \quad (4)$$

$$Dye^*_{ads} + TiO_2 \rightarrow Dye^+_{ads} + TiO_2(e^-) \quad (5)$$

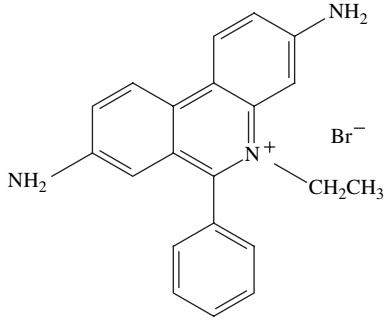
Earlier studies [9–14] have shown that heterogeneous photocatalytic oxidation processes can be used for removing colouring material from dye effluent in the presence of light. Dyes constitute the largest class of constituents used in the textile industries. The dye derivatives **1** and **2** have been used extensively in biological stains. The release of this colored wastewater in the ecosystem is a dramatic source of water pollution, eutrophication and perturbation in aquatic life. In view of the advantages of heterogeneous photocatalysis in the treatment of wastewater we have done a detailed study on the photodegradation of the dye derivatives such as Acridine Orange (**1**) and Ethidium Bromide (**2**) sensitized by TiO_2 in aqueous solution under a variety of conditions.

(a)



Acridine Orange (1)

(b)



Ethidium Bromide (2)

2. Experimental methods

2.1. Reagent and chemicals

The dye derivative Acridine Orange (**1**) was obtained from Ottokemi, Bombay, India, whereas Ethidium Bromide (**2**) was obtained from Sigma–Aldrich. They were used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, TiO_2 P25 (Degussa AG) was used for the degradation of Acridine Orange and Ethidium Bromide in most of the experiments. Other catalyst powder namely, UV100 (Hombikat) 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 [15]. Hombikat UV100 consists of 100% anatase with a specific BET-surface area >250 $m^2\,g^{-1}$ and primary particle size of 5 nm [16]. 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 [17]. The other chemicals used in this study such as $(NH_4)_2S_2O_8$, H_2O_2 and $KBrO_3$ were obtained from Merck.

2.2. Procedure

Aqueous solutions of the dye 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 the supply of air was used.

For irradiation experiment, 250 mL solution of desired concentration of the dye 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 as the irradiated solution. The suspensions were continuously purged with air throughout in each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp. IR-radiation and short-wavelength UV-radiation were eliminated by water circulated Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation. They were centrifuged before analysis.

The sunlight experiments were carried out by illuminating an aqueous suspension of the dye containing TiO_2 in the immersion well photochemical reactor vessel (which is used for UV light irradiation) with constant stirring and bubbling of air. Samples (10 mL) were collected before and at regular intervals during the illumination for analysis.

2.3. Analysis

The degradation of the dye was monitored using UV–Vis Spectrophotometer (Shimadzu 1601). The concentrations of the dye derivatives **1** and **2** were calculated by calibration curve obtained from the absorbance of the dye derivatives **1** (λ_{max} 449 nm) and **2** (λ_{max} 482 nm) at different concentrations. It was calculated in terms of [mole L^{-1} min^{-1}].

3. Results and discussion

3.1. Photolysis of TiO_2 suspensions containing dye derivatives **1** and **2**

Irradiation of an aqueous suspension of the 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. Figs. 1 and 2 show the change in concentration upon irradiation of an aqueous solution of Acridine Orange (1, 0.4 mM) and Ethidium Bromide (2, 0.2 mM) containing 1 g L^{-1} of TiO_2 in the presence of air, respectively. The concentration was found to decrease with increasing irradiation time and nearly total decomposition was observed within 75 min of irradiation for dye **1** and 195 min in case of dye **2**. Control experiments were carried out in both the cases employing UV-irradiated blank solutions. It has been found that there was no observable loss of the dyes due to adsorption on TiO_2 in unirradiated blank solutions. The zero irradiation times were obtained from blank solutions kept in the dark, but otherwise treated similarly as 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 linear regression from a plot of the natural logarithm of the dye as a function of time. The resulting first order rate constant has been used in all the subsequent plots to calculate the degradation rate for the decomposition of the compounds using formula given below

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

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

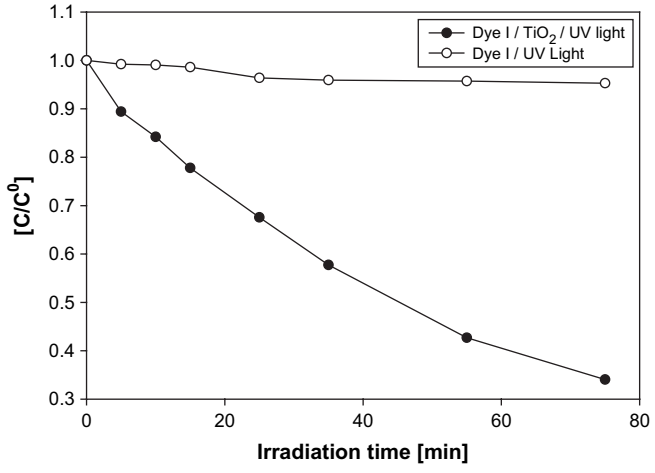


Fig. 1. Change in concentration as a function of irradiation time of air saturated aqueous suspensions of TiO_2 (1 g L^{-1}) containing Acridine Orange (1, 0.4 mM). Light source: 'Pyrex' filtered output of a 125 W medium pressure mercury lamp. Irradiation time = 75 min.

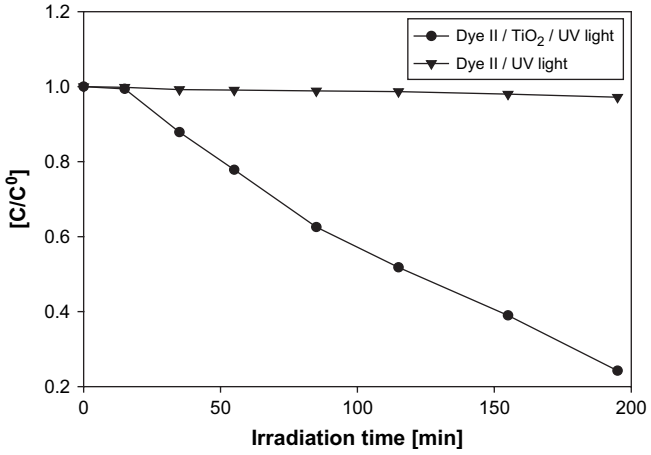


Fig. 2. Change in concentration vs. irradiation time of air saturated aqueous suspensions of TiO_2 (1 g L^{-1}) containing Ethidium Bromide (2, 0.2 mM). Light source: 'Pyrex' filtered output of a 125 W medium pressure mercury lamp. Irradiation time = 195 min.

3.2. Comparison of different photocatalysts and catalyst concentrations

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 powders (namely Degussa P25, Hombikat UV100 and PC500) on the degradation kinetics of model pollutants at different concentrations such as 0.5, 1, 2 and 3 g L^{-1}. The degradation rates for the decomposition of the dye derivatives **1** and **2** in the presence of different types of TiO_2 are shown in Figs. 3 and 4, respectively. It has been observed that the photocatalyst Degussa P25 was found to be more efficient for the degradation of both the dyes at all concentrations.

It is interesting to note that the degradation rate for the decomposition of both the dyes in the presence of Degussa P25 increases with the increase in catalyst concentration from 0.5 to 2 g L^{-1} and a further increase in catalyst concentration leads to a decrease in degradation rate. In contrast, in the presence of Hombikat UV100, better photocatalytic activity was observed at 2 g L^{-1} for both the dyes. On the other hand in the presence of PC500 activity was found to increase constantly from 0.5 to 3 g L^{-1} in case of dye derivative **2**.

This observation indicates that beyond this optimum catalyst concentration, other factors affect the degradation of dyes. At high TiO_2 concentrations, particles aggregate which in turn reduces the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface is decreased. The increase in opacity and light scattering by the particle may be the other reasons for the decrease in the degradation rate at higher catalyst concentration.

Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds [18–20].

The better photocatalytic activity of Degussa P25 could be explained on the basis of the fact that P25 being composed of small nano-crystallites of rutile disperses within an anatase

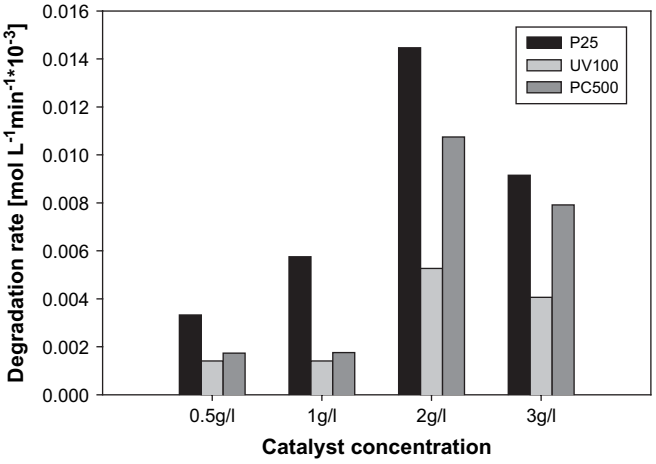


Fig. 3. Comparison of degradation rate for the decomposition of Acridine Orange (**1**) in the presence of different photocatalysts and catalyst concentrations. Experimental conditions: $V = 250$ mL, Degussa P25 (0.5, 1, 2, 3 g L^{-1}), Sachtleben Hombikat UV100 (0.5, 1, 2, 3 g L^{-1}), PC500 (0.5, 1, 2, 3 g L^{-1}). Irradiation time = 75 min.

matrix. The smaller band gap of rutile "catches" the photons, generating electron/hole pairs. The electron transfer, from the rutile CB 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 [21].

In all the following experiments, Degussa P25 was used for the degradation of both the dyes since they showed better activity for the respective dyes.

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. Therefore, the degradation of both the dyes was studied at different pH values (in the range 3–10). The degradation rate for the decomposition of dyes **1** and **2** as a function of reaction pH is shown in Fig. 5(a). In both the cases of dyes **1** and **2**, the rate decreases first and then increases with the increase in reaction pH and highest efficiency was observed at pH 10 for dye **1** and pH 4.6 for dye **2**. The highest efficiency of degradation in alkaline pH could be attributed to more efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of hydroxide ion.

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 3.7, 5.1, 6.7, 8.2, 10 for dye **1** and at 4.6, 6.6, 8.4, 10.1 for dye **2**. Analysis of the samples after centrifugation indicates some observable loss of the dye **1** at pH 8.2 and 10 as shown in Fig. 5(b). However, in case of **2** there was no loss of the dye at any pH.

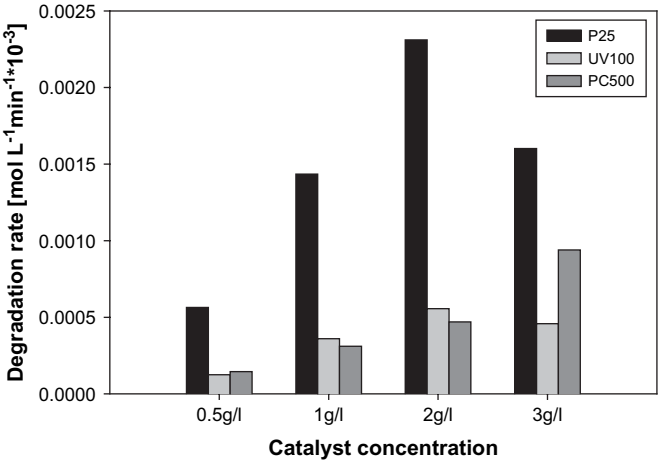


Fig. 4. Comparison of degradation rate for the decomposition of Ethidium Bromide (**2**) in the presence of different photocatalysts and catalyst concentrations. Experimental conditions: $V = 250$ mL, Degussa P25 (0.5, 1, 2, 3 g L^{-1}), Sachtleben Hombikat UV100 (0.5, 1, 2, 3 g L^{-1}), PC500 (0.5, 1, 2, 3 g L^{-1}). Irradiation time = 195 min.

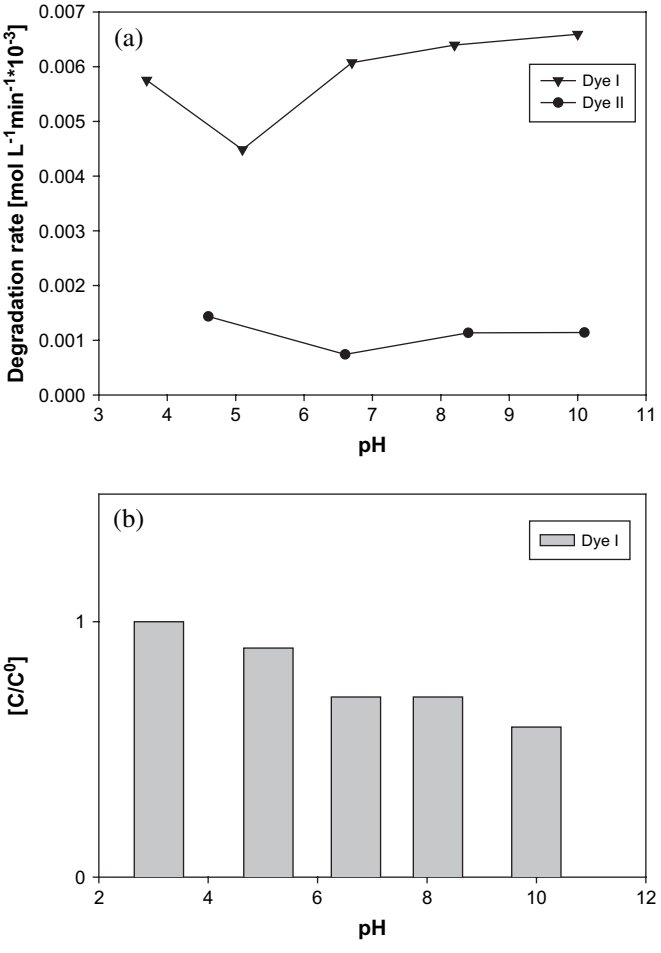


Fig. 5. (a) Comparison of degradation rate of dyes **1** and **2** vs. pH. Experimental conditions: $V = 250$ mL, Degussa P25, pH of dye **1** (3.7, 5.1, 6.7, 8.2, 10) and of dye **2** (4.6, 6.6, 8.4, 10.1). Irradiation time for dye **1** = 75 min and dye **2** = 195 min. (b) Comparison of change in concentration vs. pH for the dye derivative **1** in the dark in the presence of TiO_2 showing adsorption. Experimental conditions: $V = 25$ mL, TiO_2 (1 g L^{-1}), pH = 3.1, 5.1, 6.7, 8.2, 10.0, stirring time = 24 h.

3.4. Effect of substrate concentration

The effect of substrate concentration on the degradation rate for the decomposition of dye derivatives **1** and **2** was studied, as it is important from both the mechanistic and 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 irradiation time. Fig. 6 shows the degradation rate for the decomposition of dyes **1** and **2** as a function of initial substrate concentration containing 1 g L^{-1} of titanium dioxide.

Our results on the effect of the initial concentration on the degradation rate of the dye derivative **1** indicate that the rate increases with the increase in substrate concentration from 0.1 to 0.25 mM and then decreases with increase in concentration from 0.25 to 0.5 mM. However, for the dye derivative **2**, the degradation rate was found to decrease continuously with the increase in the substrate concentration from 0.1 to 0.4 mM. This may be due to the fact that as the initial concentrations of the dye increase, 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 $OH^{\cdot}$ and $O_2^{\cdot-}$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, 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 thus represents 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 (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 photocatalytic degradation of the model compound under investigation. These acceptors are known to generate reactive species according to the following Eqs. (7–11):

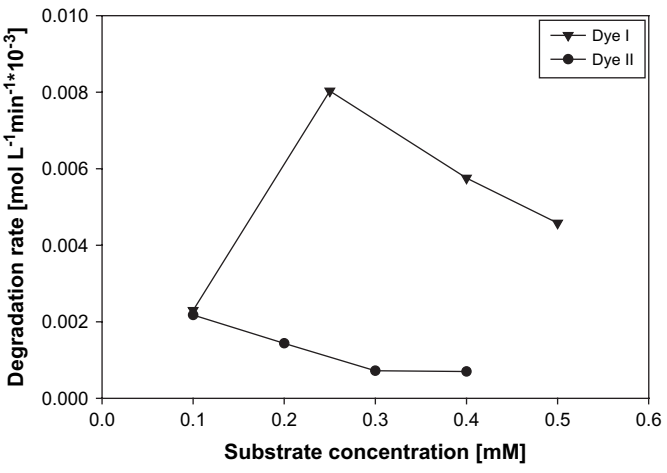


Fig. 6. Comparisons of degradation rate of dyes **1** and **2** vs. substrate concentration. Experimental conditions: $V = 250$ mL, Degussa P25, substrate concentration of dye **1** (0.1, 0.25, 0.4, 0.5 mM) and of dye **2** (0.1, 0.2, 0.3, 0.4 mM). Irradiation time for dye **1** = 75 min and dye **2** = 195 min.

$$H_2O_2 + e_{CB}^- \rightarrow OH^{\cdot} + OH^- \quad (7)$$

$$BrO_3^- + 2H^+ + e_{CB}^- \rightarrow BrO_2^{\cdot} + H_2O \quad (8)$$

$$BrO_3^- + 6H^+ + 6e_{CB}^- \rightarrow \left[BrO_2^-, HOBr\right] \rightarrow Br^- + 3H_2O \quad (9)$$

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{\cdot-} \quad (10)$$

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + OH^{\cdot} + H^+ \quad (11)$$

The respective one-electron reduction potentials of different species are: $E\ (O_2/O_2^{\cdot-}) = -155$ mV, $E\ (H_2O_2/HO^{\cdot}) = 800$ mV, $E\ (BrO_3^-/BrO_2^{\cdot}) = 1150$ mV, and $E\ (S_2O_8^{2-}/SO_4^{\cdot-}) = 1100$ mV [22]. From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than air.

Figs. 7(a) and 8 show the degradation rates for the decomposition of dyes **1** and **2** in the presence of different electron acceptors, respectively. In the case of **1** both the electron acceptors such as hydrogen peroxide and potassium bromate were found to enhance the rate markedly as shown in Fig. 7(a).

It was found that the model compound **1** is unstable in the presence of ammonium persulphate as an oxidant, which is indicated by coagulation of the dye and decrease in concentration in the dark. On the other hand, in the case of dye **2** all the additives showed beneficial effect on degradation of the dye. Blank experiments were carried out by irradiating the aqueous solution of the dye derivatives **1** and **2** containing H_2O_2 in the absence of TiO_2. Analysis of the samples showed that there was a slow decrease in the concentration of dye **1** and no observable loss of the dye **2** as shown in Fig. 7(b).

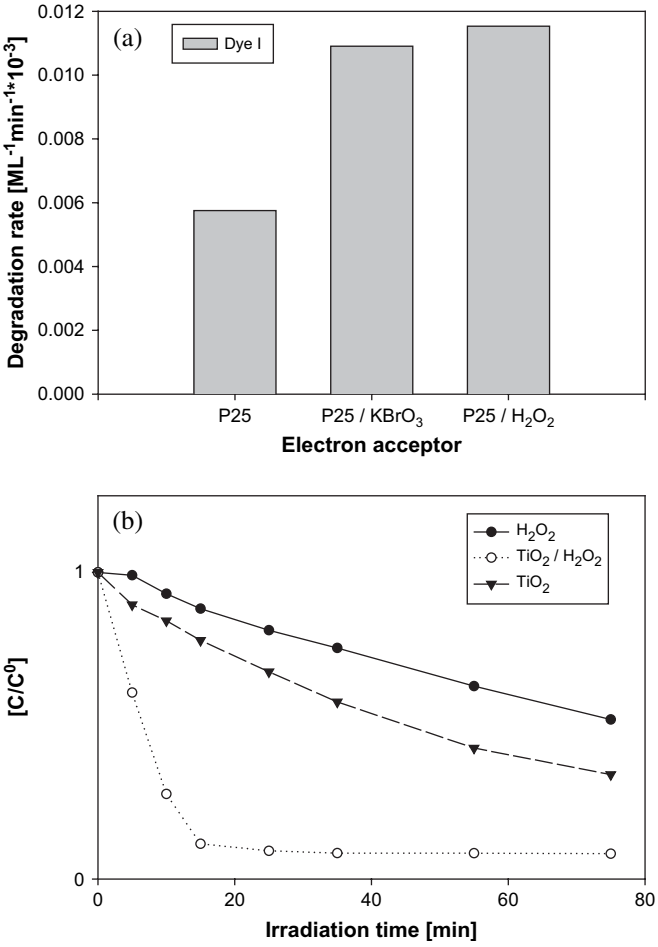


Fig. 7. (a) Comparision of degradation rate of dye **1** vs. additives. Experimental conditions: $V = 250$ mL, Degussa P25, potassium bromate, hydrogen peroxide. Irradiation time for dye **1** = 75 min. (b) Comparison of change in concentration vs. irradiation time for the dye derivative **1** under UV light source in the presence and absence of TiO_2. Irradiation time = 75 min.

*3.6. Photolysis of TiO_2 suspensions containing dye derivatives Acridine Orange (**1**) and Ethidium Bromide (**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. 9 and 10 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, respectively. 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 no observable loss of the dye derivative takes place.

4. Conclusion

TiO_2 can efficiently catalyze the decomposition of dye derivatives **1** and **2** in the presence of light and oxygen. The dye

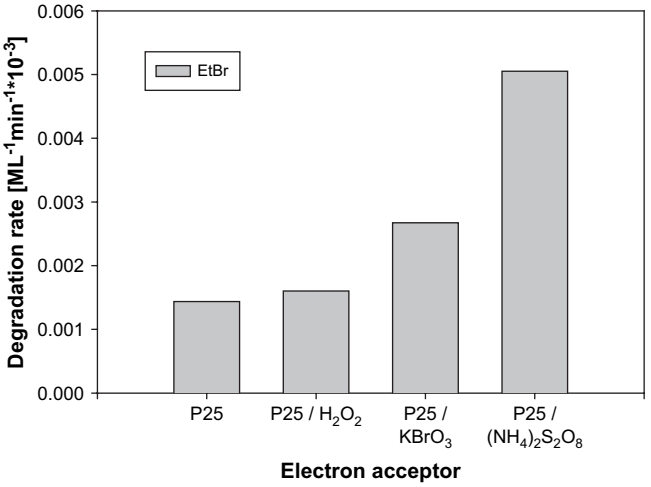


Fig. 8. Comparison of degradation rate of dye **2** vs. additives. Experimental conditions: $V = 250$ mL, Degussa P25, potassium bromate, hydrogen peroxide and ammonium persulphate. Irradiation time for dye **1** = 195.

1 was found to degrade more efficiently as compared to the dye **2**. Degussa P25 showed superior photocatalytic activity as compared with other TiO_2 powders. In the case of dye **1**, highest efficiency was observed at pH 10 whereas, in the case of dye **2**, better rate was observed at pH 4.6. The highest efficiency of degradation in alkaline pH could be attributed to more efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of hydroxide ion.

In the case of dye **1** the most appropriate concentration for the maximum degradation rate was 0.25 mM and a further increase in concentration led to a decrease in the degradation rate. On the other hand for the dye derivative **2** a decrease in the degradation rate was observed from 0.1 to 0.4 mM. 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.

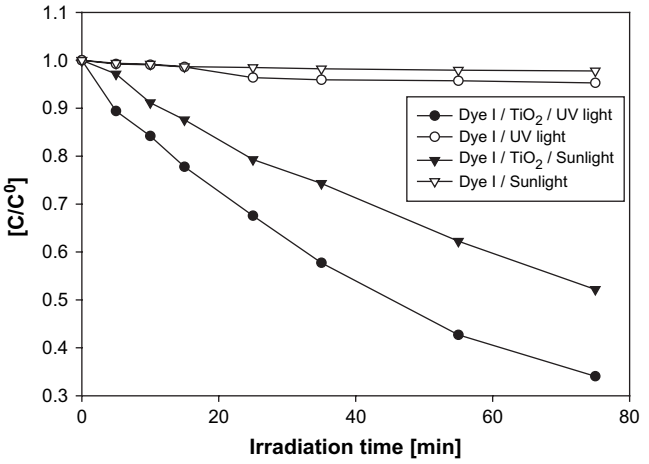


Fig. 9. Comparison of change in concentration vs. irradiation time for the dye derivative **1** under sunlight and UV light source in the presence and absence of TiO_2. Irradiation time = 75 min.

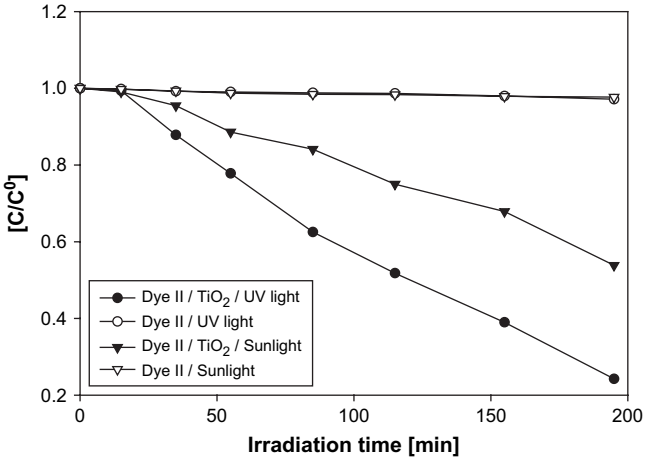


Fig. 10. Comparison of change in concentration vs. irradiation time for the dye derivative **2** under sunlight and UV light source in the presence and absence of TiO_2. Irradiation time = 195 min.

The best degradation condition depends strongly on the kind of pollutant. The investigations were conducted at the laboratory scale in order to determine the optimal degradation condition and further studies are required for the practical effluent treatment.

Acknowledgement

Financial support by the Department of Chemistry, Aligarh Muslim University, Aligarh and the Department of Science and Technology (DST), Government of India, New Delhi is gratefully acknowledged.

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