

## Photo catalytic degradation of model textile azo dyes in textile wastewater using methylene blue immobilized resin dowex-11

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This study presents degradation of textile azo dye by newly developed photo catalyst (methylene blue immobilized resin dowex-11; particle size, 20-50 mesh), which is a cheap and a very good alternative to traditional technologies for industrial application. Activity of catalyst remains unaffected on continuous use.

**Keywords:** Amido Black 10B, Azo dyes, Degradation, Methylene Blue immobilized resin Dowex-11, Photo catalyst

### Introduction

Advance oxidation process<sup>1</sup> (AOP) is best for treatment of textile industries effluent (wastewater). Methylene blue (MB) immobilized resin, a newly developed photo catalyst for degradation of azo dyes, can act as sensitizer for light induced process. Due to sensitization of photo catalyst, electron migrates from valance band (VB) to conduction band (CB) and holes formed in valance band can generate highly oxidizing hydroxyl radicals. Probably hole abstracts electron from dye molecule and degradation process starts. Bhatkhande *et al*<sup>2</sup> listed compounds degraded by photo catalysis. Studies are available on degradation of textile azo dyes and on photocatalyst<sup>3-7</sup>. Legrini *et al*<sup>8</sup> observed that purification with TiO<sub>2</sub> photo catalyst in presence of UV radiation is economical and effective in removal of organic compounds dissolved or dispersed in water. TiO<sub>2</sub>-mediated photo degradation mechanism<sup>9</sup> for Acid Orange 7 led to complete mineralization of organic molecule into naphthalene and benzene type rings, carbon into CO<sub>2</sub>, nitrogen into NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> and sulphur into SO<sub>4</sub><sup>2-</sup> ions. Degradation of Methyl Orange<sup>10</sup> has been carried out under UV Light (300 nm) illumination using ZnO/ZnO<sub>2</sub> as photo catalyst. Wang *et al*<sup>11</sup> reported enhanced photo catalytic activity for Methyl Orange

degradation using SO<sub>4</sub><sup>2-</sup>/ZnO/TiO<sub>2</sub> and ZnO as photo catalysts. Mendez-Pazet *et al*<sup>12</sup> carried out anaerobic treatment of azo dyes, Acid orange 7, under fed batch and continues condition.

This study proposes a new photo catalyst, methylene blue immobilized resin dowex-11 (MBRD-11), for oxidative degradation of textile azo dye.

### Materials and Methods

#### Dye

Dye (C<sub>22</sub>H<sub>14</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>2</sub>; mol wt, 616.49; λ<sub>max</sub>, 620 ± 4 nm; purity, 98.9%) was procured from Loba Chemicals India.

#### Photo Catalyst

Photo catalyst was prepared by using Dowex-11 resin (particle size, 20-50 mesh) (Sisco Chemicals India, Mumbai) and MB hydrate (Loba Chemicals India). MB solution (10<sup>-3</sup> M), prepared in double distilled water, was mixed with Dowex-11 resin (MB: Resin, 100:1) with shaking well. Then, mixture was allowed to stand for 3 days in dark for complete immobilization of MB inside resin pores. After 3 days, MB immobilized resin was filtered, washed by double distilled water twice and used as photo catalyst in further experiments.

#### Analytical Methods

Change in dye concentration was recorded by UV/Visible spectrophotometer (Shimadzu-160). Solution

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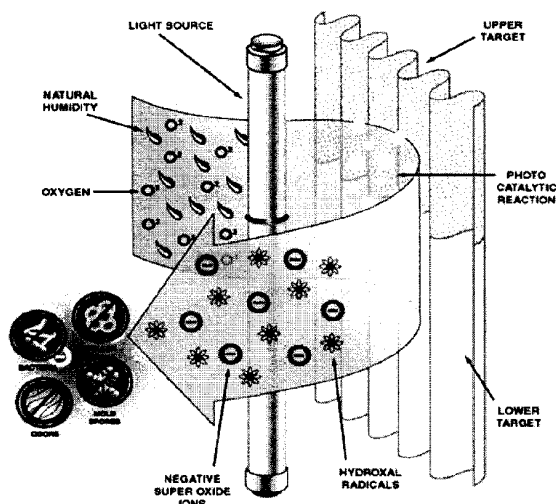


Fig. 1—Photo catalysis action: generation of holes, hydroxyl radicals and supra oxide ions ( $o^{\cdot-}$ )

(10 ml) pipetted out at 15 min interval and observed changes in percentage transparency of dye solution.

#### Experimental Set up and Experimental Procedure

Photoreaction was carried out in a glass reactor, which contains a mixture of dye (Amido Black 10B) and photo catalyst. Solution was continuously stirred by magnetic stirrer during experiment. Solution was illuminated by 500W halogen lamp placed above reactor. At 15 min interval, 10 ml solution was taken out from reaction mixture. Filtered the catalyst particles and observed variation in transparency of colored water by spectrophotometer (160UV/Visible spectrophotometer).

In all experiments, a schedule of observation was followed. In first experiment, biodegradability of dyes (without catalyst) was observed. Using dye solution in solar/lamp light for 3 days and after 3 days, changes in dye concentration was observed. If no changes are found in dye concentration then second experiment was conducted in dark to test catalyst action in dark. Reaction mixture (dye solution and catalyst) was put in dark chamber and no change was observed in dye concentration. In third experiment, pure resin was added without immobilization of MB. This experiment was carried out for test action of resin (without immobilized). It was observe that absorption process occurs. Absorption efficiency is reduced after first absorption and stops after 2-3 time of use, due to filling porosity of resin. In fourth

experiment, using MB immobilized resin, it was observed that polluted and darkly colored mixture transform into transparent water like mineral water. This catalyst can be used many times as there is no effect on efficiency of degradation of dye molecules.

## Results and Discussion

### Chemical Reaction of Dye Degradation

MB is photosensitive; when light radiation is irradiated on it, electronic transition occurs from VB to CB and through intersystem crossing (ISC) electron reach in to triplet state of MB. Intermolecular electronic transition starts between resin, MB dye molecules, water molecules, Amido Black dye molecules and dissolved oxygen, resulting through chain process into highly oxidizing holes, hydroxyl radicals and Supra oxide ions (Fig. 1), which transfer Azo dyes in simple organic compounds. Main factors influencing photo catalytic degradation of Azo dyes are variations in catalyst loading, concentration of dye, pH of solution, light intensity, and dissolved oxygen. MB becomes excited by absorbing photons of light radiations. In first electronic excitation, electron transfers into singlet state and through ISC electron can transfer to triplet state of MB. Further inter molecule electronic interaction occurs between resin, MB and solution mixture and resultant is formation of holes, hydroxyl radicals and supra oxide ions ( $o^{\cdot-}$ ), which are highly oxidative.

### Effect of Catalyst

As concentration of photo catalyst (pH 7.5) increases, rate of degradation also increases, due to availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, increase in number of holes, hydroxyl radicals and supra oxide ions ( $o^{\cdot-}$ ). These are principle oxidizing intermediates in advance oxidation process and increase rate of degradation (Fig. 2).

### Effect of Initial Dye Concentration

As dye concentration increases, rate of degradation decreases (Fig. 3), may be due to following reason: i) As dye concentration increases, number of photons reaching to catalyst surface decreases because less number of catalyst molecules undergo excitation and hence rate of formation of holes, hydroxyl radicals and supra oxide ions ( $o^{\cdot-}$ ) is decreased thereby decreasing rate of degradation; ii) Since catalyst surface area is fixed, so as concentration of dye increases rate of degradation decreases because limited number of dye molecules attach at active site of

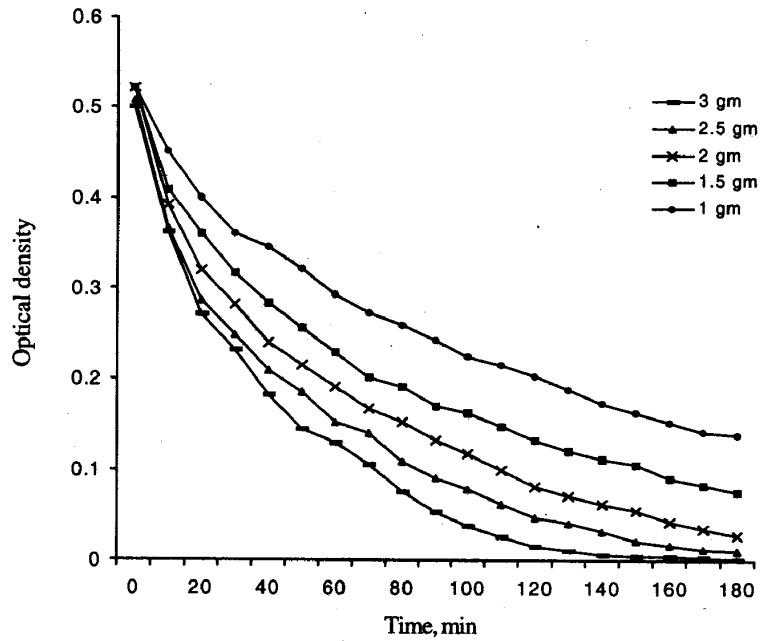


Fig. 2—Effect of catalyst loading on photo catalytic degradation (Temp. 303 K, solution vol 200 ml, initial dye conc. 40 mg/l, pH 7.5, UV/visible lamp 10.4 mWcm<sup>-2</sup>)

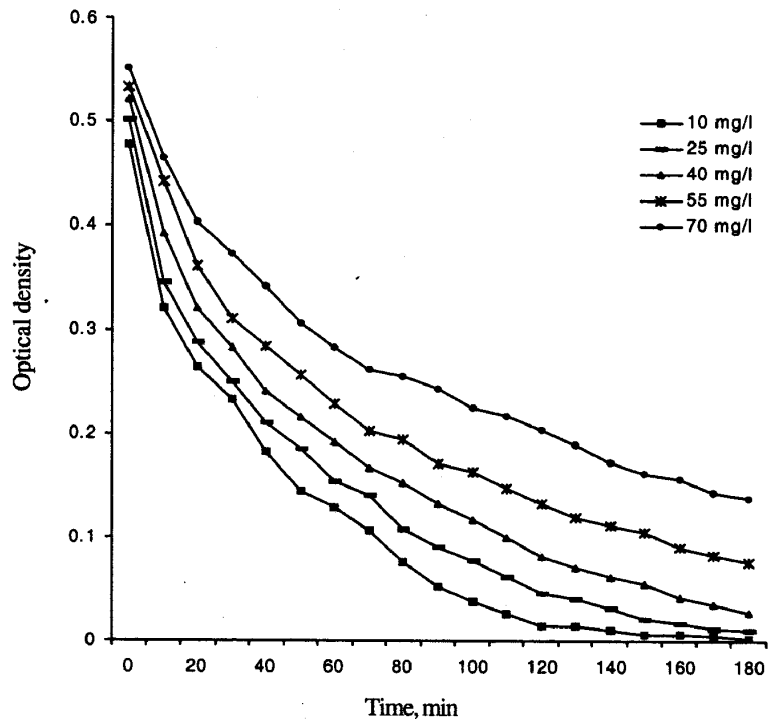


Fig. 3—Effect of initial dye concentration on degradation (Temp. 303 K, solution vol 200 ml, pH 7.5, UV/visible lamp 10.4 mW cm<sup>-2</sup>)

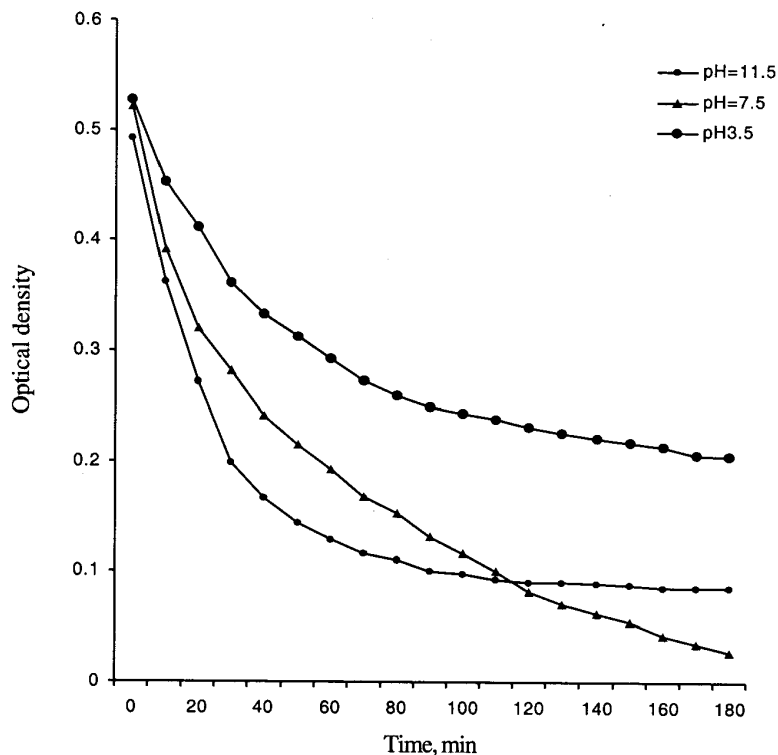


Fig. 4—Effect of pH on degradation (Temp. 303 K, solution vol 200 ml, initial dye conc. 40 mg/l, UV lamp 10.4 mW cm<sup>-2</sup>)

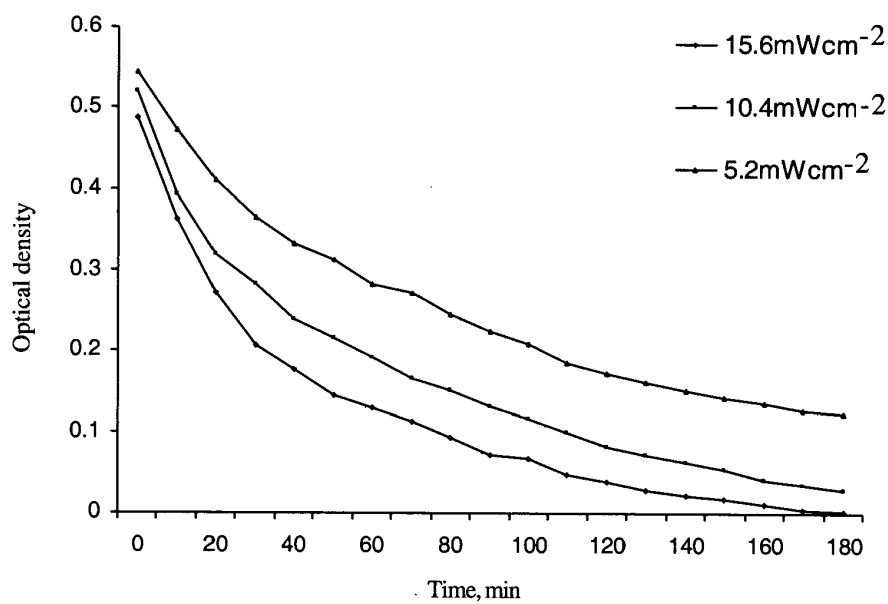


Fig. 5—Effect of variation of light intensity on degradation (Temp. 303 K, solution vol 200 ml, initial dye conc. 40 mg/l, pH 7.5)

catalyst and remaining dye molecules persist in solution until earlier attached molecules are degraded and number of active site of catalyst also decreases due less availability of photons for excitation of catalyst molecules; and iii) At higher concentration, number of dye molecules are also high so there will be more competition for attachment to active site of catalyst between dye molecules, resulting in reduction in rate of degradation.

#### Effect of pH

Rate of degradation is very low in high acidic pH. As pH increases, rate of degradation also increases. In pH range 7.5-9.0, rate of degradation is very good (Fig. 4); on further increasing pH, rate of degradation starts to decrease. Increase in rate of photo catalytic degradation may be due to more availability of  $\cdot\text{OH}$  ions by combining with holes, which are formed due to electronic excitation in catalyst in pH range 7.5-9.0. Formation of hydroxyl radicals are responsible more for photo catalytic degradation than supra oxide ( $\text{o}^-$ ).

#### Effect of Light Intensity

As light intensity increases, rate of degradation of dye molecules increases up to certain extent, and after that no changes are observed (Fig. 5). This is because as light intensity increases, number of photons reaching catalyst surface also increases, so increase in number of exited catalyst molecules result is increase in number of holes, hydroxyl radicals and Supra oxide ions ( $\text{o}^-$ ), and hence rate of degradation of dye molecules also increases.

#### Effect of Dissolved Oxygen

As dissolved oxygen increase in dye solution, rate of degradation also increase, may be due to more availability of oxygen for formation of supra oxide ( $\text{o}^-$ ) and hydroxyl radical. These are highly oxidative and increase degradation rate of dye molecules.

#### Conclusions

Photo catalyst (MBRD-11) has good potential of degradation of azo dyes/ dyes into simple molecules. It can purify textile effluent (wastewater) containing mostly non bio degradable azo dyes. As dye concentration increases, degradation rate of dye decreases. As concentration of catalyst increases, degradation rate of dye molecules also increases. Degradation rate is

optimum between pH 7.5-9.0. On increasing light intensity, degradation rate of dye molecules increases up to certain limit, after that no further changes are observed. Degradation rate increases up to some extent on increasing dissolved oxygen in dye solution.

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