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Review

Heterogeneous photocatalysed decolorization of two selected dye derivatives neutral red and toluidine blue in aqueous suspensions

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Abstract

The photocatalysed decolorization of two selected dye derivative neutral red (**1**) and toluidine blue (**2**) has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The decolorization was studied by monitoring the change in concentration of organic dyestuff employing UV spectroscopic analysis technique as a function of irradiation time. The decolorization was investigated using various parameters such as, different types of TiO_2, reaction pH, catalyst concentration, concentration of organic dyestuffs, and in the presence of electron acceptors like hydrogen peroxide (H_2O_2) and potassium bromate ($KBrO_3$) besides molecular oxygen with an aim to determine the optimal decolorization condition for the decomposition of compounds under investigation.

Keywords: Photocatalysis; Semiconductor; Titanium dioxide; Neutral red; Toluidine blue

1. Introduction

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1–20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [1–4]. The release of those colored wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase [5–8]. Decolorization of dye effluents has therefore acquired increasing attention.

The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [6,7]. Briefly, when a semiconductor such as TiO_2 absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band ($e_{cb}{}^-$) leaving behind an electron vacancy or "hole" in the valence band ($h_{vb}{}^+$). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, $h_{vb}{}^+$ may react with surface-bound H_2O or OH^- to produce the hydroxyl radical and $e_{cb}{}^-$ is picked up by oxygen to generate superoxide radical anion ($O_2{}^{\bullet -}$), as indicated in the following Eqs. (1)–(3):

$$TiO_2 + h\upsilon \rightarrow e_{cb}{}^- + h_{vb}{}^+ \quad (1)$$

$$O_2 + e_{cb}{}^- \rightarrow O_2{}^{\bullet -} \quad (2)$$

$$H_2O + h_{vb}{}^+ \rightarrow OH^\bullet + H^+ \quad (3)$$

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

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

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

Neutral red (**1**) has been used as an indicator for determining alkalinity of water, urea, nitrite, etc. It is also used for preparing neutral red paper. The dye derivative, toluidine blue (**2**) has been

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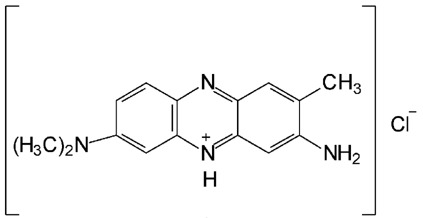
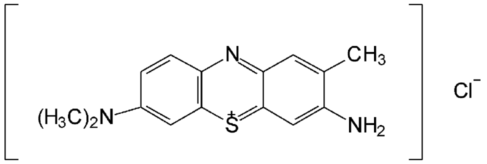


1
Neutral red



2
Toluidine blue

Chart 1.

used for direct dying, printing of wool and silk. Both the dyes are also used as a biological stain. Both the dyes are soluble in water. The solubility of toluidine blue (**2**) is 3.82 g/100 mL of water. However, no major effort has been made to study detailed decolorization kinetics of dye derivatives **1** and **2** that is essential from application point of view. With this view, we have undertaken a detailed study on the photodecolorization of neutral red (**1**) and toluidine blue (**2**) (Chart 1) sensitized by TiO_2 in aqueous solution under a variety of conditions.

2. Experimental

2.1. Reagents and chemicals

Reagent grade neutral red (**1**) was obtained from Hi-Media Labs Pvt. Ltd., Bombay, India, whereas toluidine blue (**2**) was obtained from Aldrich. These compounds were used as such without any further purification. The photocatalyst, titanium dioxide Degussa P25 (Degussa AG), was used in most of the experiment, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH), PC500 (Millennium Inorganic Chemicals) and TTP (Travancore Titanium Products, India) were used for comparative studies. 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 [9]. Hombikat UV100 consist of 100% anatase with a specific BET-surface area $>250\,m^2\,g^{-1}$ and primary particle size of 5 nm [10]. 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 [11]. The other chemical used in this study such as NaOH, HNO_3, H_2O_2 and $KBrO_3$ were obtained from Merck.

2.2. Analysis

The photocatalytic decolorization of the dye derivatives was monitored using UV spectroscopic analysis technique (Shimadzu UV–Vis 1601). The double beam spectrophotometer has an in-built tungsten and deuterium lamps, which provide the measurement of optical density (OD) in the range 200–1100 nm (near UV and visible regions). The samples were analysed using quartz cuvette, as it has zero absorption in the above wavelength regions. The change in absorbance of the dye derivatives **1** and **2** was followed at their λ_{max} as a function of irradiation time after centrifugation.

3. Results and discussions

3.1. Photocatalysis of neutral red (*1*) and toluidine blue (*2*) in aqueous suspensions of TiO_2

Irradiation of an aqueous solution of desired concentration of compounds neutral red (NR, **1**) and toluidine blue (TB, **2**) in the presence of the photocatalyst (TiO_2, Degussa P25, $1\,g\,L^{-1}$) by the pyrex filtered output of a 125 W medium pressure mercury lamp under oxygen atmosphere lead to the decrease in the absorption intensity as a function of time. Fig. 1 shows the change in the absorption intensity as a function of irradiation time for an aqueous suspension of neutral red (**1**) and toluidine blue (**2**) respectively. After centrifugation the decolorization of compounds **1** and **2** were followed at 530 and 640 nm by diluting it to 80%. Control experiments were carried out in the absence of photocatalyst where negligible loss of the compounds was observed as shown in the figures. The decolorization curves can be fitted reasonably well by an exponential decay curves suggesting the first-order kinetics. The decolorization rates for the decomposition of compounds **1** and **2** were calculated in terms of $M\,min^{-1}$. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions. For each experiment, the rate constant was calculated from the linear regression of the plot of natural logarithm of absorption intensity as a function of irradiation time, i.e., first-order kinetics. The decolorization rate for the decomposition of compounds under investigation were

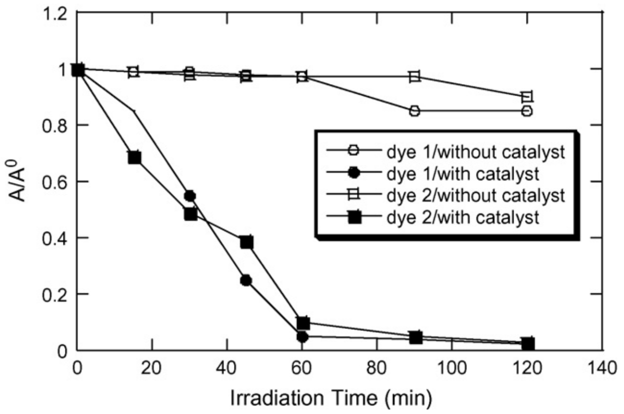


Fig. 1. Change in absorption intensity at 530 and 640 nm as a function of irradiation time for the photocatalysed decolorization of neutral red (**1**) and toluidine blue (**2**) in the presence and absence of TiO_2 in the aqueous suspensions. *Experimental conditions*: Neutral red and toluidine blue (0.5 mM), pH 5.0, $V = 250$ mL, photocatalyst: TiO_2 Degussa P25 ($1\,g\,L^{-1}$), 125 W medium pressure Hg lamp, irradiation time = 120 min.

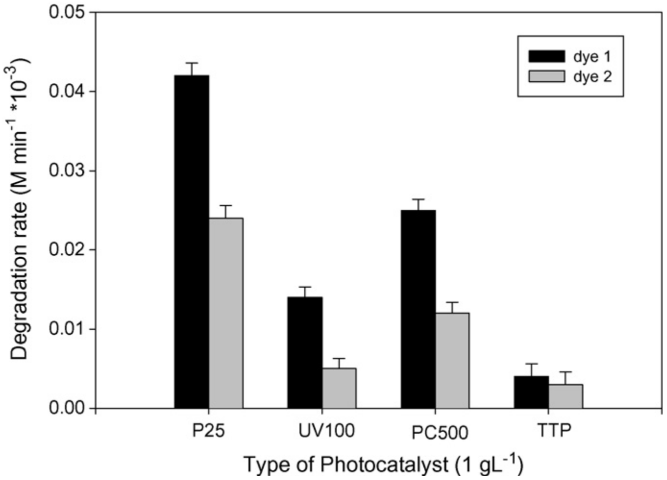


Fig. 2. Comparison of decolorization rate for the decomposition of neutral red (**1**) and toluidine blue (**2**) in the presence of different photocatalysts. *Experimental conditions*: Neutral red and toluidine blue (0.5 mM), pH 5.0, photocatalyst: TiO_2 Degussa P25 ($1\,g\,L^{-1}$), Hombikat UV100 ($1\,g\,L^{-1}$), PC500 ($1\,g\,L^{-1}$), irradiation time = 120 min.

calculated using expressions given below,

$$-\frac{d[A]}{dt} = kc^n \tag{6}$$

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

3.2. Comparison of different photocatalysts

The photodecolorization of compounds, neutral red (**1**) and toluidine blue (**2**) was tested with four different TiO_2 powders, namely, Degussa P25, Hombikat UV100, PC500 and TTP. The decolorization rate for the decomposition of compounds **1** and **2** in the presence of different types of TiO_2 powders is shown in Fig. 2.

It has been observed that the decolorization of both the pollutants proceed much more rapidly in the presence of Degussa P25 as compared with other TiO_2 samples under UV light source.

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 have also shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds [12–14]. Also Lindner et al. [15] showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. On the other hand, Hombikat UV100 was found to be better for the degradation of benzidine and 1,2-diphenyl hydrazine and remazol brilliant blue R as reported earlier [16,17]. The explanation for the greater photo effectiveness of mixed phase titania photocatalyst (here Degussa 25) could be due to three factors (1) the smaller band gap of rutile extends the useful range of photoactivity into the visible region. (2) The stabilization of charge separation by electron transfer from rutile to anatase slows the recombination. (3) The small size of the rutile crystallites facilitates the electron transfer [18].

3.3. Effect of pH

The photocatalytic decolorization of the compounds, **1** and **2** under investigations were also studied in the pH range between 3 and 9.

The decolorization rate for the decomposition of compounds, **1** and **2** as a function of reaction pH is shown in Fig. 3. It is interesting to note that the decolorization rate for the decomposition of the compounds increases significantly with the increase in the reaction pH.

The interpretation of pH effect on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as show in following equations:

$$\mathrm{TiOH} + \mathrm{H}^+ \rightarrow \mathrm{TiOH_2}^+ \tag{7}$$

$$\mathrm{TiOH} + \mathrm{OH}^- \rightarrow \mathrm{TiO}^- + \mathrm{H_2O} \tag{8}$$

The point of zero charge (pzc) of the TiO_2 (Degussa P25) is widely reported at pH ~6.25 [19]. Thus, the TiO_2 surface will remain positively charged in acidic medium (pH <6.25) and negatively charged in alkaline medium (pH >6.25). In this study it has been shown that the decolorization rate for the both model compounds under investigation is strongly influenced by the reaction pH. The efficiency of decolorization rate for the decomposition of the dye **1** and **2** was found to increase with increase in pH, from 3 to 9 and highest efficiency was observed at alkaline pH value as shown in Fig. 3. The better rate at higher pH 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

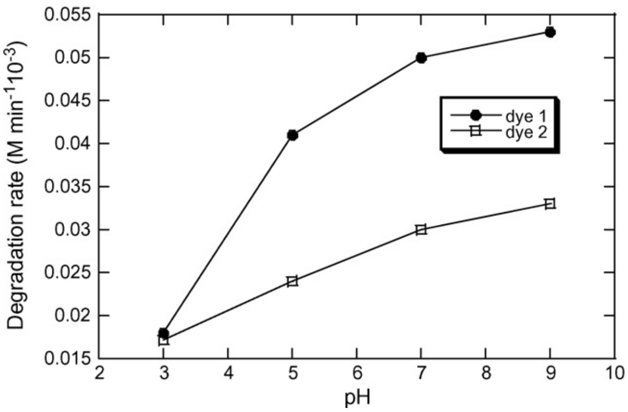


Fig. 3. Influence of pH on the decolorization rate for the decomposition of neutral red (**1**) and toluidine blue (**2**). *Experimental conditions*: Neutral red and toluidine blue (0.5 mM), photocatalysts: TiO_2 Degussa P25 ($1\,g\,L^{-1}$), irradiation time = 120 min.

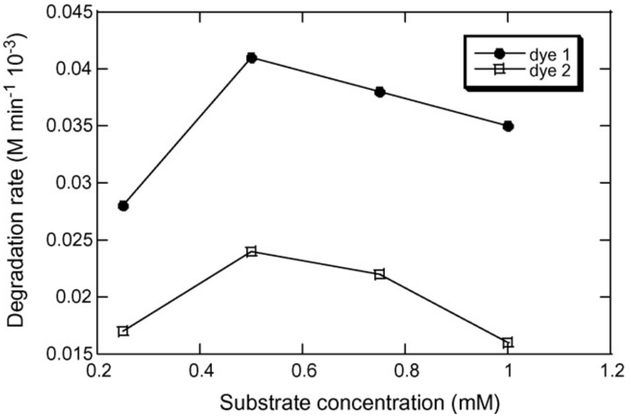


Fig. 4. Influence of concentration of organic dyestuff on the decolorization rate for the decomposition of neutral red (**1**) and toluidine blue (**2**). *Experimental conditions*: Photocatalyst: TiO_2 Degussa P25 ($1\,g\,L^{-1}$), pH 5.0, concentration of organic dyestuff (0.25, 0.5, 0.75 and 1.0 mM), irradiation time = 120 min.

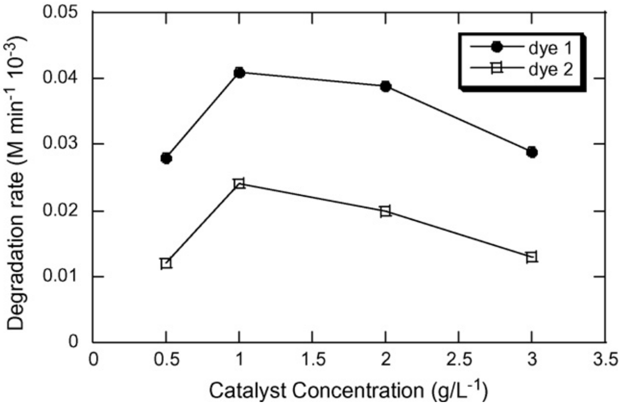


Fig. 5. Influence of catalyst concentration on the decolorization rate for the decomposition of neutral red (**1**) and toluidine blue (**2**). *Experimental conditions*: Neutral red and toluidine blue (0.5 mM), pH 5.0, photocatalysts: TiO_2 Degussa P25, catalyst concentrations (0.50, 1.0, 2.0 and $3.0\,g\,L^{-1}$), irradiation time = 120 min.

radicals have to diffuse away and degrade the dye in the bulk solution.

3.4. *Influence of concentration of organic dyestuff*

It is important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the initial concentration of organic dyestuff. Hence the effect of initial concentration of organic dyestuff on the decolorization of compounds **1** and **2** was studied at different initial concentration of organic dyestuffs in the range of 0.25–1.0 mM. Fig. 4 shows the decolorization rate for the decomposition of **1** and **2** as a function of concentration of organic dyestuff in the presence of Degussa P25 as a photocatalyst.

The decolorization rate for both the compounds was found to increase with the increase in the initial concentration of organic dyestuffs from 0.25 to 0.5 mM and a further increase in concentration of organic dyestuff, the rates were found to decrease. This may be due to the fact that as the initial concentrations of the dye increases, the color of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generation of relative amount of $OH^{\bullet}$ and $O_2^{\bullet -}$ on the surface of the catalyst do not increase as the intensity of light and irradiation times 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 decolorization efficiency of the dye decreases as the dye concentration increases.

3.5. *Effect of catalyst concentration*

The influence of the photocatalyst concentrations on the decolorization rates for the compounds **1** and **2** was also investigated in the range between 0.5 and $3\,g\,L^{-1}$. Decolorization rate for the decomposition of compounds **1** and **2** in the presence of different concentrations of Degussa P25 is shown in Fig. 5. The rates were found to enhance with the increase in catalyst concentration from 0.5 to $1\,g\,L^{-1}$ and a further increase in catalyst loading lead to decrease in the decolorization rates of the compounds. This may be due to the fact that at high TiO_2 concentrations, particles aggregate, which reduces the interfacial area between the reaction solution and the catalyst. Thus, they decrease the number of active sites on the surface. Light scattering by the particles and the increase in opacity may be the other reason for the decrease in the decolorization rate.

3.6. *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 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, i.e., (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds and (4) to avoid problems caused by low oxygen concentration. In highly toxic wastewater where the decolorization of organic pollutants is the major concern, the addition of electron acceptors to enhance the decolorization rate may often be justified. With this view, we have studied the effect of electron acceptors such as potassium bromate and hydrogen peroxide in presence of TiO_2 and air on the decolorization of the dyes under investigation.

The effect of electron acceptors such as hydrogen peroxide and potassium bromate in addition to molecular oxygen was studied on the decolorization kinetics of compounds **1** and **2** in the presence of Degussa P25. Fig. 6 shows the decolorization rate for the decomposition of compounds, **1** and **2** in the presence of two different electron acceptors in addition to molecular oxygen. As expected both the additives showed beneficial effect on the decolorization rate of the compounds under investigation.

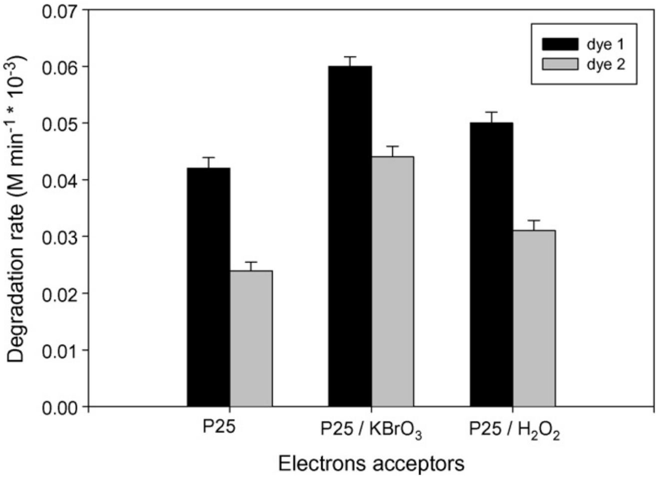


Fig. 6. Decolorization rate for the decomposition of neutral red (**1**) and toluidine blue (**2**) in the presence of electron acceptors. *Experimental conditions*: Neutral red and toluidine blue (0.5 mM), pH 5.0, photocatalysts: TiO_2 Degussa P25 (1 g L^{-1}), H_2O_2 and $KBrO_3$ concentrations (3 mM), irradiation time = 120 min.

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

$$H_2O_2 + e_{CB}{}^- \rightarrow OH^\bullet + OH^- \tag{9}$$

$$BrO_3{}^- + 2H^+ + e_{CB}{}^- \rightarrow BrO_2{}^\bullet + H_2O \tag{10}$$

$$BrO_3{}^- + 6H^+ + 6e_{CB}{}^- \rightarrow [BrO_2{}^-, HOBr] \rightarrow Br^- + 3H_2O \tag{11}$$

The respective one-electron reduction potentials of different species are: $E(O_2/O_2{}^{\bullet-}) = -155$ mV, $E(H_2O_2/OH^\bullet) = 800$ mV and $E(BrO_3{}^-/BrO_2{}^\bullet) = 1150$ mV [20]. From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen and as explained both additives enhanced the rate as shown in Fig. 6.

Simultaneously the experiments in the presence of electrons acceptors such as $KBrO_3$ and H_2O_2 without photocatalyst were carried out. These experiments show the decolorization of the dye with respect to time but the decolorization rate was found to be better when the photocatalyst was added along with the electrons acceptors as compared to the decolorization rate when only electron acceptors are added.

4. Conclusion

The results of these studies clearly indicate that TiO_2 can efficiently catalyze the decolorization of organic compounds in the presence of light and oxygen. The results also indicate that decolorization rate could be influenced by a number of parameters such as type of photocatalyst, pH, concentration of organic dyestuff and catalyst concentration and in the presence of electron acceptors. The TiO_2 sample obtained from Degussa P25 was found to be more efficient photocatalyst for the decolorization of both the compounds studied neutral red and toluidine blue were found to degrade faster under alkaline pH range. Our results also suggests that catalyst concentration 1–2 g L^{-1} would give better results as compared to higher catalyst concentrations and electron acceptors such as bromate ions and hydrogen peroxide can enhance the decolorization.

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