

A Study on Rate of Decolorization of Textile Azo Dye Direct Red 5B by Recently Developed Photocatalyst

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Abstract- In present study the photocatalytic degradation of commercial azo dye Direct Red 5B (DR5B dye) has been carried out in presence of recently developed photocatalyst: methylene Blue immobilized resin Dowex-11, under visible light. The effect of process parameters such as variation of the dye concentration, pH, light intensity and amount of catalyst loading on the reaction rate has been studied .The rate constant has an optimal conditions at 30 oC , pH 7.5,2.0gm/L catalyst loading, light intensity 200 watt & 40mg/L concentration of the dye. Kinetic study of photo degradation follows pseudo first order kinetics. A Tentative mechanism of the photocatalytic degradation of DR5B dye has also been proposed.

Index Terms- DR5B, photo catalyst, photo degradation, Methylene Blue Immobilized resin Dowex -11

I. INTRODUCTION

Textile azo dyes like Reactive dye, Direct dyes and other industrial dye stuffs constitute one of the largest groups of organic compounds that represent growing environmental pollution. Considering the volume and chemical compounds of the discharged effluents the textile dyeing and finishing is one of the major pollutants in industry¹⁻². Studies indicate that manufacturing and processing operations adds substantial amounts of dye stuffs and the resultant color enters the environment through effluents from industrial wastewater treatment plants. Adsorption and chemical coagulation are common technique used in treatment of such wastewater. However these methods transfer dyes from liquid to solid phase and produce secondary pollution and requiring further treatment. Textile wastewater treatment processes by means of coagulation, flocculation, ultra filtration and adsorption of the dyes aiming at the destruction of wastewater's color.³⁻⁵. Another wastewater treatment process like Advance Oxidation Process (AOPs) have been proposed⁶. AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade by traditional physico chemical and biological methods.⁷. Among AOPs photo catalytic oxidation processes have been paid more attention to degrade various organic compounds & pollutants in water in the recent years.⁸⁻¹¹

Maria et al¹² investigate the complete mineralization of acid orange 7 dye into simple organic molecules using TiO₂ as photo catalyst. Enhanced photo catalytic performance of nano sized coupled ZnO/SnO₂ photo catalyst has been reported by Wang et al.¹³

Ameta et al¹⁴ studied the photo bleaching of basic blue-24 and orange – G over ZnO powder in presence of surfactants.

Degradation of methyl orange dye under UV light (300nm) illumination using ZnO/ZnO₂as photo catalyst has been investigated by Chin et al¹⁵.

Yau et al¹⁶ used combination of TiO₂ and activated fiber for the degradation of methylene blue dye. Purification with TiO₂ mediated photo catalysis under UV light has been shown to be potentially advantageous as it may lead to complete mineralization of pollutant to CO₂, water and mineral acids.¹⁷⁻¹⁸

Although TiO₂ is the most widely used catalyst, mainly because of its photo stability, low cost and non toxicity and insoluble in water under most environmental conditions.¹⁹, but this technology has not yet been successfully commercialized in past because of problems connected to the separation of TiO₂ particles from suspension .To solve this problem, supported photo catalysts have been developed²⁰⁻²¹.

In present study MB immobilized resin, a newly developed photo catalyst for degradation of azo dyes can act as photo sensitizer induced process. As photo catalyst sensitizes, electron migrates from VB to CB and follows inter system crossing(ISC) and electronic transition starts between resin, MB dye molecules, water molecules,DR5B molecules and dissolved oxygen ,and via a chain process into highly oxidizing hole ,hydroxyl radicals and super oxide ions.

II. MATERIAL AND METHODS

Dye

The Dye Direct Red 5B (a sulfonated azo dye) mol.wt, 663; λ_{max} 510 nm figure-1 was collected from the near by textile industry and used as such.



Figure-1

Photo catalyst

Preparation of the photo catalyst was done by using Dowex-11 resin (particle size, 20 -50 mesh) (sisco chemicals India , Mumbai) and MB hydrated (Loba Chemicals India).All other laboratory reagents were analytical grade and the solutions were prepared by dissolving the calculated amounts of appropriate chemicals in double distill water.

MB solution of concentration 10⁻³ M in double distill water, was mixed with Dowex-11 resin (MB: resin, 100:1) with shaking well and allowed the mixture to stand for 3 days in dark for complete immobilization of resin by MB. After 3 days the

resin was filtered washed by double distill water twice and used as photo catalyst. The immobilization takes place it can be identified by its characteristic IR spectrum Figure-2 shows the peaks of the resin (without grafting) before immobilization and Figure-3 shows the peaks after immobilization the bands at 2987, 2905, 1600-1430 cm^{-1} were attributing to Ar-H, C-H, C=C and C=N respectively, peaks at 1270, 1220-1020 cm^{-1} and others peaks show bending of various groups (Spectro Jasco Corp. /IR-610 over the range 599.7532 – 4000.605 cm^{-1}). These peak shows that the immobilization of the photo sensitized dye (methylene blue) in the resin has been taken place.

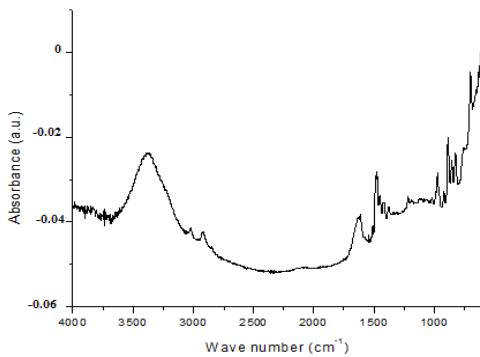


Figure-2. The IR spectra of Dowex-11 resin without grafting.

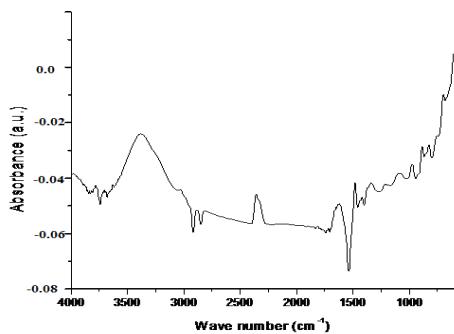


Figure-3. The IR spectra of Dowex-11 resin after immobilization by Methylene blue dye.

Stability of the catalyst

In order to know the stability of the catalyst, the catalyst was recycled five times by using dye solution at optimum conditions, after each experiment the catalyst was separated from solution by filtration, washed with deionized water for several times, derived at 35°C for over night and than used for next run, observed after cycles of the experimentation, the catalysis efficiency of the catalyst was still higher than 98%, and the catalytic performance was not effected by the time of reuses. So the catalytic effect of the prepared catalyst (MB immobilized resin Dowex-11) was as successful as conventional catalyst.

Analytical methods

The photocatalytic degradation of DR5B was observed by making aqueous solution of the desired concentration from the stock solution. Irradiation was carried out by using 200 watt tungsten lamp (Philips) having intensity 10.4 mWcm^{-2} . The optical density of solution was measured by using

spectrophotometer (Systronic model 106). The pH conditions of the desired solution were adjusted by using standardized 1N NaOH and 1N H_2SO_4 solution. pH of the solution was measured by digital pH meter(Fisher Scientific Accument 50). All the experiments were performed at room temperature and magnetically stirred and aerated throughout the experiment.

Procedure

To carry out the photochemical reaction 50ml of the dye solution (DR5B dye) of desired concentration (40mg/L) was taken and appropriate amount (2.0gm) of MB immobilized Dowex -11 catalysts was added to it. The mixture was irradiated under visible light using 200watt tungsten lamp.

3 ml aliquot of the dye solution was withdrawn after a specific time interval and absorbance was measured using spectrophotometer (Systronic model 106) at 510 nm .The rate of decrease of color was monitored after specific time interval.

III. RESULT AND DISCUSSION

The photo catalytic degradation of direct dye (DR5B) was observed at λ_{\max} 510nm. The optimum condition for the removal of the dye is, dye concentration at 40mg/L, pH-7.5, catalyst loading 2.0gm, light intensity 200 watt.

Rate of the reaction (k) was determined using the expression

$$\text{Rate } (k) = 2.303 * \text{slope}$$

Figure- 4 shows the semi logarithmic plot of $1+\log O.D$ versus exposure time was found to be straight line suggesting the bleaching of the dye follows pseudo first order kinetics.

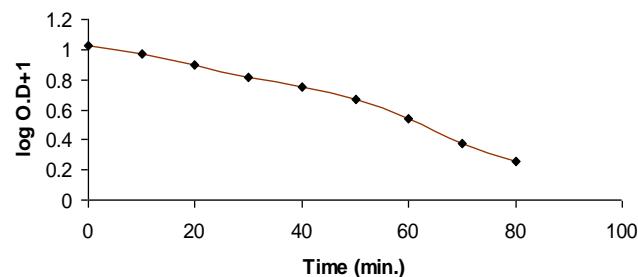


Figure-4: A Typical run of photo catalytic degradation of DR5B (λ_{\max} 510 nm) under optimum conditions.

Effect of variation in pH

The photo degradation of the dye was studied at different pH values ranges from 3.5 to 11.5 .Degradation rate of the dye is very low in acidic pH range As pH range increases, degradation rate increases. In pH range 7.5-9.0 rate of bleaching was very good. It has been reported graphically in figure 5.

On further increasing pH, rate of degradation starts to decrease. Increase in rate of photo catalytic degradation in the neutral to alkali range (pH 7.5-9.0) may be due to more availability of OH^- ions by combining with holes, which are formed due to electronic excitation in catalyst. These hydroxyl radicals were considered responsible for the photo catalytic bleaching.

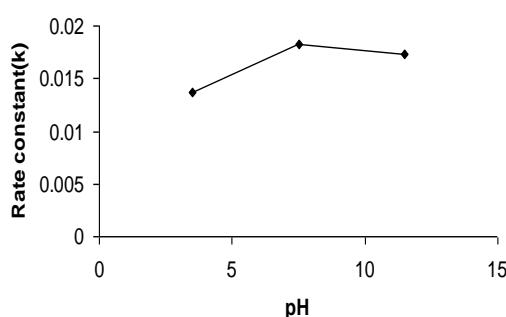


Figure 5: A typical run of effect of pH on photo catalytic bleaching of the dye (Temp.30°C, dye conc. 40mg/L, light intensity 200watt , catalyst loading 2.0gm)

Effect of catalyst loading

As catalyst loading increase the rate constant increases from 1.0gm to 3.0gm, by taking other parameters constant. This can be due to more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst , resulted increase in number of holes , hydroxyl radicals and supra oxide ions(o^-). Since these are principle oxidizing intermediates in AOP and rate of degradation increases. This can be shown graphically in figure 6.

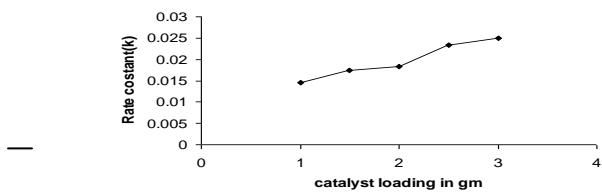


Figure- 6. A typical run of effect of catalyst loading on photo catalytic bleaching of the dye(Temp.30°C, dye conc. 40mg/L, light intensity 200 watt)

Effect of concentration of dye

Degradation rate of the dye decrease with increase in concentration of the dye from 10mg/L to 70mg/L . As shown in figure 7. The rate constant revealed that the maximum degradation observed at low concentration of the dye. As concentration increases the rate constant decreases above the optimal value. At high concentration the decrease in degradation phenomenon can be explained in terms of the increased concentration of the dye However, the irradiation time and amount of catalyst have been kept constant hence the production of OH⁻ radicals and supra oxide radicals was limited.

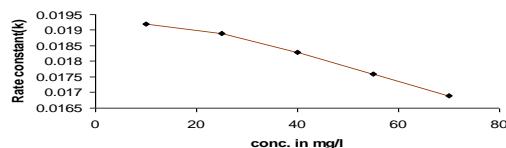


Figure 7 - A typical run of effect of variation of concentration on photo catalytic bleaching of the dye (Temp.30°C, light intensity 200 watt, catalyst loading 2.0gm)

Effect of light intensity

The influence of light intensity was studied in the range 60 to 500 watt an almost linear plot between the rate constant and light intensity was observed, that indicates an increase in the light intensity will increase the rate of reaction. Figure -8. This may be due to increase in number of photons reaching catalyst surface area so increase in number of excited catalyst molecules resulted in increase in number of holes, hydroxyl radicals and supra oxide ions(o^-) .As a consequence ,an over all increase in the rate of degradation of dye molecules has been observed.

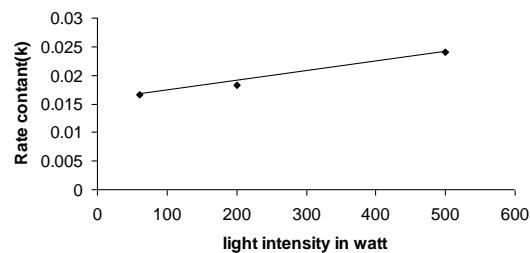
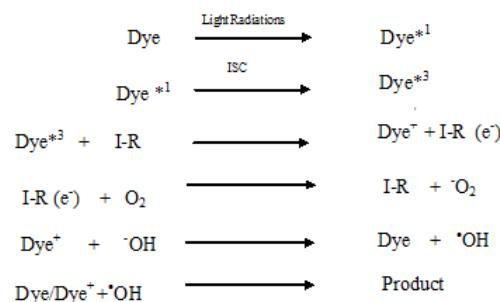


Figure-8. A typical run of effect of light intensity on photo catalytic bleaching of the dye(Temp.30°C, conc. 40mg/L, catalyst loading 2.0 gm)

Mechanism

Tentative mechanism has been proposed on the basis of above experimental observation.

On irradiation the dye molecules absorb photons and get excited, resulted electrons jump to singlet state. Then these excited singlet state molecule is convert into triplet state through intersystem crossing. The triplet dye may donate its electron to the photo catalyst and the dye becomes positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of photo catalyst. The positively charged molecules of the dye will immediately react with hydroxyl ion to form hydroxyl radicals and these hydroxyl radicals will oxidize the dye molecule in to the product.



IV. CONCLUSIONS

In conclusion, this study has proved that MB immobilized Dowex -11 is an efficient catalyst .For degradation of DR5B Dye in the presence of solar light. The optimal reaction condition for the photo catalytic degradation of DR5B Dye were determined to be, 30° C, pH 7.5, 2.0gm/l catalyst loading, 40mg/l concentration

of the dye and 90 minute solar irradiation time. The degradation of DR5B by MB immobilized Dowex -11 catalyst, followed the Pseudo-first order Kinetics with respect to the concentration of DR5B dye. No obvious decline in efficiency of the catalyst was observed after 5 respected cycles and this shows the stability and reusability of the catalyst.

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