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# Photocatalytic degradation of two selected dye derivatives, chromotrope 2B and amido black 10B, in aqueous suspensions of titanium dioxide

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## Abstract

The photocatalytic degradation of two selected dye derivatives, chromotrope 2B (**1**) and amido black 10B (**2**), has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions which is essential from an 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. In these studies, a number of byproducts are formed during the photooxidation process which can potentially be harmful to the environment, therefore, we have studied the mineralization of the pollutants by measuring the total organic carbon (TOC) as a function of irradiation time. The degradation of dyes were 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 molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient as compared with other photocatalysts. The dye derivative (**1**) was found to degrade faster as compared to the dye derivative (**2**).

*Keywords:* Photocatalysis; Dye; Chromotrope 2B; Amido black 10B; Titanium dioxide

## 1. Introduction

Water contamination is caused by various sources such as industrial effluents, agricultural runoff and chemical spills. Industrial effluents contain several non-biodegradable substrates that can be harmful to the environment [1]. One major source of these effluents is the waste arising from the industrial processes, which utilize dyes to colour paper, plastic and natural and artificial fibres [2]. A substantial amount of dyestuff is lost during the dyeing process in the textile industry [2], which poses a major problem for the industry as well as a threat to the environment [2–6]. Decoulourization of dye effluents has therefore acquired increasing attention. During the past two decades, photocatalytic processes involving $TiO_2$ semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of wastewater pollutants.

There are several studies related to the use of semiconductors in the photomineralization of photostable dyes [7–23]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [24,25]. Briefly, when a semiconductor such as $TiO_2$ absorbs a photon of energy equal to or greater than its band gap width, an

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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 ($OH^•$) and $e^-_{cb}$ is picked up by oxygen to generate superoxide radical anion ($O_2^{-•}$), as indicated in Eqs. (1)–(3).

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

$$O_2 + e^-_{cb} \rightarrow O_2^{-•} \qquad (2)$$

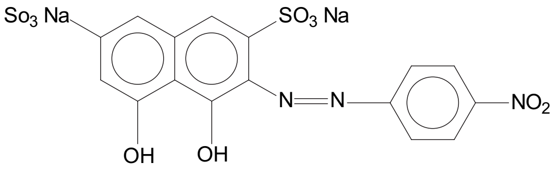
$$H_2O + h^+_{vb} \rightarrow OH^• + H^+ \qquad (3)$$

It has been suggested that the hydroxyl radicals ($OH^•$) and superoxide radical anions ($O_2^{-•}$) 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:

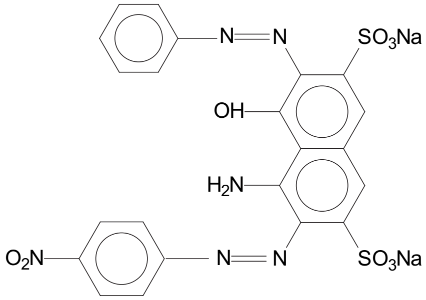
$$Dye_{ads} + h\nu \rightarrow Dye^*_{ads} \qquad (4)$$

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

Earlier studies [7–23] have shown that heterogeneous photocatalytic oxidation processes can be used for removing colouring material from dye effluent in the presence of light. The azo dye derivatives **1** and **2** have been used extensively in biological staining and colouring fibres. The degradation of amido black 10B (Naphthol Blue Black) in the presence of $TiO_2$ semiconductor nanoparticle using visible diffuse reflectance transient absorption and FTIR technique has been studied earlier [26]. No major efforts have been made to study the detailed degradation kinetics, which is essential from an application point of view. In many of these studies, although the initial disappearance of the pollutant is rapid, a number of byproducts are formed, which can potentially be harmful to the environment. We plan to determine the total organic carbon (TOC) content as well as to determine methods to enhance the mineralization process. Therefore, we have undertaken a detailed study on the photodegradation of the dye derivative chromotrope 2B (**1**) and amido black 10B (**2**) sensitized by $TiO_2$ in aqueous solution under a variety of conditions.



Chromotrope 2B (**1**)



Amido black 10 B (**2**)

## 2. Experimental methods

### 2.1. Reagent and chemicals

Chromotrope 2B (**1**) and amido black 10B (**2**) were obtained from from Hi-Media, Bombay, and Central Drug House (private) Ltd., New Delhi, India, and used as such without any further purification. The water employed in all the studies was double distilled. Titanium dioxide Degussa P25 was used as photocatalyst in most of the studies. Other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH) and PC500 (Milenium inorganic chemicals) were used for comparative study. P25 consist 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 [27]. Hombikat UV100 consists of 100% anatase with a specific BET-surface area $>250\ m^2\ g^{-1}$ and primary particle size of 5 nm [28]. 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 [29]. 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

Stock solutions of the dye containing desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, a water circulating jacket and an opening for supply of molecular oxygen was used.

For irradiation experiment 250 mL solution of desired concentration of the dye was taken into the photoreactor and the required amount of photocatalyst was added and the solution was stirred and bubbled with molecular oxygen for at least 15 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 a blank solution kept in the dark but otherwise treated similar 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 water circulated Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation. They were centrifuged before analysis.

### *2.3. Analysis*

The mineralization of the dye was monitored by measuring the total organic carbon (TOC) content with a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solution, whereas the degradation was monitored by measuring the absorbance on a Shimadzu UV–Vis Spectrophotometer (Model 1601). The absorption maxima of the dye derivatives **1** and **2** have been found to be 519 and 618 nm, respectively. Therefore, the degradation of the dyes was followed at these wavelengths as a function of irradiation time with appropriate dilution. For each experiment, the degradation rate for the mineralization and decomposition of the model pollutants was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of TOC and absorbance of the dye as a function of irradiation time, i.e. first order degradation kinetics. It was calculated in terms of $\mathrm{mol\,L^{-1}\,min^{-1}}$.

## 3. Results

### *3.1. Photolysis of $TiO_2$ suspensions containing chromotrope 2B (1) and amido black 10B (2)*

Figs. 1 and 2 show the change in absorption intensity and depletion in TOC on irradiation of an aqueous solution of chromotrope 2B (**1**, 0.25 mM) and amido black 10B (**2**, 0.25 mM) in the presence and absence of titanium dioxide by the "Pyrex" filtered output of a 125 W medium pressure mercury lamp. It was observed that the azo dye derivative **1** degrades much faster as compared to the amido black 10B (**2**). Both degradation curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the rate constant was calculated from the plot of natural logarithm of TOC and dye concentration as a function of irradiation time. The degradation rate for the mineralization and decomposition was calculated using the formula given below,

$$-\mathrm{d[TOC]}/\mathrm{d}t = kc^n$$

$$-\mathrm{d[A]}/\mathrm{d}t = kc^n$$

where TOC = total organic carbon, $A$ = absorbance, $k$ = rate constant, $c$ = concentration of the pollutant, $n$ = order of reaction.

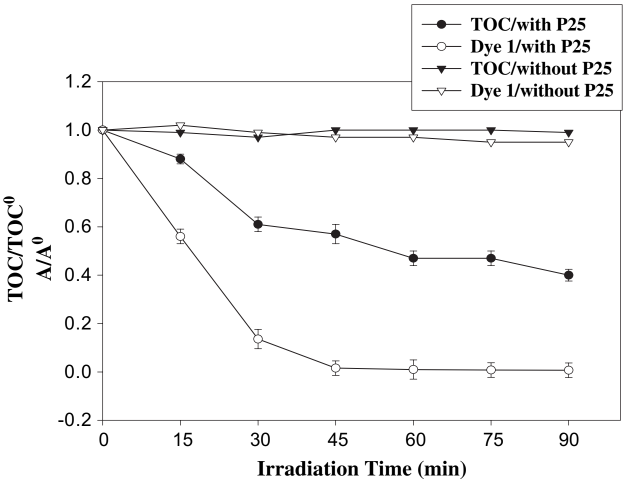


Fig. 1. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of chromotrope 2B (**1**) in the presence and absence of $TiO_2$. Experimental condition: dye concentration (0.25 mM), $V$ = 250 mL, pH = 5, Degussa P25 ($1\ \mathrm{g\,L^{-1}}$), absorbance was followed at 519 nm after 50% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging and stirring, irradiation time = 90 min.

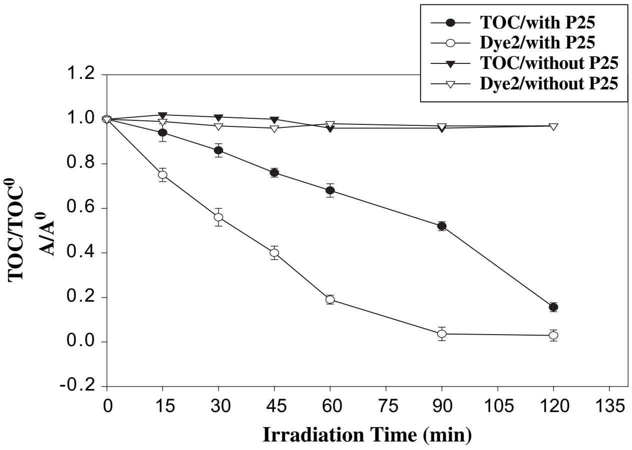


Fig. 2. Depletion in TOC and change in absorption intensity as a function of irradiation time for an aqueous solution of amido black 10B (**2**) in the presence and absence of $TiO_2$. Experimental condition: dye concentration (0.25 mM), $V$ = 250 mL, pH = 5, Degussa P25 ($1\ \mathrm{g\,L^{-1}}$), absorbance was followed at 618 nm after 40% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging and stirring, irradiation time = 120 min.

Blank experiments were carried out by irradiating the aqueous solution of the dye derivatives in the absence of $TiO_2$, where no observable loss of the dye was found as shown in Figs. 1 and 2, respectively.

### 3.2. Comparison of different photocatalysts

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity, is non-toxic, relatively inexpensive and stable in aqueous solution. Several reviews have been written, regarding the mechanistic and kinetic details 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 [30]. We have tested the photocatalytic activity of three different commercially available $TiO_2$ powders (namely P25, UV100 and PC500) on the degradation kinetics of chromotrope 2B (**1**) and amido black 10B (**2**). Figs. 3 and 4 show the degradation rate for the TOC depletion and decomposition of the dye in the presence of different types of $TiO_2$ for the dye derivative **1** and **2**, respectively. It has been observed that the degradation of both dyes proceeds much more rapidly in the presence of Degussa P25 as compared with other $TiO_2$ samples.

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

### 3.3. pH effect

The mineralization and decomposition of chromotrope 2B (**1**) and amido black 10B (**2**) in the aqueous suspensions of Degussa P25 were studied in the pH range between 3 and 9. The degradation rate for the TOC depletion and decomposition of **1** and **2** as a function of reaction pH is shown in Figs. 5 and 6, respectively. It is interesting to note that the degradation rates for both the dyes increases with the increase in reaction pH and highest efficiency was observed at pH 9.

The adsorption of both the dye derivatives **1** and **2** on the surface of the photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h in a round bottomed flask containing varying amounts of $TiO_2$ such as 0, 0.5, 1, 2 and 5 g $L^{-1}$. Analysis of the solution after centrifugation using UV spectroscopic

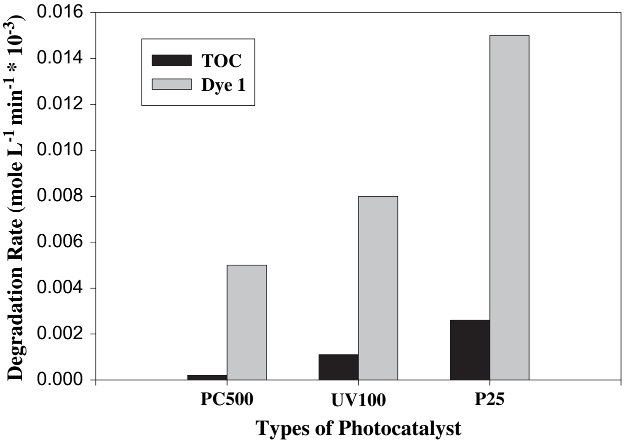


Fig. 3. Comparison of degradation rate for the mineralization and decomposition of chromotrope 2B (**1**) under different photocatalysts. Experimental conditions: dye concentration (0.25 mM), $V$ = 250 mL, pH = 5, Degussa P25 (1 g $L^{-1}$), Sachtleben Hombikat UV 100 (1 g $L^{-1}$) and PC 500 (1 g $L^{-1}$), absorbance was followed at 519 nm after 50% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 90 min.

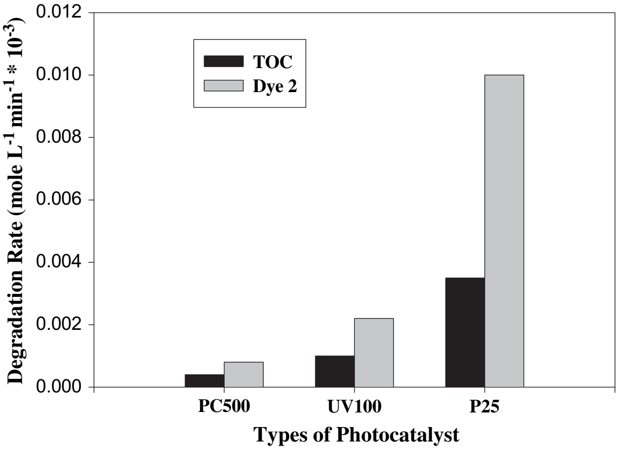


Fig. 4. Comparison of degradation rate for the mineralization and decomposition of amido black 10B (**2**) under different photocatalysts. Experimental conditions: dye concentration (0.25 mM), $V$ = 250 mL, Degussa P25 (1 g $L^{-1}$), Sachtleben Hombikat UV 100 (1 g $L^{-1}$) and PC 500 (1 g $L^{-1}$), absorbance was followed at 618 nm after 40% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 120 min.

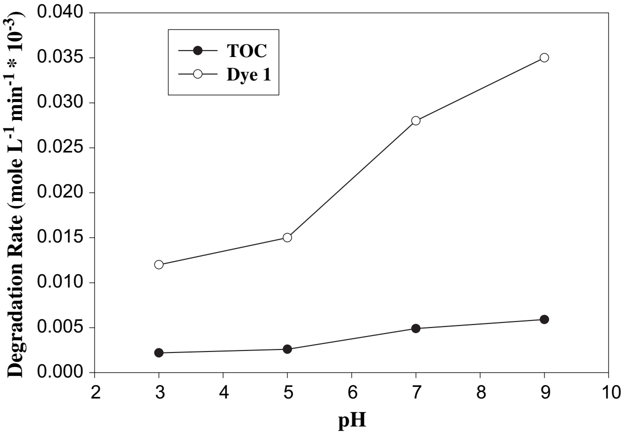


Fig. 5. Influence of pH on the degradation rate for the mineralization and decomposition of chromotrope 2B (**1**). Experimental conditions: dye concentration (0.25 mM), $V$ = 250 mL, pH (3, 5, 7 and 9), Degussa P25 (1 g $L^{-1}$), absorbance was followed at 519 nm after 50% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 90 min.

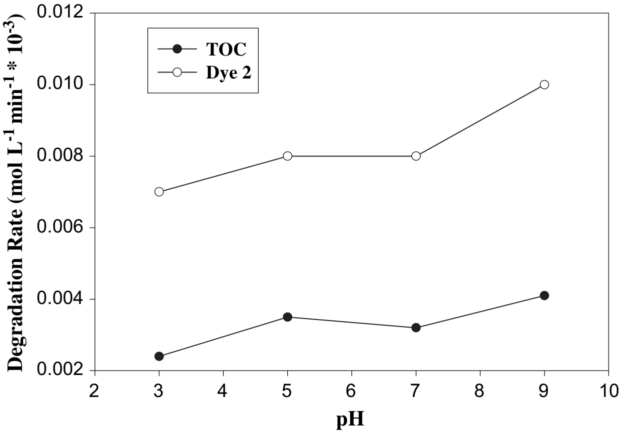


Fig. 6. Influence of pH on the degradation rate for the mineralization and decomposition of amido black 10B (**2**). Experimental conditions: dye concentration (0.25 mM), $V$ = 250 mL, pH (3, 5, 7 and 9), Degussa P25 (1 g L$^{-1}$), absorbance was followed at 618 nm after 40% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 120 min.

technique and TOC measurement showed no appreciable adsorption of the dyes on the surface of photocatalyst as shown in Figs. 7 and 8 for the dye derivatives **1** and **2**, respectively.

### 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 chromotrope 2B (**1**) and amido black 10B (**2**) was studied at different concentrations such as 0.25, 0.35, 0.5 and 0.75 mM. Figs. 9 and 10 show the degradation rate for the TOC depletion and decomposition of dyes **1** and **2** as a function of substrate concentration employing Degussa P25 as photocatalyst. It is interesting to note that for the dye derivative **1**, the degradation rate increases with the increase in substrate concentration from 0.25 to 0.35 mM and a further increase in substrate concentration led to a decrease in the degradation rate. However, for the dye derivative **2**, the degradation rate was found to decrease continuously with the increase in substrate concentration from 0.25 to 0.75 mM.

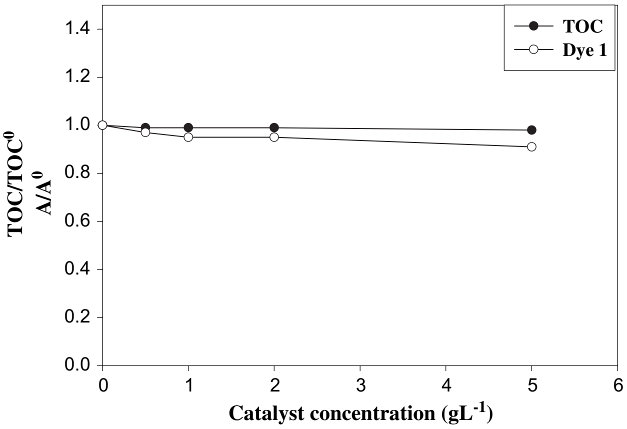


Fig. 7. Change in absorbance and TOC content on stirring the solution of chromotrope 2B (**1**) with different amounts of $TiO_2$ in the dark for 24 h. Experimental conditions: dye concentration (0.25 mM), $V$ = 20 mL, pH = 5, Degussa P25 (0, 0.5, 1, 2 and 5 g L$^{-1}$), absorbance was followed at 519 nm after 50% dilution.

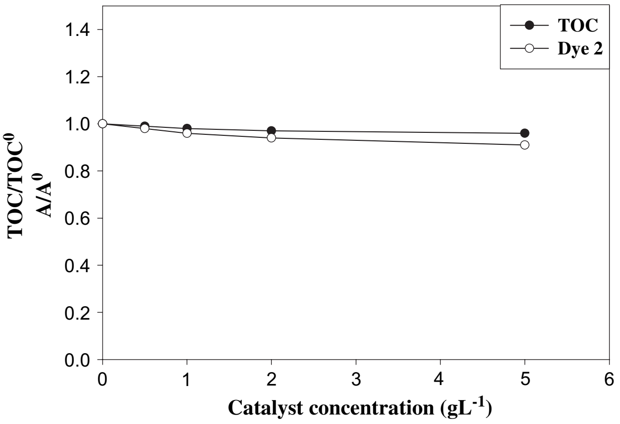


Fig. 8. Change in absorbance and TOC content on stirring the solution of amido black 10B (**2**) with different amounts of $TiO_2$ in the dark for 24 h. Experimental conditions: dye concentration (0.25 mM), $V$ = 20 mL, pH = 5, Degussa P25 (0, 0.5, 1, 2 and 5 g L$^{-1}$), absorbance was followed at 618 nm after 40% dilution.

### 3.5. Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of dye derivatives **1** and **2** was

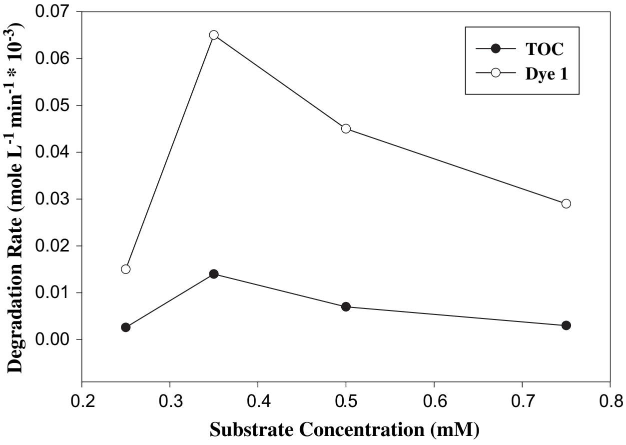


Fig. 9. Influence of substrate concentration on the degradation rate for the mineralization and decomposition of chromotrope 2B (**1**). Experimental conditions: dye concentration (0.25, 0.35, 0.5 and 0.75 mM), $V$ = 250 mL, pH = 5 Degussa P25 (1 g L$^{-1}$), absorbance was followed at 519 nm after 50% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 90 min.

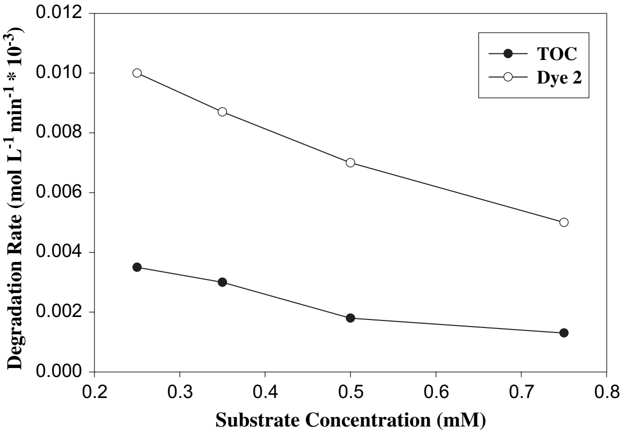


Fig. 10. Influence of substrate concentration on the degradation rate for the mineralization and decomposition of amido black 10B (**2**). Experimental conditions: dye concentration (0.25, 0.35, 0.5 and 0.75 mM), $V = 250$ mL, pH = 5, Degussa P25 (1 g $L^{-1}$), absorbance was followed at 618 nm after 40% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 120 min.

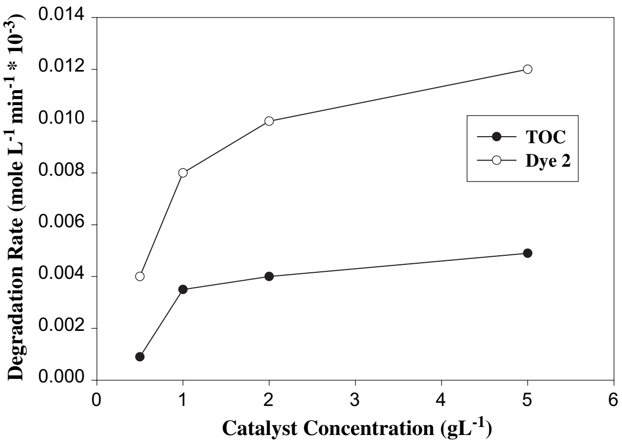


Fig. 12. Influence of catalyst concentration on the degradation rate for the mineralization and decomposition of amido black 10B (**2**). Experimental conditions: dye concentration (0.25 mM), $V = 250$ mL, pH = 5, Degussa P25 (0.5, 1, 2 and 5 g $L^{-1}$), absorbance was followed at 618 nm after 40% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 120 min.

investigated employing different concentrations of Degussa P25 varying from 0.5 to 5 g $L^{-1}$. As expected, the degradation rate for the mineralization and decomposition of the model compounds under investigation was found to increase with the increase in catalyst concentration (Figs. 11 and 12) which is the characteristic of heterogeneous photocatalysis. The results are in agreement with a number of studies reported earlier.

### 3.6. *Effect of electron acceptors*

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, 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 electron/hole ($e^-/h^+$) pair recombination. The degradation rate for the TOC depletion and decomposition of the dye derivative **1** in the presence of different electron acceptors is shown in Fig. 13. It has been observed that all the additives showed beneficial effect for the degradation of the dye. In contrast, in the photocatalytic degradation of the dye

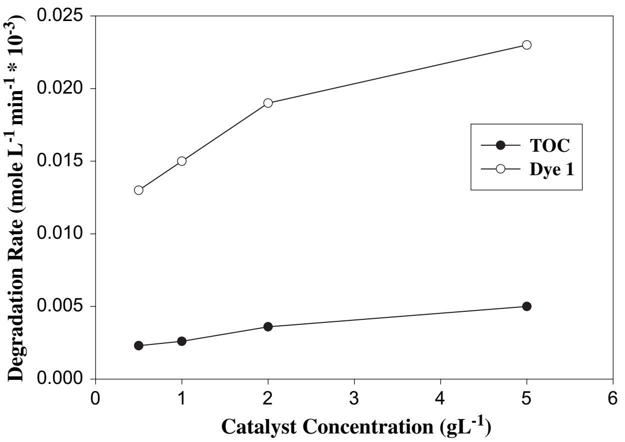


Fig. 11. Influence of catalyst concentration on the degradation rate for the mineralization and decomposition of chromotrope 2B (**1**). Experimental conditions: dye concentration (0.25 mM), $V = 250$ mL, pH = 5, Degussa P25 (0.5, 1, 2 and 5 g $L^{-1}$), absorbance was followed at 519 nm after 50% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 90 min.

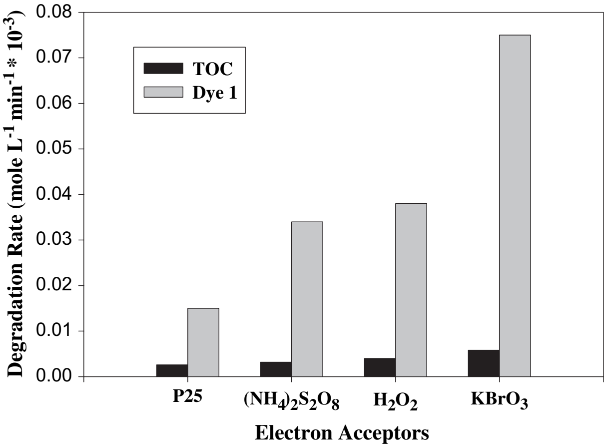


Fig. 13. Comparison of degradation rate for the mineralization and decomposition of chromotrope 2B (**1**) in the presence of different electron acceptors. Experimental conditions: dye concentration (0.25 mM), $V = 250$ mL, Degussa P25 (1 g $L^{-1}$); electron acceptors: $H_2O_2$ (10 mM), $(NH_4)_2S_2O_8$ (3 mM) and $KBrO_3$ (3 mM), absorbance was followed at 519 nm after 50% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 90 min.

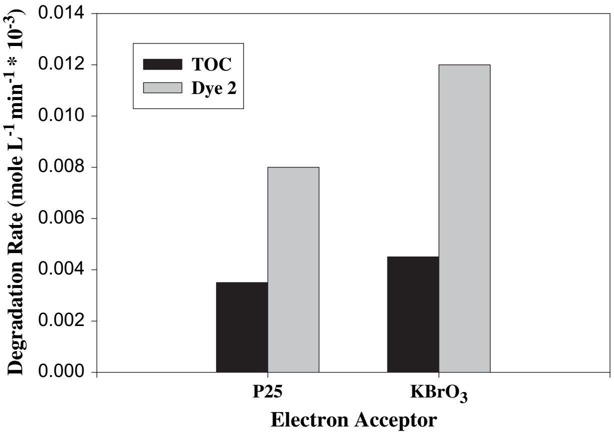


Fig. 14. Comparison of degradation rate for the mineralization and decomposition of amido black 10B (**2**) in the presence of $KBrO_3$ (3 mM). Experimental conditions: dye concentration (0.25 mM), $V$ = 250 mL, Degussa P25 (1 g $L^{-1}$), absorbance was followed at 618 nm after 40% dilution, immersion well photoreactor, 125 W medium pressure Hg lamp, cont. $O_2$ purging, irradiation time = 120 min.

derivative **2**, only the addition of $KBrO_3$ found to enhance the degradation rate as shown in Fig. 14.

## 4. Discussion

The differences in the photocatalytic activity are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron–hole pairs. Earlier studies [31] have 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.

Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds [32–34]. On the one hand Lindner et al. [35] showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. Also Hombikat UV100 was found to be better for the degradation of benzidine and 1,2-diphenyl hydrazine as shown in a recent study [36]. These results indicate that the activity of the photocatalyst also depends on the type of the model pollutant.

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. In the case of Degussa P25 photocatalyst, the zero point of charge ($pH_{zpc}$) is at pH 6.25. Hence, at more acidic pH values, the particle surface is positively charged, while at pH values above 6.25, it is negatively charged [37]. In this study it has been shown that the degradation rate for both model compounds under investigation is strongly influenced by the reaction pH. The degradation rate for the decomposition and mineralization of both dyes was found to be lower at lower pH values which increase with increase in pH and highest efficiency was observed at pH 9. This effect may be attributed to more efficient generation of hydroxyl radicals by $TiO_2$ with increasing concentration of $OH^-$. At the alkaline pH values, the hydroxyl radicals have to diffuse away and degrade the dye in the bulk solution.

The effect of substrate concentration on the degradation rate for the decomposition and mineralization of **1** and **2** (Figs. 9 and 10) was studied, as it is important both, from the 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 irradiation time. 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 the substrate concentration from 0.25 to 0.35 and a further increase in concentration leads to a decrease in the degradation rate. In contrast, in the case of **2**, the degradation rate was found to decrease continuously with the increase in substrate concentration from 0.25 to 0.75 mM. This may be due to the fact that as the initial concentrations of the dye increases, the colour of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generations of relative amount of $OH^{\bullet}$ and $O_2^{\bullet -}$ on the surface of the catalyst do not increase as the intensity of light, illumination time and concentration of the catalyst are constant. Conversely, their concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

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 hence represent the major energy-wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron–hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as (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 compounds under investigation. These acceptors are known to generate hydroxyl radicals according to Eqs. (6)–(10);

$$H_2O_2 + e_{CB}^- \rightarrow OH^{\bullet} + OH^- \qquad (6)$$

$$BrO_3^- + 2H^+ + e_{CB}^- \rightarrow BrO_2^{\bullet} + H_2O \qquad (7)$$

$$BrO_3^- + 6H^+ + 6e_{CB}^- \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \qquad (8)$$

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{-\bullet} \qquad (9)$$

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^+ \qquad (10)$$

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, $E\ (BrO_3^-/BrO_2^{\bullet}) = 1150$ mV, and $E\ (S_2O_8^{2-}/SO_4^{-\bullet}) = 1100$ mV [38]. From the thermodynamic point of view, all employed additives should therefore be more efficient electron acceptors than molecular oxygen. As expected, all the electron acceptors showed beneficial effect for the degradation of dye **1**. In contrast, in the case of dye **2**, only potassium bromate was found to enhance the degradation rate.

## 5. Conclusion

$TiO_2$ can efficiently catalyze the photomineralization of textile dye derivatives **1** and **2** in the presence of light and oxygen. The chromotrope 2B (**1**) was found to degrade more efficiently as compared to the amido black 10B (**2**). The photocatalyst Degussa P25 showed superior photocatalytic activity as compared with other two $TiO_2$ samples for the degradation of both the dyes under investigation. The increase in reaction pH favoured the photodegradation efficiency for both the dyes and highest efficiency was observed at pH 9. The most appropriate concentration for the maximum degradation rate of dye **1** was 0.35 mM where as in case of dye **2**, an inhibition in the degradation rate was observed from lower substrate concentration to higher substrate concentration. 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 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.

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