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Photocatalysed decolourization of two textile dye derivatives, Martius Yellow and Acid Blue 129, in UV-irradiated aqueous suspensions of Titania

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ABSTRACT

Photocatalysed decolourization of two textile dye derivatives, Martius Yellow and Acid Blue 129, has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The decolourization was studied by monitoring the decrease in dye concentration as a function of irradiation time employing the UV spectroscopic analysis technique. The decolourization kinetics was investigated under different conditions such as types of TiO_2 (Anatase [Hombikat UV-100 and PC500]/Anatase–Rutile mixture [Degussa P25]), initial reaction pH, catalyst dosage, dye concentration and in the presence of electron acceptors such as potassium bromate, hydrogen peroxide and ammonium persulphate. The decolourization of both dyes was also investigated under sunlight. The decolourization rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the decolourization of dye derivative Martius Yellow, while UV100 was better for the decolourization of Acid Blue 129. All the electron acceptors markedly enhanced the decolourization rate of Martius Yellow, while only $KBrO_3$ as an electron acceptor shows pronounced effect for the decolourization of Acid Blue 129 in the presence of TiO_2 and air.

Keywords: Photocatalysis; Martius Yellow; Acid Blue 129; Titanium dioxide; Decolourization of dyes

1. Introduction

Water is one of the most abundantly available substances in nature. It is an important constituent of all forms of life and represents 75% of the matter of the planet. Water is distributed in nature in different forms such as groundwater, surface water, etc. These water bodies are polluted through various sources such as industrial effluents, agricultural runoff, chemical spills, etc. The major sources of industrial effluents are the wastes arising from the manufacturing processes of drug, textile, pesticides, etc. Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that pose an increasing environmental danger, which utilize dyes to colour paper, plastic and natural and artificial fibres. Studies indicate that approximate 12% of synthetic dyes are lost during manufacturing and processing operations [1] and that 20% of the resultant colour enter into the environment through the effluents that come from industrial wastewater treatment plants [1]. The 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 to the environment [3–7]. The remediation of these coloured compounds from different water sources has

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been of great interest to the scientific communities. Therefore, decolourization of dyes effluents has been attracting the attention of many researches during the last few decades.

There are several studies related to the use of semiconductors for the decolourization of dyes [8–14]. Hitherto has studied the degradation of several classes of dyes under different parameters in order to obtain the optimum degradation conditions [15–18]. The results of our earlier studies indicate that degradation kinetics strongly depend on the type of chromophore present on the pollutants. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed in detail in the literature [19]. Briefly, when a semiconductor such as TiO_2 absorbs light that is equal to or greater than its band gap width, it leads to the generation of electron–hole (e^-–h^+) pair. If the 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 water to produce the hydroxyl radical and e^-_{cb} is picked up by oxygen to generate the superoxide radical anion as indicated in Eqs. (1)–(3):

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

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

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

The dye derivative (Dye) on absorption of light goes to an excited state (Dye*), which can either donate an electron to TiO_2 surface or accept an electron from the excited TiO_2 surface to generate a radical cation or a radical anion of the dye derivative as summarized below [20]:

$$\mathrm{Dye} + h\nu \rightarrow \mathrm{Dye}^* \tag{4}$$

$$\mathrm{Dye}^* + TiO_2 \rightarrow \mathrm{Dye}^{\cdot +} + TiO_2(e) \tag{5}$$

$$\mathrm{Dye}^* + TiO_2 \rightarrow \mathrm{Dye}^{\cdot -} + TiO_2 \tag{6}$$

In a heterogeneous process, a small amount of suspended TiO_2 powder is sufficient to carry out the reaction due to the large surface area of the catalyst available for the reaction. However, in large-scale applications, the separation and recycling of the suspended catalyst powder should be done from the treated wastewater prior to discharge, which is a time-consuming and expensive process. In addition, the depth of penetration of UV light is limited because of strong absorption by both catalyst particles and dissolved dyes [21].

The model compounds, Acid Blue 129 (AB 129) and Martius Yellow (MY) are used as textile dyes [22,23]. Earlier, Shirin and Balakrishnan [22] studied the zerovalent Fe-mediated reduction of Acid Blue 129. The sonochemical decolourization of the MY dye in aqueous solution [23] and wet oxidation of AB 129 at various temperatures using combined $FeCl_2$/$NaNO_2$ as a catalyst has also been investigated earlier by Peng et al. [24]. To the best of our knowledge, there has not been any study relating to the decolourization of these dyes in the presence of TiO_2. Therefore, we have undertaken a detailed study on the photodecolourization of MY and AB 129 sensitized by TiO_2 in aqueous solution examining various reaction parameters, such as the type of photocatalyst (Anatase/Anatase–Rutile mixture), reaction pH, dye concentration, catalyst loading and addition of electron acceptors in order to obtain the optimal degradation condition, which is essential for any practical application of photocatalytic oxidation processes.

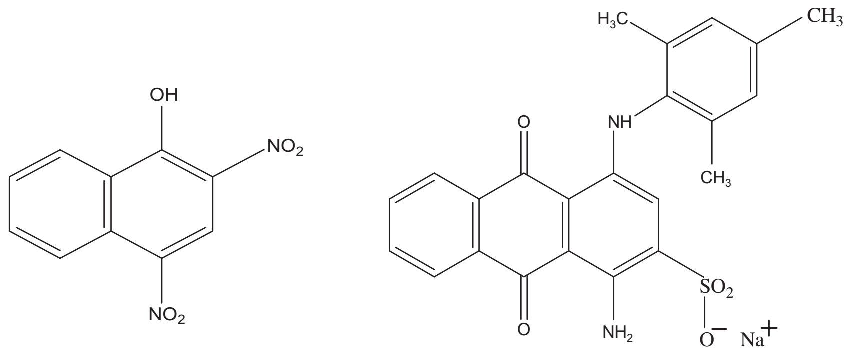
2. Experimental methods

2.1. Reagents

Analytical-grade Martius Yellow and Acid Blue 129 (Chart 1) were obtained from Sigma-Aldrich. Double-distilled water was employed to make dye solutions for conducting all experiments. Three commercially available photocatalysts namely Degussa P25 (Degussa AG), Hombikat UV-100 (Sachtleben Chemie GmbH) and PC500 (Millennium Inorganic), were used in these studies. Degussa P25 contains 80% anatase and 20% rutile with a specific BET-surface area of $50\,m^2\,g^{-1}$ and a primary particle size of 20 nm [25]. Hombikat UV-100 consists of 100% pure anatase with a specific BET surface area of $250\,m^2\,g^{-1}$ and a primary particle size of 5 nm [26]. The photocatalyst PC 500 has a BET-surface area of $287\,m^2\,g^{-1}$ with 100% anatase and a primary particle size of 5–10 nm [27]. The other chemicals such as NaOH, HNO_3, H_2O_2, ammonium persulphate and potassium bromate, used in the study, were obtained from Merck.

2.2. Procedure

For experiments under UV light, stock solutions of the compound with desired concentrations (0.2 mM for MY and 0.5 mM for AB 129, except in dye concentration experiments) were prepared in double-distilled water. An immersion well photochemical reactor made of Pyrex glass was used for irradiation experiments. For these experiments, an aqueous solution of the dye of desired concentration (250 mL) was taken into the reactor and the required amount of photocata-



Martius Yellow **Acid Blue 129**

Chart 1. Chemical structures of textile dye derivatives Martius Yellow (MY) and Acid Blue 129 (AB 129).

lyst ($1\,g\,L^{-1}$, except in catalyst dosage experiments) was added. The solution was stirred 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 dilute aqueous solution of NaOH or HNO_3 in order to obtain the required pH of the dye solutions (pH 3.1, 9.4 and 11.9 for MY and 4.1, 8.9 and 11.3 for AB 129). The zero time irradiation reading was obtained from a blank solution that was kept in the dark, but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with air throughout each experiment, except for those which were done in the absence of air. Irradiations were carried out using a 125 W medium pressure mercury lamp. The light intensity falling on the solution was measured using a UV-light intensity detector (Lutron UV-340) and was found to be 1.60–1.86 $mW\,cm^{-2}$. IR radiation and short wavelength UV radiation were eliminated by a water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation and analysed after centrifugation.

2.3. Analysis

The decolourization was monitored by measuring the change in absorption intensity at their λ_{max} 435 nm (MY) and 629 (AB 129) [23,24] using Shimadzu UV–vis Spectrophotometer (Model 1601).

The rate constant was calculated from the plot of natural logarithm of dye concentration as a function of irradiation time.

3. Results and discussion

3.1. Photolysis of TiO_2 suspensions containing Martius Yellow (MY) and Acid Blue 129 (AB 129)

Irradiation of an aqueous solution of dyes under investigation in the presence of TiO_2 and air leads to a decrease in absorption intensity as a function of irradiation time. Fig. 1 shows the change in the concentration of MY in the presence and absence of photocatalyst as a function of time on irradiation with a Pyrex-filtered output of a 125 W medium pressure mercury lamp. Fig. 1 also shows the change in dye concentration on the irradiation of MY without bubbling of air in the presence of photocatalyst (Degussa P25). Insets A and B of this figure show the change in absorption intensity at 435 nm at different time intervals and change in colour of the dye as a function of time for irradiation of MY in the presence of TiO_2 with continuous air bubbling.

Fig. 2 shows the change in dye concentration in the presence and absence of photocatalyst (with and without air bubbling) for irradiation of AB 129 under analogous irradiation conditions. Insets A and B of this figure show the change in absorption intensity of AB 129 at 629 nm at different time intervals and change in colour of the dye as a function of time for irradiation of AB 129 in the presence of TiO_2.

It could be seen from the figure that 53% decolourization of MY and 78% decolourization of AB 129 take place after 35 and 135 min of irradiation, respectively, in the presence of TiO_2 and air. On the other hand, in the absence of photocatalyst, no observable decrease in the dye concentration could be seen. In contrast, when the irradiation of the dyes was carried out in the presence of photocatalyst without bubbling of air, a slight decrease in dye concentration was observed for both MY and AB 129 as shown in Figs. 1 and 2, respectively.

Control experiments were carried out in all cases, employing unirradiated blank solutions. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

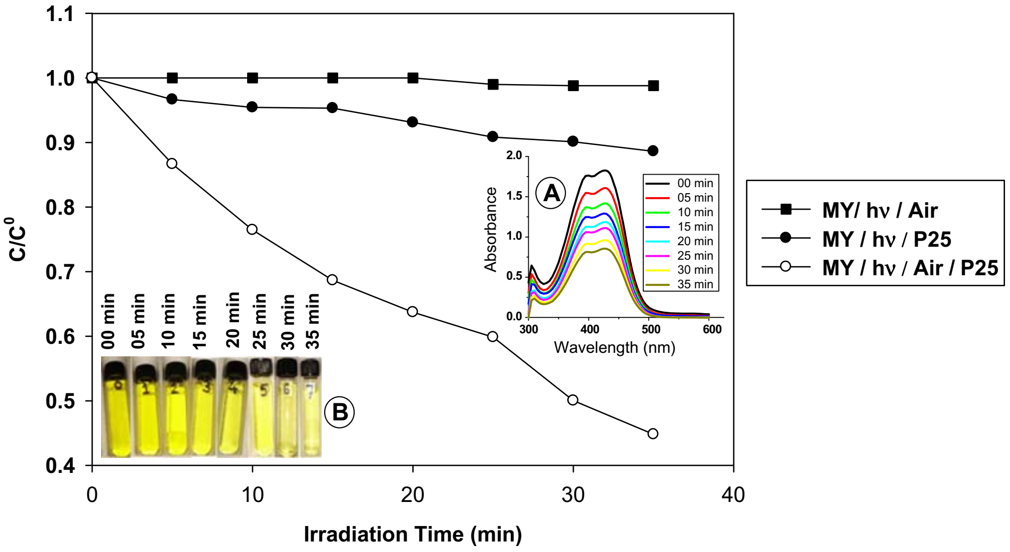


Fig. 1. Change in concentration as a function of time for irradiation of an aqueous solution of Martius Yellow (MY) in the presence and absence of photocatalyst with and without bubbling of air. Inset: (A) Change in absorbance as a function of irradiation time in the presence of photocatalyst with bubbling of air, (B) change in colour of the dye with respect to irradiation time in the presence of photocatalyst with bubbling of air. Experimental conditions: 0.20 mM MY, $V = 250$ mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 435 nm with and without bubbling of air, continuous stirring, irradiation time = 35 min.

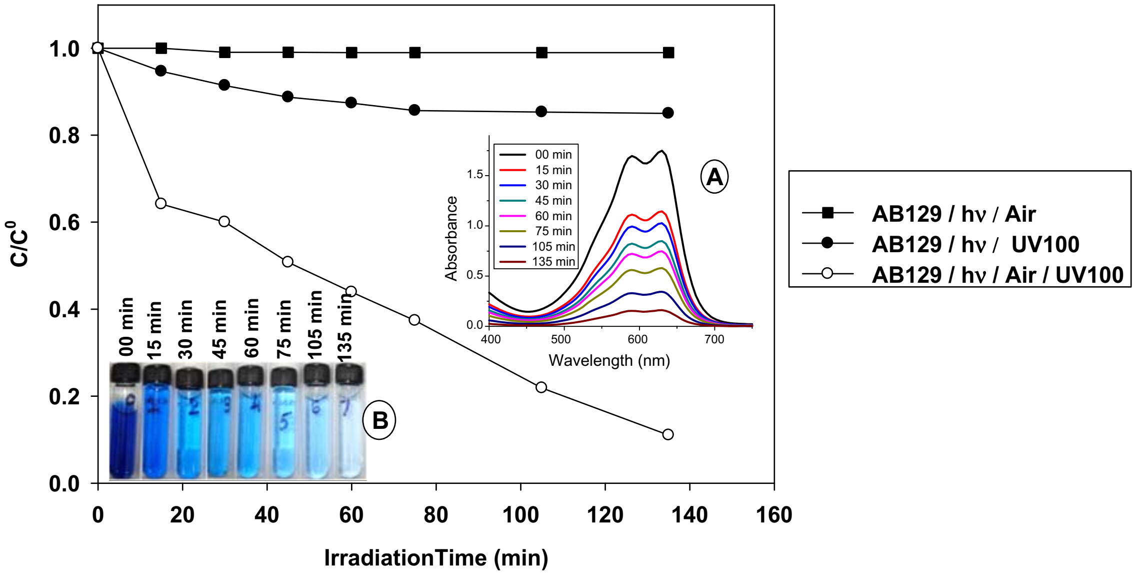


Fig. 2. Change in concentration as a function of time for irradiation of an aqueous solution of Acid Blue 129 (AB 129) in the presence and absence of photocatalyst. Inset: (A) Change in absorbance as a function of irradiation time in the presence of photocatalyst, (B) change in initial colour of the dye with respect to irradiation time in the presence of photocatalyst. Experimental conditions: 0.5 mM AB 129, $V = 250$ mL, photocatalyst: TiO_2 (UV100, 1 g L^{-1}) immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 629 nm continuous purging of air and stirring, irradiation time = 135 min.

For each experiment, the rate constant was calculated from the plot of natural logarithm of dye concentration as a function of irradiation time. The decolourization curve can be fitted reasonably well by an exponential decay curve, suggesting pseudo-first-order kinetics. The decolourization rate was calculated using the formula given below [28]:

$$-d[c]/dt = kc^n \tag{7}$$

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

3.2. Comparison of photocatalytic activity of different photocatalysts

The decolourization of MY and AB 129 was tested with three different commercially available TiO_2 powders, namely Degussa P25, Hombikat UV-100 and PC500. Fig. 3 shows the decolourization rate for the decomposition of MY and AB 129 in the presence of different photocatalysts. It has been observed that the decolourization of MY proceeds slightly faster in the presence of Degussa P25, while UV-100 shows a better decolourization rate for AB 129 as compared with other samples.

The reason for the better photocatalytic activity of Degussa P25 could be attributed to the fact that Degussa P25 is composed of small nano-crystallites of rutile dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron-hole pairs [29]. The electron transfer, from the rutile conduction band to electron traps in anatase phase, takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react [29]. The reason for better photocatalytic activity of Hombikat UV-100 is due to fast interfacial electron transfer rate [30]. For Hombikat UV-100, we would expect a higher efficiency when the adsorption/desorption of the dye derivative is relatively fast and recombination of electron and hole is prevented by the reaction of electrons with suitable electron acceptors or by reactions of the holes with adsorbed pollutants.

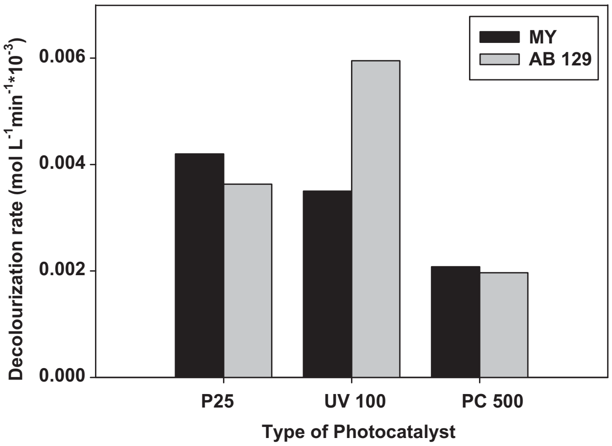


Fig. 3. Decolourization rate of MY and AB 129 in the presence of different photocatalysts. Experimental conditions: 0.20 mM MY, 0.5 mM AB 129, $V = 250$ mL, photocatalysts: TiO_2 Degussa P25 (1 g L^{-1}), Sachtleben Hombikat UV-100 (1 g L^{-1}), PC500 (1 g L^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 435 nm and 629 nm for MY and AB 129, respectively, with constant bubbling of air, continuous stirring, irradiation time = 35 min (MY) and 75 min (AB 129).

The photocatalyst Degussa P25 has been reported to degrade a large number of compounds with better effeciency [19,28,31]. On the other hand, earlier studies have also shown that Hombikat UV-100 was more effective than Degussa P25 for the degradation of Fast Green FCF [32], benzidine and 1,2-diphenyl hydrazine [33] and dichloroacetic acid [34]. These results indicate that the activity of the photocatalyst also depends on the type of the model pollutant.

In all following experiments, the photocatalyst Degussa P25 was used for the decolourization of MY and UV100 for AB 129 since this material exhibited the highest overall activity for the decolourization of dyes under investigation.

3.3. pH effect

Employing Degussa P25 as a photocatalyst for the decolourization of MY and photocatalyst Hombikat UV-100 for the decolourization of AB 129 in aqueous suspensions was studied in the pH range between 3 and 12 under UV-light radiation. Fig. 4 shows the decolourization rate for decomposition of MY and AB 129 as a function of reaction pH. The results indicate that the decolourization rate of MY was better at lower pH values, which decreases with increase in initial reaction pH and the highest efficiency was observed at pH 3.1. This could be explained on the basis of the fact that the zero point of charge (pH_{ZPC}) of Degussa P25 is at pH 6.25 [35]. Hence at pH values below 6.25, the particle surface is positively charged, while at pH values above 6.25, it is negatively charged. Due to the low pK_a value (2.12) of MY [36], the molecule will be present in its anionic form within the pH range studied. With increasing pH, the negative charges on the titanium dioxide would repel MY, and this repulsion would increase with increasing pH, resulting in a decrease in the photodecolourization efficiency.

In the case of AB 129, the decolourization rate was found to increase with increase in pH from acidic to neutral and further increase in pH leads to decrease in the decolourization rate. As we can see from the chemical structure of the AB 129 dye shown in Chart 1, the electron-donating group such as $–NH_2$ at α-position of the carbonyl group is capable of forming intramolecular hydrogen bonding at high pH values [37]. Therefore, the dye structure becomes chemically

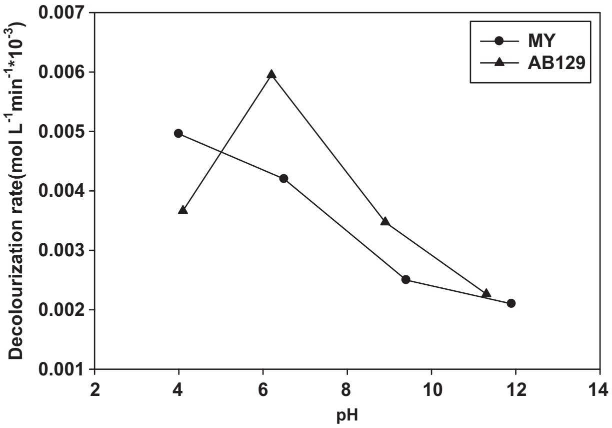


Fig. 4. Influence of pH on the decolourization rate of MY and AB 129. Experimental conditions: 0.20 mM MY, 0.5 mM AB 129, $V = 250$ mL, photocatalyst TiO_2 (Degussa P25, 1 g L^{-1}), reaction pH (3.1, 6.5, 9.4 and 11.9), for MY and (UV 100, 1 g L^{-1}), reaction pH (4.1, 6.2, 8.9, 11.3) for AB 129, immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 435 nm and 629 nm for MY and AB 129, respectively, with constant bubbling of air, continuous stirring, irradiation time = 35 min (MY) and 75 min (AB 129).

stable at high pH. The chromophores of the dye remain intact after light irradiation and hence, reduce the degradation rate of the dye [38].

3.4. Effect of dye concentration

It is important both from a mechanistic and an application point of view to study the dependence of dye concentration on the photocatalytic reaction rate. The influence of dye concentration on the decolourization rate for MY and AB 129 was studied at different concentrations varying from 0.12 to 0.25 mM and 0.2 to 0.6 mM, respectively. Table 1 shows the decolourization rate of MY and AB 129 as a function of dye concentration employing Degussa P25 (1 g L for MY) and UV100 (1 g L for AB 129). It was observed that in the case of MY the decolourization rate was found to increase with increase in dye concentration from 0.12 to 0.20 mM and further increase in dye concentration from 0.20 to 0.25 mM leads to a decrease in the decolourization rate. In the case of AB 129, the rate was found to increase with the increase in the initial concentration of the dye from 0.20 to 0.40 mM, which decreases on further increase in the dye concentration from 0.40–0.60 mM. This may be due to the fact that on increasing the dye concentrations, the colour of the stock solution becomes more and more intense, which prevents the penetration of light to the surface of the catalyst during the irradiation process. Hence, the generation of relative amount of $OH^{\bullet}$ and $O_2^{\bullet-}$ on the surface of the catalyst does not increase, as the intensity of light and irradiation time are constant. As a result, the decolourization efficiency of the dye decreases with increase in the dye concentration.

Table 1
Influence of dye concentration on the decolourization rate of MY and AB 129. Experimental conditions: $V = 250$ mL, photocatalyst: TiO_2, 1 g L^{-1} (Degussa P25 for MY and UV100 for AB 129), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 435 nm and 629 nm for MY and AB 129, respectively, with constant bubbling of air, continuous stirring, irradiation time = 35 min (MY) and 75 min (AB 129)

Dyes	Dye concentration (mM)	Decolourization rate (mol L^{-1} min^{-1} $\times 10^{-6}$)
MY	0.12	3.55
	0.15	3.81
	0.20	4.38
	0.25	3.70
AB 129	0.20	6.24
	0.40	11.28
	0.50	5.95
	0.60	3.80

3.5. Effect of catalyst concentration

The influence of photocatalyst concentration on the decolourization rate of MY and AB 129 was investigated using different concentrations of Degussa P25 (for MY) and UV100 (for AB 129) varying from 0.5 to 3 g L^{-1}. Fig. 5 shows the decolourization rate of MY and AB 129 as a function of catalyst concentration. It could be seen from the figure that the addition of photocatalyst improves the decolourization rate of the pollutant from 0.5 g L^{-1} to 1 g L^{-1} for MY and up to 2 g L^{-1} of AB 129. Further increase in the catalyst loading leads to decrease in the decolourization rate. This may be due to the fact that at higher catalyst loading, the tendency towards agglomeration (particle-to-particle interaction) also increases due to reduction in the surface area available for light absorption and hence a drop in the photocatalytic decolourization rate was observed at higher catalyst loading.

Dark adsorption of MY and AB 129 on the surface of the photocatalyst was investigated by stirring their aqueous solution of desired concentration (10 mL) in an Erlenmeyer Volumetric flask for 24 h at different catalyst loadings ranging from 0.5 to 3.0 g L^{-1}. Analysis of the samples after centrifugation indicates a maximum of 10% adsorption in MY and 8% in AB 129 on the surface of the catalyst as shown in the inset of Fig. 5.

3.6. Effect of electron acceptor

We have studied the effect of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate on the photocatalytic decolourization of dye derivative MY and AB 129.

Fig. 6 shows the decolourization rate of MY in the presence of electron acceptors such as $KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$ in aqueous solutions in the presence and absence of TiO_2 by continuous purging of air. All the additives were found to enhance the decolourization rate markedly. Fig. 7 shows the decolourization rate of AB 129 in the presence of $KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$ as electron acceptors under analogous condition. In this case, only $KBrO_3$ showed a beneficial effect on the decolourization rate, while the other two additives such as hydrogen peroxide and ammonium persulphate did not show any enhancement in the decolourization rate. Blank experiments were also carried out in the absence of TiO_2 containing additives where very low degradation rates were observed.

The electron acceptors such as hydrogen peroxide, bromate and persulphate ions are known to generate hydroxyl radical by trapping the electron from the conduction band by the mechanism shown in Eqs. (8)–(12):

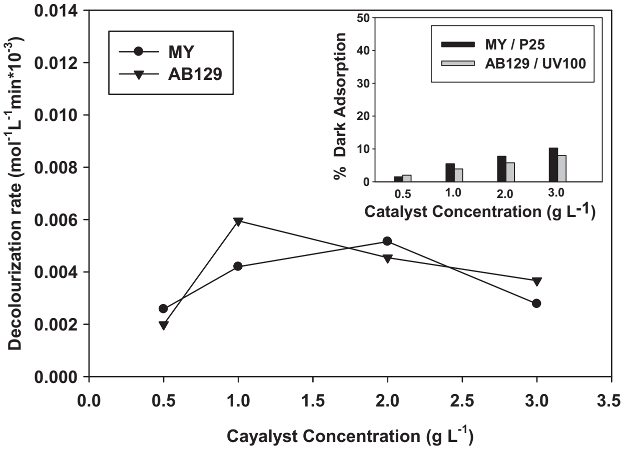


Fig. 5. Influence of catalyst concentration on the decolourization rate of MY and AB 129. Inset: Comparison of dark adsorption at different catalyst concentrations of MY and AB 129. Experimental conditions: 0.20 mM MY, 0.5 mM AB 129, $V = 250$ mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1, 2 and 3 g L^{-1}) for MY and UV100 (0.5, 1, 2 and 3 g L^{-1}), for AB 129, immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 435 nm and 629 nm for MY and AB 129, respectively, with constant bubbling of air, continuous stirring, irradiation time = 35 min (MY) and 75 min (AB 129). For dark adsorption: stirring time = 24 h.

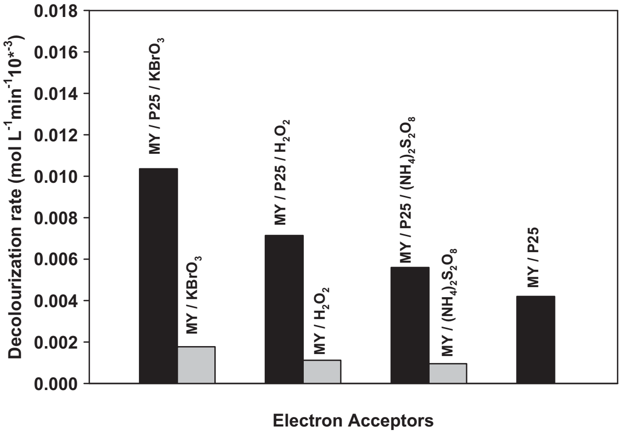


Fig. 6. Comparison of decolourization rate of MY in the presence and absence of photocatalyst containing electron acceptors $KBrO_3$, H_2O_2, and $(NH_4)_2S_2O_8$. Experimental conditions: 0.20 mM MY, $V = 250$ mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}) electron acceptor: $KBrO_3$ (3 mM), H_2O_2 (10 mM), $(NH_4)_2S_2O_8$ (3 mM), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 435 nm with constant bubbling of air, continuous stirring, irradiation time = 35 min.

$$H_2O_2 + e^-_{CB} \rightarrow OH^{\bullet} + OH^- \quad (8)$$

$$BrO_3^- + 2H^+ + e^-_{CB} \rightarrow BrO_2^{\bullet} + H_2O \quad (9)$$

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

$$S_2O_8^{2-} + e^-_{CB} \rightarrow SO_4^{2-} + SO_4^{\bullet -} \quad (11)$$

$$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^+ \quad (12)$$

The respective one-electron reduction potentials of different species are: $E(O_2/O_2^{\bullet -}) = -155$ mV, $E(H_2O_2/HO^{\bullet}) = 800$ mV, $E(BrO_3^-/BrO_2^{\bullet}) = 1{,}150$ mV and $E(S_2O_8^{2-}/SO_4^{\bullet -}) = 1{,}100$ mV [39]. From the thermodynamic point of view, all the additives should therefore be more efficient electron acceptors than molecular oxygen. The addition of bromate ions markedly enhanced the decolourization of both the dyes MY and AB 129, as they can react to a large number of electrons as shown in Eq. (10). Another possible explanation might be a change in the reaction mechanism of photocatalytic decolourization, since the reduction of bromate ions by electron does not lead

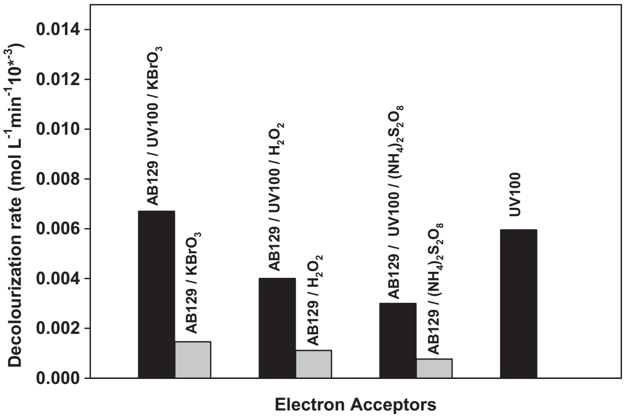


Fig. 7. Comparison of decolourization rate of AB 129 in the presence and absence of photocatalyst containing electron acceptors $KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$. Experimental conditions: 0.5 mM AB 129, $V = 250$ mL, photocatalyst: TiO_2 (UV100, 1 g L^{-1}) electron acceptor: $KBrO_3$ (3 mM), H_2O_2 (10 mM), $(NH_4)_2S_2O_8$ (3 mM), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 629 nm with constant bubbling of air, continuous stirring, irradiation time = 75 min.

directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing reagents e.g. BrO_2^- and HOBr. Furthermore, bromate ions themselves can act as oxidizing agents.

3.8. Photolysis of TiO_2 suspensions containing dye derivatives MY and AB 129 under sunlight

For practical application of wastewater treatment based on these processes, the utilization of sunlight is preferred. Hence, the aqueous suspensions of dye derivatives MY and AB 129 containing TiO_2 (Degussa P25 for MY and UV100 for AB 129) were exposed to solar radiation in the same reaction vessel under constant bubbling of air and continuous stirring. The samples were collected at different time intervals and analyzed after centrifugation. The degradation was followed by measuring the change in concentrations of MY and AB 129, using a Shimadzu UV–vis spectrophotometer (model 1601). Figs. 8 and 9 show the change in concentration as a function of irradiation time on illumination of an aqueous suspension of dye derivatives MY and AB 129, respectively, in the presence and absence of TiO_2 under sunlight and UV-light source. It was found that 38% decolourization of MY and 31% decolourization of AB 129 take place when the irradiation was carried out in the presence of sunlight.

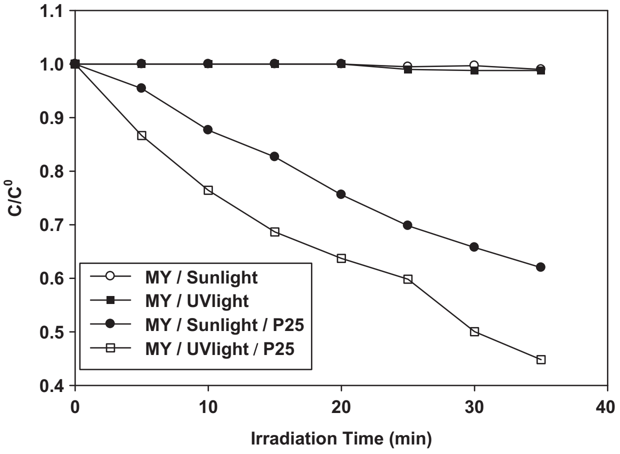


Fig. 8. Comparison of change in concentration as a function of time for irradiation of an aqueous solution of MY in the presence and absence of photocatalyst under sunlight and UV-light source. Experimental conditions: 0.20 mM MY, V = 250 mL, photocatalyst: TiO_2 (Degussa P25, 1 g L^{-1}), immersion well photoreactor, UV light source: 125 W medium pressure Hg lamp, absorbance was followed at 435 nm with constant bubbling of air, continuous stirring, irradiation time = 35 min.

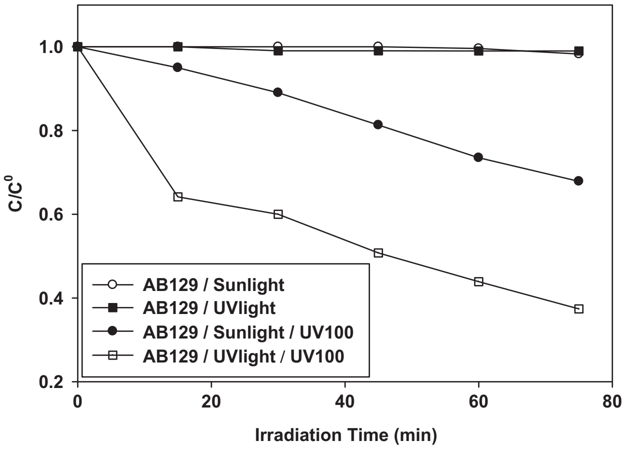


Fig. 9. Comparison of change in concentration as a function of time for irradiation of an aqueous solution of AB 129 in the presence and absence of photocatalyst under sunlight and UV light source. Experimental conditions: 0.5 mM AB 129, $V = 250$ mL, photocatalyst: TiO_2 (UV100, 1 g L^{-1}), immersion well photoreactor, UV-light source: 125 W medium pressure Hg lamp, absorbance was followed at 629 nm with constant bubbling of air, continuous stirring, irradiation time = 75 min.

4. Conclusion

TiO_2 can efficiently catalyse the photodecolourization of two textile dye derivatives Martius Yellow and Acid Blue 129 in the presence of light and air.

Conclusions derived from this study are summarized as follows.

- Degussa P25 and UV 100 were found to be more efficient photocatalysts for the decolourization of the dye derivatives MY and AB 129, respectively.
- The catalytic efficiency of TiO_2 powder for the decolourization of these dyes was enhanced by air bubbling and addition of electron acceptors.
- The decolourization of MY and AB 129 was found to be better at pH 3.1 and 6.2, respectively.
- The catalyst loading for efficient decolourization of MY and AB 129 was found to be 2 and $1\,g\,L^{-1}$, respectively.
- The decolourization rate was enhanced markedly by adding $KBrO_3$ as an electron acceptor.

The results of this study clearly demonstrate the importance of choosing the optimum decolourization parameters to obtain high decolourization rates of the model compound, which is essential for any practical application of photocatalytic oxidation processes. The best decolourization condition depends strongly on the kind of pollutant.

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