The effect of operational parameters on the photoinduced decoloration of dyes using a hybrid catalyst V_2O_5/TiO_2

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Abstract

The decoloration of three dyes namely Toludine Blue, Safranin Orange and Crystal Violet was studied in the presence of UV radiation using a heterogeneous hybrid catalyst, namely titanium oxide impregnated with vanadium oxide. The advantage of using a hybrid catalyst lies in the fact that the decoloration increased by more than five times as compared to in a neat catalyst. The influence of operational parameters, such as dye concentration, amount of catalyst and pH of the solution were thus determined for dye decoloration using a hybrid catalyst. Rate of photoinduced catalytic decoloration was calculated from the observed absorption changes and the induced effects were explained on a mechanistic model involving the generation of $^\bullet OH$ radicals which are responsible for the decoloration of dye solution. The kinetic data fitted well to pseudo first order equation and the Langmuir–Hinshelwood model. Dye decoloration was also investigated in the presence of some ions and their role was discussed in terms of chemical reactions.
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1. Introduction

The effluents of many industrial activities such as paper and pulp manufacturing, dyeing of cloth, leather treatment, printing, etc. contain substantial amount of organic dye macromolecules. Since some of these dyes are toxic in nature, their removal from the industrial effluents is a major environmental problem [1–4]. The wastewater which is colored in the presence of these dyes can block both sunlight and oxygen penetration, which are essential for aquatic life. Besides this, some dyes in particular can undergo anaerobic decoloration to potentially carcinogenic amines [5]. Consequently there is a considerable need to treat these colored effluents before discharging them to various water bodies. Literature review on this subject matter has revealed the importance of various approaches to handle such effluents. These include biodecoloration, photocatalytic, photolytic and advanced oxidative decoloration of various dye solutions [6–9]. Semiconductors such as TiO_2, ZnO, Fe_2O_3, CdS, ZnS and V_2O_5 have been reported in the literature for their use in reducing color of the dye solutions [10,11]. The major advantage in using these materials in decoloration of dye solutions is that they all absorb energy and as a result of subsequent reactions produce $^\bullet OH$ radicals which are a strong oxidizing reagent and can attack organic molecules. The detailed mechanism is narrated in the relevant section of this paper. However, limited literature is available on the use of impregnated forms of catalysts for decomposing dye solutions. The purpose of this study is to focus attention on the photocatalytic decoloration of three different dyes namely, Toludine Blue, Safranin Orange and Crystal Violet in the presence of hybrid catalyst (impregnated form of a catalyst), namely V_2O_5/TiO_2 and UV light, and the various factors which effect the percentage decoloration. The results were also subjected to kinetic analysis.

2. Experimental

2.1. Materials

The dyes under investigation namely Toludine Blue, Safranin Orange and Crystal Violet with a labeled purity of more than 90% were obtained from either Sigma or Aldrich and used as such. Deionized water was used to make the dye solutions of desired concentration. The primary catalyst namely Titanium oxide was Degussa P-25 and it was mainly in the anatase form

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(approximately 75% anatase and 25% rutile). The BET surface area of the catalyst was found to be 50 m^2/g by using the nitrogen adsorption method.

The primary catalyst was loaded with 2% vanadium oxide, and used to study the effect on dye decoloration. The V$_2$O$_5$/TiO$_2$ catalyst was prepared by incipient wetness impregnation technique using ammonium meta-vanadate as a precursor. The nominal surface coverage in this case was 33%. The concentration of the catalyst in all the dye solutions for this work was kept constant at 10 mg/20 mL of dye solution unless otherwise stated. This value was chosen so as to avoid the opacity of the solution and also to avoid the possibility of light scattering and thereby decreasing the amount of light passing through the solution.

2.2. Preparation of samples and decoloration studies

Dye stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water in a 250 mL flask. Necessary dilutions of this stock were done with deionized water. A 0.01 g of the catalyst (V$_2$O$_5$/TiO$_2$) was added to 20 mL of this diluted solution. The contents of the dye solution were allowed to equilibrate for a given time (usually 15–30 min) in the dark before irradiating with a UV light of 254 nm for a given period of time. During irradiation, the contents of the solution were agitated continuously so as to maintain a homogeneous environment. After a certain time interval, the cell was drawn away from the UV light and centrifuged and the absorbance of the supernatant solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the rate of decoloration. UV/vis studies were done on a CARRY UV/vis spectrophotometer, using a 1 cm quartz cell. For photolytic experiments, the samples were irradiated with a UV lamp (UVGL-58, J-129, Upland make). The instrument operates at 0.12 A with a UV output at 365 and 254 nm, however, the lamp was used in the 254 nm output mode for these studies.

3. Results and discussion

In the present work, decoloration and kinetic behavior of three dyes namely Toludine Blue, Safranin Orange and Crystal Violet, was investigated. The structure of the three dyes is given in Fig. 1. The λ_{max} values for these dyes are as follows: Toludine Blue (TB) = 623 nm Safranin Orange (SO) = 530 nm and Crystal Violet (CV) = 593 nm. For decoloration studies, the λ_{max} of each dye was chosen for further investigations. Initially, experiments were carried out in the absence and presence of either UV light or the catalyst alone. The result showed that UV light alone was not sufficient for the decoloration of this dye.

3.1. Decoloration of dye solution

Dye solution of known concentration was prepared in water and subjected to UV light in the presence of a given amount of a catalyst. The change in the absorption spectra of the dye solution was monitored at regular intervals of time. It was noted that the absorption value of dye became less with irradiation time,
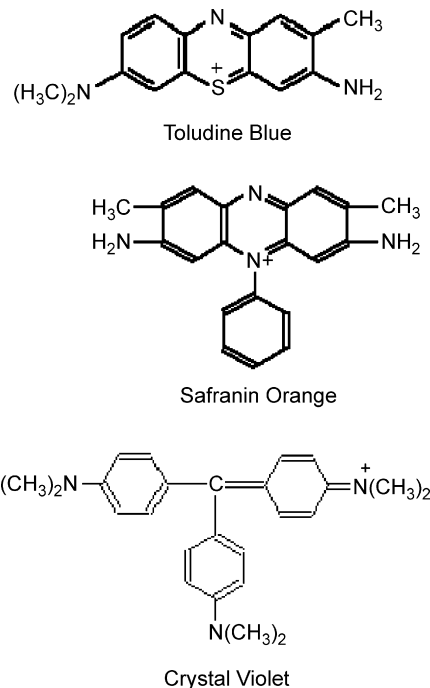

Fig. 1. Chemical structures of Toludine Blue, Safranin Orange and Crystal Violet.

thus indicating the decoloration of dye solution. The decrease in absorption value of dye solution can be related in terms of percentage decoloration as follows:

$$\%\text{decrease in absorption} = \left(1 - \frac{A_f}{A_i}\right) \times 100 \qquad (1)$$

where A_i and A_f are the initial and the final absorption values. The evolution of absorption for the decoloration of the dye solution as a function of irradiation time is shown in Fig. 2.
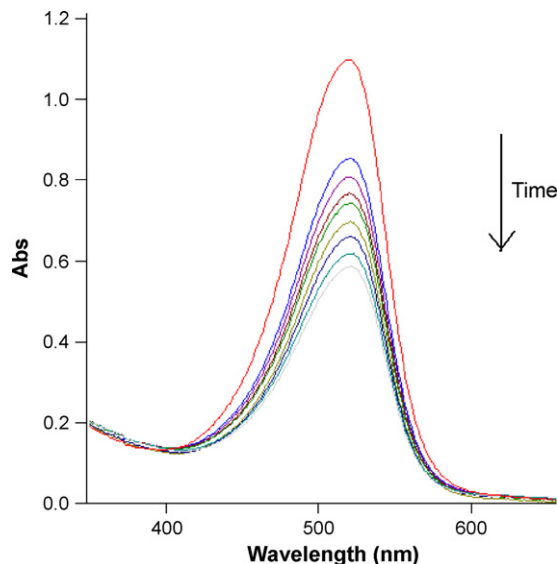

Fig. 2. Representative spectra showing change in absorbance values of dye solution with time in the presence of a catalyst.

3.2. Mechanism of dye decoloration

The photocatalytic decoloration of dye is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this phenomenon, an electron-hole pair is produced [12]
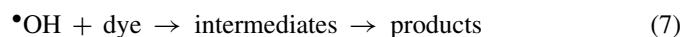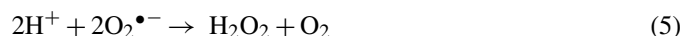
$$\text{Catalyst} + h\nu \rightarrow \ e_{cb}^- + h_{vb}^+ \tag{2}$$
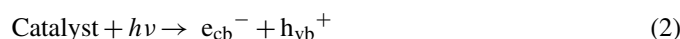
where e_{cb}^- and h_{vb}^+ are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases h_{vb}^+ can react easily with surface bound H_2O molecules to produce $^\bullet OH$ radicals, whereas, e_{cb}^- can react with O_2 to produce superoxide radical anion of oxygen.

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

$$O_2 + e_{cb}^- \rightarrow \ O_2^{\bullet -} \tag{4}$$

This reaction prevents the combination of the electron and the hole which are produced in the first step.

The $O_2^{\bullet -}$ produced in the above manner can then react with H^+ to produce H_2O_2 which again in turn can produce $^\bullet OH$ and these can react with dye and is thus responsible for its decoloration [13]

$$2H^+ + 2O_2^{\bullet -} \rightarrow \ H_2O_2 + O_2 \tag{5}$$

$$H_2O_2 + h\nu \rightarrow \ 2^\bullet OH \tag{6}$$

$$^\bullet OH + \text{dye} \ \rightarrow \ \text{intermediates} \rightarrow \ \text{products} \tag{7}$$

3.3. Effect of dye concentration, catalyst amount and pH

The dye concentration and amount of catalyst were changed to see the effect on decoloration of dye solution. It was observed that percentage decoloration decreased with increasing amount of dye concentration, while keeping a fixed amount of catalyst in these studies. The decoloration percentage values for the dyes increased when dye concentration was less in solution as shown in Table 1. This can be rationalized on the basis that as dye concentration increases, less number of photons are available to reach the catalyst surface thus causing an inhibition in decoloration percentage. Likewise, when catalyst amount was altered in the solution containing a fixed amount of dye concentration, the decoloration percentage increased with the catalyst amount, however, beyond a certain amount, this value started decreasing. Table 2 summarizes this trend for all the dyes. The increase in catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the number of $^\bullet OH$ radicals which can take part in actual decoloration of dye solution. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage decoloration starts decreasing. Since pH of the solution can have a great impact on decoloration, it is necessary to check the effect of pH on % decoloration. In this regard the solution pH was changed by adding small volumes of either HCl or NaOH solution. The solution was then charged with the catalyst and irradiated in the usual way. Percentage decoloration was calculated after a given interval of time. It was found that the dye decolorized more in neat solution as compared to in acidic or basic media. The results are shown in Table 3. It was also interesting to note that dye decoloration was very less when only TiO_2 was used as a catalyst instead of V_2O_5/TiO_2, e.g., in the case of Toludine Blue

Table 1

Apparent rate constants and percentage decoloration of dye solution (amount of V_2O_5/TiO_2 = 10 mg/20 mL, irradiation time = 20 min)

[Dye] (μM)	TB		SO		CV	
	k_{app} (min^{-1})	% decoloration	k_{app} (min^{-1})	% decoloration	k_{app} (min^{-1})	% decoloration
80	0.0065	15	0.0063	8.0	–	–
70	0.0070	22	–	–	–	–
60	0.0076	30	–	–	–	–
50	0.0412	57	–	–	–	–
40	–	–	0.0124	13.5	0.0039	6.5
30	–	–	0.0190	15.5	0.0067	8
20	–	–	0.0240	16.5	0.0106	19

Table 2

Effect of V_2O_5/TiO_2 on % decoloration of dye solution in the presence of UV (concentration of TB = SO = 80 μM, CV = 40 μM, irradiation time = 20 min)

Dye	V_2O_5/TiO_2 (mg/20 mL)				
	10	20	25	30	40
TB	15	40	47	41	27
SO	8	11	21	12	–
CV	6.5	12	–	17	15

Table 3
Effect of pH on % decoloration of dyes[a]

TB		SO		CV	
pH	% decoloration	pH	% decoloration	pH	% decoloration
3.6	22	3.5	10	4.1	3
5	7	4	8	4.3	5
6.1 (Neat dye)	40	6.2 (Neat dye)	21	6.1 (Neat dye)	17
10	18	10.5	16	9.1	11
10.5	8	–	–	9.3	6

[a] $[TB] = 80\,\mu M$, $V_2O_5/TiO_2 = 20\,mg/20\,mL$; $[SO] = 80\,\mu M$, $V_2O_5/TiO_2 = 25\,mg/20\,mL$; $[CV] = 40\,\mu M$, $V_2O_5/TiO_2 = 30\,mg/20\,mL$.

the % decoloration was 40% in the presence of V_2O_5/TiO_2, but this value was only 7% in the presence of TiO_2 under similar conditions. Similar trend was observed for the other two dyes. Thus the impregnated form of a catalyst is more efficient for dye decoloration.

3.4. Kinetics of photocatalytic decoloration

The decoloration of dye solutions was also subjected to kinetic analysis. Firstly, the data was subjected to first order kinetics, which in its usual form is given by

$$\ln\left(\frac{C_0}{C}\right) = k_{app}t \tag{8}$$

where C_0 is the equilibrium concentration value of the dye, C the concentration at time t and k_{app} is the apparent rate constant. It was found that for all dyes, the absorption data fitted well to the above kinetic equation as shown in Fig. 3. The apparent rate constant values and % decoloration for various concentrations of the dyes used in this work are given in Table 1. One can see from this table that k_{app} decreases and % decoloration increases with increasing concentration of dye solution. These changes are seen most in the case of TB and least for CV. Thus TB is more prone to oxidative changes as compared to other dyes studied in this work.

In terms of heterogeneous photocatalysis, the kinetic data can be further analyzed by using the normalized form of Langmuir–Hinshelwood (L-H) model which describes the solid–liquid reaction successfully. This model assumes that the dye is strongly adsorbed on the catalytic surface and that the surface reaction is directly proportional to the surface coverage of the dye. The normalized L-H kinetic expression is
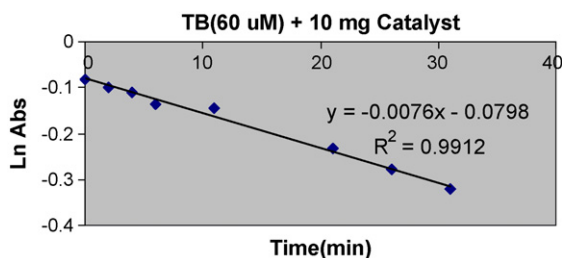

Fig. 3. First order kinetics of TB decoloration in the presence of V_2O_5/TiO_2 (similar trends were obtained for other dyes).

Table 4
Application of Langmuir–Hinshelwood model to the kinetic behavior of dye decoloration

| Dye	k_T (mg/L min)	k_a (L/mg)	R^2
Toluidine Blue	0.274	0.003	0.991
Safranin Orange	0.456	0.002	0.970
Crystal Violet	0.09	0.011	0.993

given by [14]

$$\frac{1}{r} = \frac{1}{k_T k_a C} + \frac{1}{k_T} \tag{9}$$

where $1/r$ is reciprocal value of the initial rate, C dye concentration at time t, k_T the specific reaction rate constant for the oxidation of the reactant and k_a is the equilibrium constant of the reactant. A linear fitting of the data for all the dyes to the above equation confirmed the applicability of this model with reasonable correlation coefficient values as shown in Table 4. The plot for the dyes is shown in Fig. 4A–C.

3.5. Effect of additives on dye decoloration

The decoloration of dyes was also investigated in the presence of certain ions which are generally present in dye wastewater. Among the ions chosen for this purpose were Fe^{2+}, Zn^{2+}, Ag^+, Na^+, Cl^-, PO_4^{3-}, SO_4^{2-}, BrO_3^-, CO_3^{2-}, HCO_3^- and persulphate ions. These ions were individually added to the dye solution along with the catalyst. The other experimental conditions were kept the same as for neat dye decoloration study. Each of these added ions caused a certain decrease in percentage decoloration of the dye solution. The results of this study are shown in Table 5. The change in dye decoloration in the presence of some selective ions is explained below on the basis of their chemical reactions in solution, for example, Fe^{2+} ions most likely undergoes the following chemical reaction in solution with •OH radicals already produced in solution.

$$\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \tag{10}$$
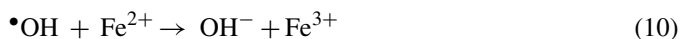
The above reaction has an appreciably high rate constant value of $3.5 \times 10^8\,M^{-1}\,s^{-1}$ [15]. Thus in the presence of Fe^{2+}, •OH radicals are easily converted into OH^-, thereby decreasing their concentration and thus less decoloration of dye solution is observed.

Likewise, the presence of CO_3^{2-} and HCO_3^- ions were also investigated in terms of their role on dye decoloration.
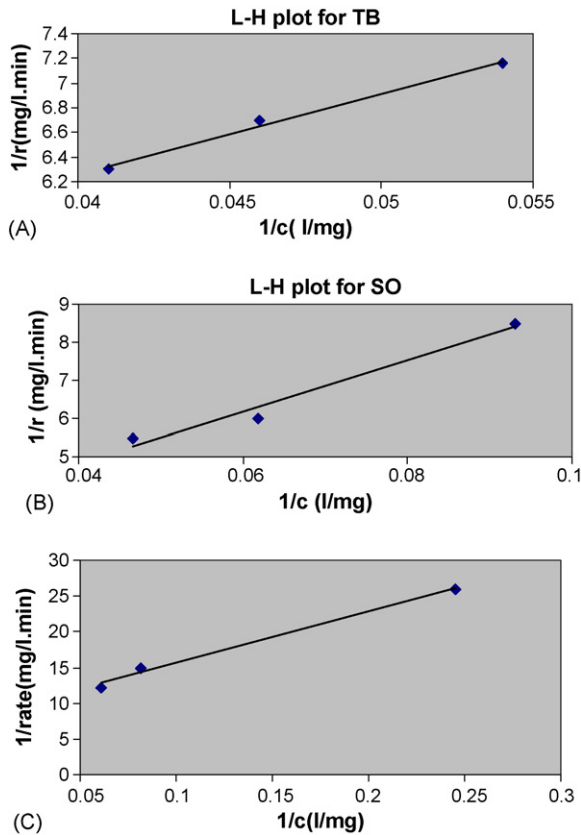
Fig. 4. (A) Langmuir–Hinshelwood plot for Toludine Blue. (B) Langmuir–Hinshelwood plot for Safranin Orange. (C) Langmuir–Hinshelwood plot for Crystal Violet.
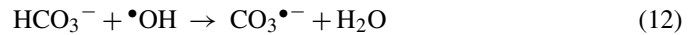
These ions are usually added to the dye bath to adjust the pH of the dye solution. In the presence of these ions, dye decoloration decreased slightly. This can be explained on the basis that the presence of these ions scavenge the $^\bullet$OH radicals according to the following reactions thus causing a decrease in

Table 5
Change in percent decoloration of dye solution in the presence of various ions (ion concentration = 50 mg/L, irradiation time = 20 min)[a]
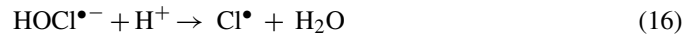
[Ions]	% decoloration		
	TB	SO	CV
–	40	21	17
Fe^{2+}	6	3.5	8.5
Zn^{2+}	11	–	7.5
Ag^+	23	7.5	10
CO_3^{2-}	23	7	10
HCO_3^-	23	12.5	10
Cl^-	11	9	15
BrO_3^-	29	–	9.5
$S_2O_8^{2-}$	12	11	12
SO_4^{2-}	38	9	12.5
PO_4^{3-}	33	17	9
NO_3^-	24	10	13

[a] The studies correspond to [TB] = 80 μM, V_2O_5/TiO_2 = 20 mg/20 mL; [SO] = 80 μM, V_2O_5/TiO_2 = 25 mg/20 mL; [CV] = 40 μM, V_2O_5/TiO_2 = 30 mg/20 mL.

percentage decoloration.

$$CO_3^{2-} + {}^\bullet OH \rightarrow CO_3^{\bullet -} + OH^- \qquad (11)$$

$$HCO_3^- + {}^\bullet OH \rightarrow CO_3^{\bullet -} + H_2O \qquad (12)$$

Similarly, the decrease in decoloration value in the presence of Cl^- is due to its hole and hydroxyl radical scavenging effect, which occurs as follows:

$$Cl^- + h_{VB}^+ \rightarrow Cl^\bullet \qquad (13)$$

$$Cl^- + Cl^\bullet \rightarrow Cl^{\bullet -} \qquad (14)$$

$$^\bullet OH + Cl^- \rightarrow HOCl^{\bullet -} \qquad (15)$$

$$HOCl^{\bullet -} + H^+ \rightarrow Cl^\bullet + H_2O \qquad (16)$$

The presence of sulphate ions in solution can cause a slight decrease in percentage decoloration because these ions can react with $^\bullet$OH radicals in solution and result in their depletion as follows [16]:

$$SO_4^{2-} + {}^\bullet OH \rightarrow SO_4^{\bullet -} + OH^- \qquad (17)$$

Addition of a strong oxidizing agent such as persulphate ions ($S_2O_8^{2-}$) also decreases the decoloration percentage because of the reason that it can produce sulphate ions in solution.

$$S_2O_8^{2-} + e_{cb}^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} \qquad (18)$$

The sulphate ions can then react with $^\bullet$OH radicals as shown in reaction (17). The sulphate radical ions can further react with water molecules to produce more sulphate ions as follows:

$$SO_4^{\bullet -} + H_2O \rightarrow {}^\bullet OH + SO_4^{2-} + H^+ \qquad (19)$$
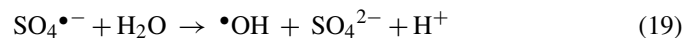
Since $SO_4^{\bullet -}$ is less reactive than $^\bullet$OH radicals, therefore SO_4^{2-} concentration increases in solution which leads to less dye decoloration.

The addition of bromate ion (BrO_3^-) also decreased the percentage decoloration. This can be explained on the basis that BrO_3^- is an efficient electron scavenger and can react in the solution as follows:

$$BrO_3^- + 6e_{cb}^- + 6H^+ \rightarrow Br^- + 3H_2O \qquad (20)$$
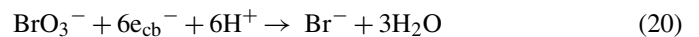
The bromide ions produced in the reaction can react with $^\bullet$OH radicals in solution (rate constant value = $1.1 \times 10^9 \, M^{-1} \, s^{-1}$ [15]) thus decreasing their concentration which result in less decoloration.

$$Br^- + {}^\bullet OH \rightarrow {}^\bullet Br + OH^- \qquad (21)$$

4. Conclusion

Photolytic decoloration of Toludine Blue, Safranin Orange and Crystal Violet was carried out in the presence of a hybrid catalyst, i.e. titanium oxide impregnated with Vanadium oxide. The decoloration of the dye solution was found to increase by almost five times using a hybrid catalyst as compared to a neat catalyst. It was found that first order kinetics and Langmuir–Hinshelwood model fitted well to the decoloration scheme of the dyes. The addition of many ions such as chloride, carbonate, bicarbonate,

persulphate and bromate ions decreased the percent decoloration. This was explained on the basis of $^\bullet$OH scavenging in the presence of these ions.

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