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Photocatalytic decoloration of Coomassie Brilliant Blue with titanium oxide

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Abstract

Coomassie Brilliant Blue dye was subjected to UV radiation in the presence of titanium oxide. The change in the color of the dye was monitored spectrophotometrically. The apparent rate of decolorization was calculated from the observed data and was found to fit the first order equation. The added amounts of Zn^{2+} ions caused a decrease in dye decoloration. A plausible explanation involving the radical initiated reaction is forwarded. Langmuir–Hinshelwood model was also used to describe the photocatalytic kinetics of the dye.

Keywords: Photocatalysis; Titanium oxide; Coomassie Blue

1. Introduction

Dyes are an important class of chemicals which are widely used in many chemical industries for various purposes, such as paper and pulp manufacturing, dyeing of cloth, leather treatment, printing, etc. Most of the used solutions containing such dyes are discarded as effluents. Since some of these dyes are toxic in nature, their removal from the industrial effluents is a major environmental problem [1–4]. Quite apart from the aesthetic desirability of colored streams resulting from dye waste, some dyes in particular can undergo anaerobic decoloration to potentially carcinogenic amines [5]. Literature review on this subject matter has revealed the importance of various approaches to handle such wastes. These include biodecoloration, photocatalytic, photolytic and advanced oxidative decoloration of various dye solutions [6–10]. The purpose of this study is to focus attention on the heterogeneous photocatalytic decoloration of Coomassie Blue, in the presence of titanium oxide. Titanium oxide is chosen because of its high photocatalytic activity and stability and is also reported widely in the literature as a photocatalyst for the removal of organic pollutants [11,12]. The present investigation also looks at the kinetic parameters and the effect of added ions on the decoloration of sample dye solution.

2. Experimental

The dye under investigation was Coomassie Blue with a labeled purity of more than 90% obtained from Biorad and used as such. Deionized water was used to make the dye solutions of desired concentration. The catalyst namely titanium oxide was Degussa P-25 and it was mainly in the anatase form (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 amount of catalyst in all the dye solutions for this work was kept constant at 30 mg/100 ml unless otherwise mentioned. 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. UV/vis studies were done on a CARRY

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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 nm and 254 nm. In the present work, the instrument was used in the 254 nm output mode.

2.1. Preparation of samples and decoloration/decoloration studies

Coomassie Blue stock solution of 1.2×10^{-2} 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 30 mg of the catalyst (titanium oxide) was added to this solution. The contents of the dye solution were allowed to equilibrate for 1 h 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. A series of such solutions were taken in different tubes and subjected simultaneously to UV radiation. After a certain time interval, a given tube 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 order of discoloration rate.

3. Results and discussion

In the present work, the kinetics of catalyst assisted photochemical decoloration of Coomassie Blue was investigated. The structure of the dye is given in Fig. 1. The initial investigation of the dye revealed two main peaks in its absorption spectra in aqueous solution, one at 285 nm and the other at 585 nm as shown in Fig. 2. These can be assigned to $n \rightarrow \pi^*$ transition (attributed to the color of the dye) and the $\pi \rightarrow \pi^*$ transition (attributed to the delocalized aromatic structure of the dye), respectively. For decoloration studies, 585 nm wavelength was chosen for further investigations.

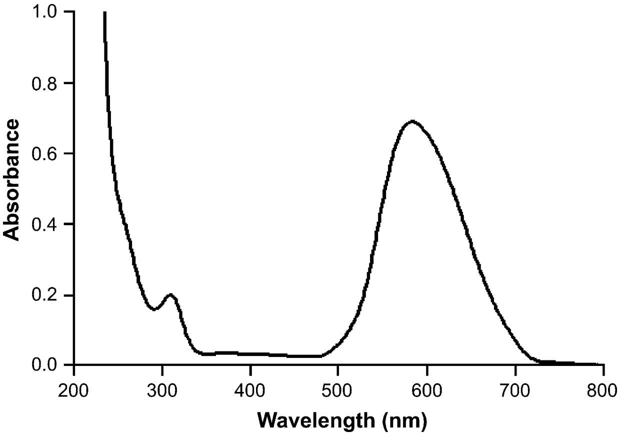

Fig. 2. UV/vis spectrum of Coomassie Blue.

Decoloration of this dye in the presence of a catalyst with UV light was carried out. Deionized water was used as a reaction media. Initially experiments were carried out in the absence and presence of either UV light or the catalyst alone. The results showed that mere UV light did not cause any decoloration of the dye. On the other hand, the addition of a catalyst in the absence of UV light did cause some changes in the absorption value of the dye solution, but remained constant after 1 h. Thus all photolytic experiments were done after this equilibration time of 1 h.

A solution of 40 μM of the dye in water was prepared and subjected to UV light in the presence of a catalyst. The dye started decolourising immediately in the presence of a catalyst and UV radiation. The rate of decolorization was monitored with respect to the decrease in absorption value of the dye solution, which has a distinct peak at 585 nm in the visible region. The dye concentration in solution was kept low so as to enhance the light triggered catalytic reaction. However, during the course of the experiments, effect of dye concentration on its decoloration rate was also monitored. The decrease in the absorption spectra of the dye solution was noted at regular intervals of time.

The evolution of absorption for the decoloration of dye solution as a function of irradiation time is given in Fig. 3.

The absorption data were found to fit well to a first order rate equation.

$$(A_t/A_0) = \exp(-kt) \tag{1}$$

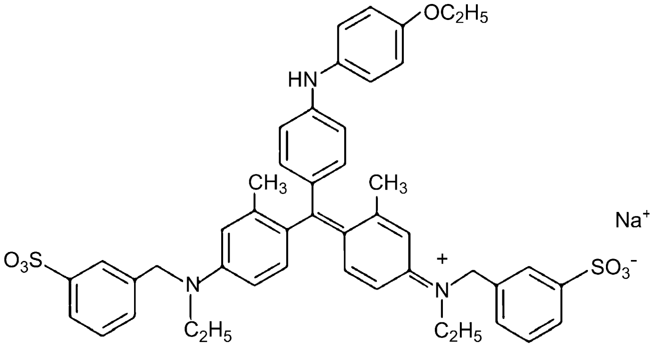

Fig. 1. Chemical structure of Coomassie Blue.

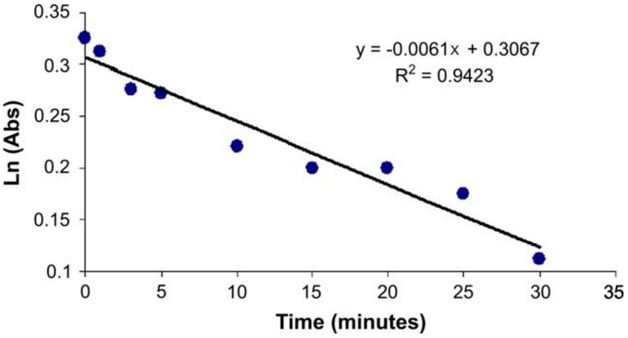

Fig. 3. Change in absorption value of Coomassie Blue with time (dye conc. = 30.7 mg/l, TiO_2 = 30 mg/100 ml).

Where k is the apparent rate constant, t is the irradiation time and A_0 and A_t are the initial and the final absorbance values of the dye solution, respectively. This is graphically depicted in Fig. 3. The slope of the line corresponds to the apparent rate constant value of 6.3×10^{-3} for the decoloration of the dye.

The photocatalytic decoloration of Coomassie Blue is believed to take place according to the following mechanism. When TiO_2 is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this, an electron–hole pair is produced [13].

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \tag{2}$$

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 a redox reaction with other species present on the surface. In most cases h^+_{vb} can react easily with surface bound H_2O to produce OH radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen.

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

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

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

The $OH^{\bullet}$ and $O_2^{-\bullet}$ produced in the above manner can then react with the dye to form other species and are thus responsible for the decoloration of the dye [14].

$$O_2^{\bullet -} + H_2O \rightarrow H_2O_2 \tag{5}$$

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

$$OH^{\bullet} + Dye \rightarrow Dye_{ox} \left(k = 10^9 - 10^{10} M^{-1} s^{-1}\right) \tag{7}$$

$$Dye + e^-_{cb} \rightarrow Dye_{red} \tag{8}$$

The decoloration of Coomassie Blue was also investigated with respect to its concentration in the presence of a fixed amount of catalyst. The results are shown in Table 1. It can be seen from this table that with increasing concentration of dye solution, its percent decoloration decreases. This is because of the reason that there is not enough catalyst surface available to react with the dye to cause its decoloration. Similarly the effect of catalyst amount on percent decoloration was also evaluated and the results are presented in Table 2. Increasing amount of the catalyst with a fixed amount of dye causes a substantial change in its decoloration. This is due to the reason that increasing amounts of the catalyst cause more light photons to be absorbed thus causing more decoloration of the dye as per the mechanism illustrated above.

Table 1
Change in percent decoloration of dye solution in the presence of various concentrations of dye

Dye conc. (μM)	%Decoloration
10	75.35
20	28.00
30	20.65
40	19.00

Amount of TiO_2 = 30 mg/100 ml, irradiation time = 30 min.

Table 2
Effect of TiO_2 on decoloration of dye solution in the presence of UV

TiO_2 (mg/100 ml)	%Decoloration
20	14.15
30	19.00
50	51.00

Amount of dye = 40 μM, irradiation time = 30 min.

The decoloration of Coomassie Blue was also investigated in the presence of certain salts which were added to the dye solution along with the catalyst. This is because of the reason that the presence of transition metals may increase the photocatalytic activity by either scavenging electrons that reduces the combination of charges and therefore favors the formation of OH, or by the intermediates of Fenton type reactions [15]. The other experimental conditions were kept the same as for neat Coomassie Blue decoloration study. Among the salts chosen for this purpose was $Zn(NO_3)_2$. A detailed study was performed when $Zn(NO_3)_2$ was added to the dye solution.

The change in apparent rate value of the dye in the presence of various concentrations of $Zn(NO_3)_2$ is shown in Fig. 4. Decoloration of the dye in the presence of Zn^{2+} followed a similar trend as without its presence, however, the overall decoloration efficiency is reduced in the presence of Zn^{2+} ions as shown in Table 3. This is also reflected in the rate constant values which are lower in magnitude as compared to the one without Zn^{2+} ions. This may well be due to the reason that Zn^{2+} ions are preferentially adsorbed on the catalyst surface thus inhibiting its role towards dye decoloration. As Zn^{2+} ion concentration increases in the solution, the dye decoloration also decreases, thus confirming the above

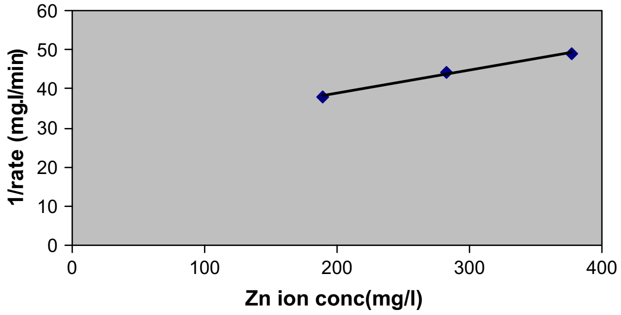

Fig. 4. Change in apparent rate of dye with varying concentrations of zinc ion (dye = 30.7 mg/l).

Table 3
Change in percent decoloration of dye solution in the presence of various amounts of Zn^{2+} ions

$Zn(NO_3)_2$ conc. (mg/l)	%Decoloration	Rate constant (k, min^{-1})
0.0	63.2	6.3×10^{-3}
188.80	54.2	263×10^{-4}
283.08	49.7	228×10^{-4}
377.25	46.0	204×10^{-4}

Irradiation time = 30 min, amount of TiO_2 = 30 mg/ml.

reasoning. This type of behaviour has been reported in the literature for other cases[16]

Heterogeneous photocatalysis can be explained in terms of its behaviour using the Langmuir–Hinshelwood expression [17], which in its simpler form is given by:

$$1/r = 1/k_r + 1/(k_r k_a C) \tag{9}$$

where, r is the reaction rate for the oxidation of reactant (mg/l min), k_r is the specific reaction rate constant for the oxidation of the reactant (mg/l min), k_a is the equilibrium constant of the reactant (l/mg) and C is the dye concentration.

A plot of $1/r$ versus $1/C$ gave a straight line with $R^2 = 0.9949$, a slope of $1/(k_r k_a)$ and an intercept of $1/k_r$. This is shown in Fig. 5, from which k_r and k_a values were calculated to be 0.0378 mg/l min and 0.0352 l/mg, respectively.

In the presence of constant concentration of Zn^{+2} and different dye concentrations, the above equation was used in its modified form as below [16]:

$$1/r = 1/k_r + [(1 + k_{ion} C_{ion})/(k_r k_a)]/C \tag{10}$$

where, C_{ion} is the concentration of the added ion. In this case a plot of $1/r$ versus $1/C$ also gave a straight line with $R^2 = 0.9987$ as shown in Fig. 6. The high correlation coefficient value in this case is an indication that the TiO_2 mediated photocatalytic decoloration of the dye undergoes the same kinetic behaviour in the presence or absence of added ions.

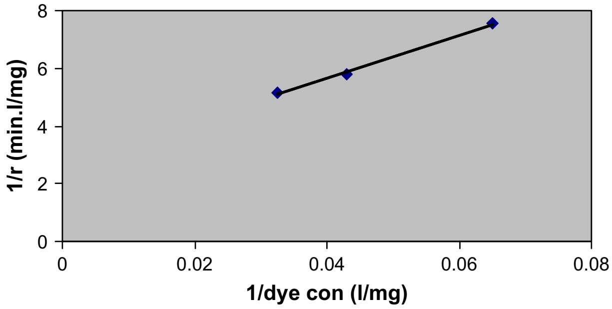

Fig. 5. Langmuir–Hinshelwood plot in the absence of Zn^{2+} ions.

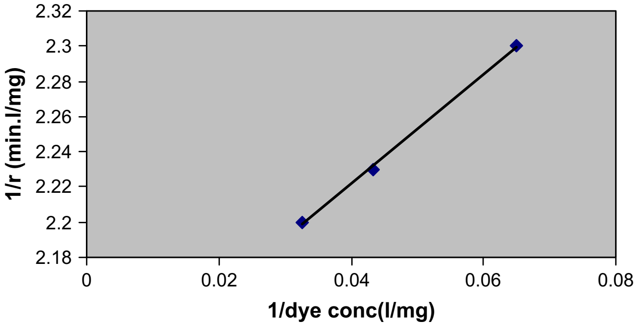

Fig. 6. Langmuir–Hinshelwood plot in the presence of Zn^{2+} ions (ion conc. = 94.5 mg/l).

4. Conclusion

Photolytic oxidation of Coomassie Blue was carried out in the presence of titanium oxide. The decoloration of the dye solution was observed by monitoring the absorption values of the solution. It was found that the dye is resistant to direct photolysis but can undergo some decoloration in the presence of a catalyst without light. The dye undergoes less decoloration in the presence of Zn ions. This may well be due to the reason that Zn^{2+} ions are preferentially adsorbed on the catalyst surface thus inhibiting its role towards dye decoloration. The photocatalytic decoloration of the dye obeys the first order kinetics and can also be described in terms of Langmuir–Hinshelwood model.

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