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# Photo catalytic bleaching of Amaranth by Methylene Blue immobilized resin Dowex-11

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## Abstract

*Methylene Blue immobilized resin Dowex-11 has been employed for photo catalytic decolorization of Acid Red 27 (Amaranth) dye. The effect of process parameters such as initial dye concentration, catalyst loading, pH and light intensity on the extant of decolorization have been observed. Decolorization of azo dyes using Methylene Blue immobilized resin Dowex-11 photo catalyst is a cheap method and very good alternate to replace costly traditional methods. Activity of photo catalyst remains un-affected on continuous use.*

**Key words:** Decolorization, Methylene Blue immobilized resin Dowex-11, Acid Red 27.

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## INTRODUCTION

Today most of water resources are polluted. Water pollution is increasing steadily, due to rapid population growth, industrialization, urbanization, increasing living standard and wide sphere of human activities. Large volume of discharge and effluents and wastewater of textile industries are most polluting among all industrial sectors.

Advance oxidation process is used to decompose many hazardous chemical compounds to acceptable levels and provide very good results, without producing hazardous by-products which require further handling. To oxidize the organic pollutants especially azo dyes in wastewater by advance oxidation process had been valued in recent years. Most synthetic dyes are not degrade by conventional physical and chemical processes like adsorption and chemical coagulation because these methods merely transfer dyes from liquid to solid phase causing secondary pollution [1-3]. Tang and An [4] investigated the treatment of five commercial dyes with suspended UV/TiO2 photo catalytic process and showed the color removal ratio varied at different pH values. Hachem et al.[5] have been investigated the photo catalytic transformation of various dyes (Orange G, Indigo Carmine, Congo Red, Malachite Green, Crystal Violet, Rhomazole Blue and Methyl Yellow). The subject of research work related to dye transformation has been excellently reviewed by Yashodharam et al. [6], Kalyanasundram [7], Kamat [8] and Frewd and Gomes [9].

A photo catalyst which has extensively been used is TiO2 with a 3.0-3.2eV band gap between valence band and conduction band. The discovery of photo-assisted water cleaves at semiconductor electrode, first time reported by K. Honda and A. Fujishima [10-11] in 1972, achieved UV light induced water cleaves using a TiO2 photo anode in combination with a platinum counter electrode soaked in an electrolytic aqueous solution.

Titanium dioxide is a semiconductor material that becomes involved in oxidation-reduction process when excited by ultraviolet light energy. UV light energy activates the catalyst surface by exciting an electron from the valence band to the conduction band, leaving behind an electron hole. An electron scavenger is needed to prevent recombination of the electron and hole in valence band. The adsorption and photocatalytic degradation of diazo Direct Yellow 12 and Direct Black 38 in aqueous suspension of semiconductor oxide TiO2 under UV light has been investigated by Toor et al. and Regina et al. [12-13]. Chat et al. [14] have been reported photo degradation of 2,4,6 Trinitrotoluene and nitrobenzene mixture in TiO2 suspension.

Degradation of Acid Green 16 was studied by Sakthivel et al. [15] using ZnO irradiated with sunlight. Here the photo degradation efficiency decreased with an increase in initial dye concentration. Optimum catalyst loading was found to be 250mg in 100 ml. Akyol et al. [16] was studied the photo catalytic transformation of Remazol Red by ZnO. Pandurangan et al. [17] carried out the photo catalytic transformation of Basic Yellow Auramine O in a batch reactor, using ZnO exposed to solar radiation. The process follows pseudo-first order kinetics. Pachwarya and Meena [18] have been studied the degradation of azo dye Amido Black 10B by recently developed photo catalyst (Methylene Blue immobilized resin Dowex-11.

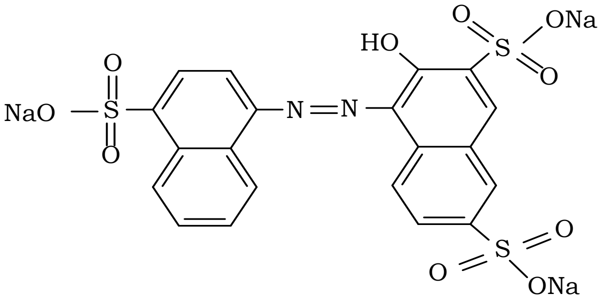
Amaranth (Acid Red 27) which is the most common among all other dyes of its category is generally used as colorant in textiles, color photography and in food stuffs. Though Amaranth is not strongly hazardous but it can cause some harmful effects. Therefore the removals of such dyes from effluents become environmentally important. In the present work Methylene Blue immobilized resin Dowex –11 used as photo catalyst for the bleaching of Amaranth dye and investigate the influence of operational parameters like pH, initial concentration of dye, catalyst loading and intensity of light etc. on the decolarization kinetics of Amaranth dye.

## MATERIALS AND METHODS

The reaction was carried in a photo catalytic reactor to study the decolarization of Acid Red 27. The dye used in this experiment was purchased from LOBA Chemicals (India). Dye solution was prepared by dissolving dye in double distilled water. The pH of the solution was measured by pH meter (Fisher Scientific Accument 50) and adjusted by adding NaOH or $H_2SO_4$ solution. All the experiments were performed at room temp. and magnetically stirrer continuously (REMI M1L-S). The model solution for the reactor was taken in glass tube (Pyrex 100ml.). Irradiation was carried with a 200W tungsten lamp. The intensity of the irradiation was 10.4mW/cm$^2$ which was measured with the help of solar meter and optical density of the solution was measured with the help of Shimadzu-160 UV/Vis spectrophotometer at optimal wavelength 520 nm.

## RESULTS AND DISCUSSION

The photo catalytic decolorization of Acid Red 27 was carried out at $\lambda_{max}$ = 520nm using UV/Vis spectrophotometer at optimal pH=7.5. The decolorization of dye solution was increased up to 98.81% after 2.5 hrs. The results for a typical run are given in figure 1. (Structure given below)



Acid Red 27

It was observed that optical density of Acid Red 27 solutions decreased with the increase in time of irradiation. This increase in the transparency was due to the increase in degradation of the dye. The highest decolarization was observed at pH=7.5. A plot of 2+log O.D. v/s time was found to be linear which determined that the reaction was of pseudo first order. Rate constant was obtained with slope such as:

$$k = 2.303 * \text{slope}$$

The optimum rate constant with photo catalyst was determined to be $4.41*10^{-4}$. Photo catalytic reactor with novel developed photo catalyst Methylene Blue immobilized resin Dowex -11 gave new results of decolorization of non biodegradable azo dye. After these observations we conclude that this reactor with new photo catalyst is capable to decolorize the dye solution.

**3.1. Effect of the dye concentration**: - Effect of variation of dye concentration was studied by taking different concentration of Acid Red 27. Results are reported in table 1. We found as the concentration of dye increased the rate of degradation increased up to a limit and then decreased. It is determined by changing the dye concentration from 10mg/litre to 70mg/litre. This effect may be due to more dye molecules are available to degrade. On further increasing the concentration of Acid Red 27 above 40mg/litre the rate of degradation decreased. Because as the dye concentration increased the number of photons reaching to catalyst surface decreased and hence less number of catalyst were excited results in less number of cationic molecule to react with hydroxyl ions.

Secondly the increase in dye concentration there should be an extreme competition for attachment to catalyst between dye molecules. Hence the movement of dye molecule toward the catalyst was hindered results in the decrease in the rate of degradation.

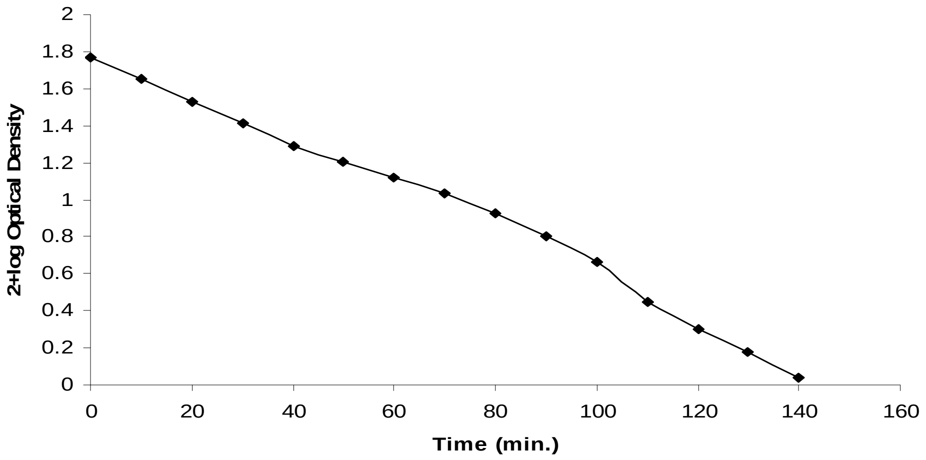


**Fig. 1. Kinetics for Acid Red 27 – Photo catalyst system**

*(Initial dye con. = 40mg/lt., Catalyst loading= 2.0gm, pH= 7.5, Solution volume= 50ml. Light intensity=10.4mW/cm$^2$)*

**3.2. Effect of the Photo catalyst loading:**-The amount of photo catalyst affects the rate of photo catalytic bleaching of Acid Red 27 and hence different amount of photo catalyst were used. The reaction rates were analyzed in the range 1.0gm to 3.0gm. The results are summarized in table 1. It has been observed that the rate of decolarization increased with increase in amount of catalyst. This may be attributed to availability of more surface area for adsorption of photon and increased interaction of dye molecules with catalyst. On further increase of catalyst amount the rate of reaction was almost constant because the number of exposed catalyst would not increase as the exposed surface was limited and the reaction was almost constant after this limit.

**3.3. Effect of the pH- The** pH of the solution is likely affect the bleaching of the Acid Red 27 dye. The effect of pH was investigated in the pH range 3.5-11.5. The results are reported in table 1. To examine the effect of pH, the dye solution was adjusted to the desired pH for each experiment by adding NaOH or $H_2SO_4$. Results clearly confirm that pH has prominent effect on photo catalytic bleaching, as high rate of degradation at basic pH 7.5-9 and it was very low at acidic pH i.e. less than 3.5. So we conclude that photo catalytic bleaching is very high at pH 7.5-9 but on further increasing the pH rate of transformation of dye decreased. Photo catalytic bleaching results at basic pH because of the generation of more hydroxyl radicals by reaction between the hydroxyl ions and cationic form of dye (holes) which are produced by electronic excitation of dye. This effect decreased at higher pH because of the competition, inhibition of attachment of cationic dye between large no. of hydroxyl ions and hence the rate of degradation also decreased.

**3.4. Effect of the light intensity**: - We have been investigated the influence of light intensity on the decolorization efficiency at constant dye concentration 40 mg/l and catalyst loading 2.0 gm/50ml.The reaction rates were analyzed in the range 5.2 to15.6 mWcm$^{-2}$. The results are reported in table 1. We observed that as light intensity increased the rate of reaction of photo catalytic bleaching also increased. This was because of the increase in the number of photons with increase in light intensity and hence large number of photons striking per unit area of the exposed surface of catalyst. So number of excited catalyst molecules increased and hence more hydroxyl radicals were produced. Since an increase in light increases the temperature of dye solution and a thermal reaction may occur, therefore higher intensities were avoided.

**Table- 1: Effect of variation of different parameters**

| **Effect of Acid Red 27 concentration** | | **Effect of amount of catalyst** | | **Effect of pH** | | **Effect of light intensity** | |
|---|---|---|---|---|---|---|---|
| Catalyst=2.0gm<br>pH=7.5<br>Light intensity=10.4mW/cm$^2$ | | Dye conc.=40mg/L<br>pH=7.5<br>Light intensity=10.4mW/cm$^2$ | | Dye conc.=40mg/L<br>Catalyst=2.0gm<br>Light intensity=10.4mW/cm$^2$ | | Dye conc.=40mg/L<br>Catalyst=2.0gm<br>pH=7.5 | |
| Dye conc. (mg/L) | Rate constant *10$^{-2}$ | Amount of catalyst (gm) | Rate constant *10$^{-2}$ | pH | Rate constant *10$^{-2}$ | Light intensity (mW/cm$^2$) | Rate constant *10$^{-2}$ |
| 10 | 2.74 | 1.0 | 2.09 | 3.5 | 1.03 | 5.2 | 1.72 |
| 25 | 2.66 | 1.5 | 2.22 | 7.5 | 2.64 | 10.4 | 2.64 |
| 40 | 2.64 | 2.0 | 2.64 | 11.5 | 1.61 | 15.8 | 2.78 |
| 55 | 2.21 | 2.5 | 2.80 | | | | |
| 70 | 1.55 | 3.0 | 2.88 | | | | |

**3.5. Recycling studies: -** In order to know the stability of the catalyst, the catalyst was recycled five times by using Acid Red 27 dye solution at optimum conditions. After each experiment, the catalyst was separated from the solution by filtration, washed with deionized water for several times and dried over a night and then used for next run. Noticeably after five cycles of experimentation, the catalyst efficiency was still higher and the catalytic performance was not affected by the times of reuse. So, the catalytic effect of the newly developed photo catalyst was successful.

## 1. **Mechanism**

On the basis of results a tentative mechanism has been proposed for photo catalytic decolorization of Acid Red 27 with catalyst Methylene Blue immobilized Resin Dowex -11 in the presence of light -:

$$\text{Dye} \xrightarrow{\text{Light Radiations}} \text{Dye*}^{1}$$

$$\text{Dye *}^{1} \xrightarrow{\text{ISC}} \text{Dye*}^{3}$$

$$\text{Dye*}^{3} + \text{I-R} \longrightarrow \text{Dye}^{+} + \text{I-R (e}^{-}\text{)}$$

$$\text{I-R (e}^{-}\text{)} + O_2 \longrightarrow \text{I-R} + {}^{-}O_2$$

$$\text{Dye}^{+} + {}^{-}\text{OH} \longrightarrow \text{Dye} + {}^{\bullet}\text{OH}$$

$$\text{Dye/Dye}^{+} + {}^{\bullet}\text{OH/ (}^{-}O_2\text{)} \longrightarrow \text{Product}$$

The dye molecule absorbs photons and electrons become excited and its 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.

## CONCLUSION

From the results of the study it can be concluded that Methylene Blue immobilized resin Dowex 11 can be effectively used to decolorize Acid Red 27 dye in aqueous solution. To obtain maximum color removal of the dye, basic pH (7.5-9), high light intensity and minimum dye concentration are required. For a solution with dye concentration of 40 mg/l, color elimination was 98.81% when the pH was 7.5, catalyst amount was 2.0 gm and light intensity was 10.4mW/cm$^2$. These results show that this newly developed photo catalyst provides a promising technology to improve the quality of effluent from textile wastewater treatment plants.

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