



Photocatalytic Decolorization of Acid Red 186 Using Alternative Developed Photocatalyst MBIR Dowex 11

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Abstract

Methylene blue immobilized resin (MBIR) Dowex 11 was used as a photocatalyst for the removal of Acid Red 186 (C.I. 18810) from aqueous solutions. The rate of decolorization of dye was investigated under various parameters such as catalyst dose, concentration of dye, pH of the solution, light intensity and dissolved oxygen was systematically studied. The heterogeneous photocatalyst MBIR Dowex 11 is cheap and a very good alternative to replace costly traditional treatment technologies for industrial application. The size of catalyst particle is 20-50 mesh can filter easily. The kinetics of photocatalytic degradation of the dye was found to follow pseudo first-order kinetics according to Langmuir-Hinshelwood model. The results showed that the dye removal efficiency found 98% after 160 min of reaction time. The possible reaction mechanism and recycle study of catalyst are also discussed.

Keywords: Methylene blue, immobilization, degradation, acid red 186, dowex 11.

Introduction

The textile processing industry is putting a severe burden on the environment, through the release of heavily polluted wastewaters. The removal of the non-biodegradable organic chemicals is a crucial ecological problem. Azo Dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial pollutants. Various approaches have been developed to remove organic dyes from the natural environment. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultra filtration can be used for color removal from textile effluents¹⁻³. Among chemical technologies, a novel method that has been growing in recent decades is the advanced oxidation processes (AOPs) which are very potent in oxidization, decolorization, mineralization, and degradation of organic pollutants. Due to high oxidation rate of the chemical reactions caused by AOPs, the behaviour of chemicals is significantly changed after the treatment. The degradation makes organic chemicals smaller and biodegradable. AOPs for wastewater treatment are not an economical process due to their high operating cost, thus; it is suggested to integrate these technologies with other post-treatment methods such as biological processes. The integration of advanced oxidation technologies and biological processes has been reviewed by Scott and Ollis⁴, Tabrizi and Mehrvar⁵ and Mantzavinos and Psillakis⁶.

AOPs were based on the generation of very reactive species such as hydroxyl radicals ($\bullet\text{OH}$) that oxidize a broad range of pollutants quickly and non selectively. AOPs such as Fenton and photo-Fenton catalytic reactions⁷⁻¹⁰, $\text{H}_2\text{O}_2/\text{UV}$ processes¹¹ and TiO_2 mediated photo-catalysis¹² have been studied under a

broad range of experimental conditions in order to reduce the color and organic load of dye containing effluent waste waters. Among AOPs, heterogeneous photocatalysis using TiO_2 as photo-catalyst appears as the most emerging destructive technology¹³. Decolorization of textile industry wastewater and degradation of C.I. Reactive Orange⁴ and its simulated dye bath wastewater by heterogeneous photocatalysis^{14,15}. The photocatalytic degradation of reactive black⁵ using different semiconducting oxides, TiO_2 , UV-100 TiO_2 , ZnO , and TiO_2/WO_3 four parallel black light blue fluorescent tubes were used as the UV-light source¹⁶. Degradation of Acid Green 16 using ZnO irradiated with sunlight, here the photodegradation efficiency decreased with an increase in initial dye concentration, optimum catalyst loading was found to be 250 mg in 100 ml¹⁷. Photocatalytic degradation of various textiles azo dyes with nanoparticles, activated charcoal adsorption and electrocoagulation and ultrasound assisted semiconductor are suggested by various researchers¹⁸⁻²². Use of semiconducting iron (II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta *et al.*²³.

The degradation is more with solar/ ZnO process than with solar/ TiO_2 -P25 process at pH 9 reported by Krishnakumar and Swaminathan²⁴. The photodegradation of azo dyes acid red 14 by chitosan capped CdS composite nanoparticles and in aqueous phase nanophotocatalysts^{25,26}. Degradation of Ponceau-S and Sudan IV with methylene blue immobilized resin Dowex 11 photocatalyst²⁷. The visible light induced photocatalyst MBIR Dowex 11 is an impressive task in order to utilize the solar energy effectively. In the present work we have undertaken a detailed study on the photodegradation of toxic azo dye Acid Red 186 employing methylene blue immobilized resin (MBIR)

Dowex 11 as a photocatalyst in aqueous solution under solar and UV light sources examining the impact of various experimental parameters.

Material and Methods

Photocatalytic studies and design of photoreaction chamber:

We prepared photocatalyst by following materials Dowex 11 resin 20-50 mesh (Sisco Chemicals, India Mumbai), and Methylene blue hydrates (Loba Chemicals India). For immobilization we prepare approximately M/1000 concentration solution of methylene blue in double distilled water and add Dowex 11 resin in this solution and shake well for immobilization of pores of resin up to 4-5 days. All the process carried out in dark place. Then filter prepared resin from solution, wash this resin by double distilled water twice and used it as photocatalyst. Photochemical degradation experiments were carried out in glass reactor which containing solutions of Acid Red 186 dye, molecular formula $C_{20}H_{14}N_4Na_2O_8S_2$, λ_{max} 455 nm (figure-1) and photocatalyst.

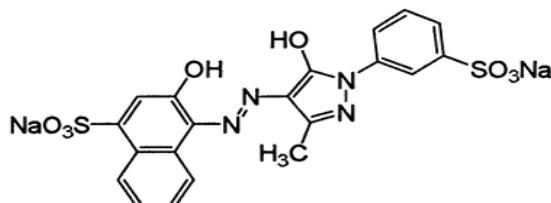
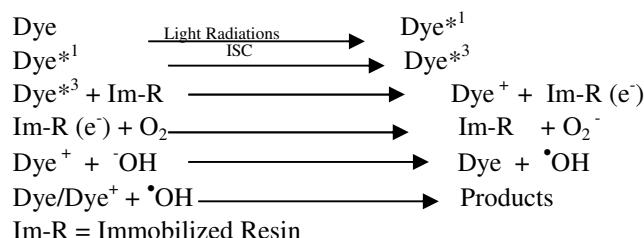


Figure-1
Structure of Acid Red 186

Solution of reactor is continuously stirred by magnetic stirrer during the experiment and illuminated by halogen lamp (Philips, India) above the reactor which emitted irradiation comparable to visible light (figure-2). The lamp was surrounded with aluminium reflector in order to avoid loss of irradiation. The intensity was measured by photometer (IL1400A) and pH of the solution was monitored by Fisher Scientific Acumen 50.

Mechanism of degradation: The mechanism of Acid red 186 dye degradation process under UV-Vis/Solar light illumination involves an electron excitation and generation of very active oxygenated species that attack the dye molecules leading to photodegradation. Methylene blue immobilizes resin Dowex-11 is newly developed photocatalyst, due to photosensitive nature

of methylene blue, when light radiation is irradiated on it, electronic transition occurs from valence band (VB) to conduction band (CB) and through (ISC) electrons reach into triplet state of methylene blue. After it intermolecular electronic transition start between resin, methylene blue dye molecules, water molecules, acid red 186 dye molecules and dissolved oxygen, resultant through chain process, holes, hydroxyl radicals ($\cdot OH$) and super oxide ions (O_2^-) are formed and these are highly oxidizing in nature, by the action of holes, hydroxyl radicals and super oxide ions on azo dye, are transformed in simple organic compounds like CO_2 and H_2O etc.



We shook out 10 ml solution of reaction mixture with the help of a syringe at 10 min time interval, and filtered the catalyst particles through Millipore syringe and change in concentration of dye solution is observed simply by Shimadzu-1600 UV/visible spectrophotometer at λ_{max} 455nm. Calculate the dye removal efficiency (X %) of dye solution by this equation.

$$X\% = (C_i - C_t / C_i) \times 100$$

Where, C_i and C_t are optical densities of dye solution at initial time and at time t respectively.

Kinetic Study: Photocatalytic degradation of Acid red 186 was observed at $\lambda_{max} = 455$ nm. The optimum conditions were obtained at initial dye concentration: 40 mg/L, catalyst loading: 2.0gm/100ml, solution volume: 100ml, light intensity: 10.4 mWcm⁻², pH: 7.5 and temperature 303 K. The plot of 1 + log optical density versus exposure time is a straight line (Figure-3). This indicates that the photocatalytic degradation of Acid red 186 follows pseudo first-order kinetics²⁸⁻³⁰. The rate constant (K) for the reaction was determined using the expression. Rate = K [Acid red 186], $K = 2.303 \times$ Slope. The rate constant for this reaction is $K = 1.33 \times 10^{-2} \text{ min}^{-1}$.

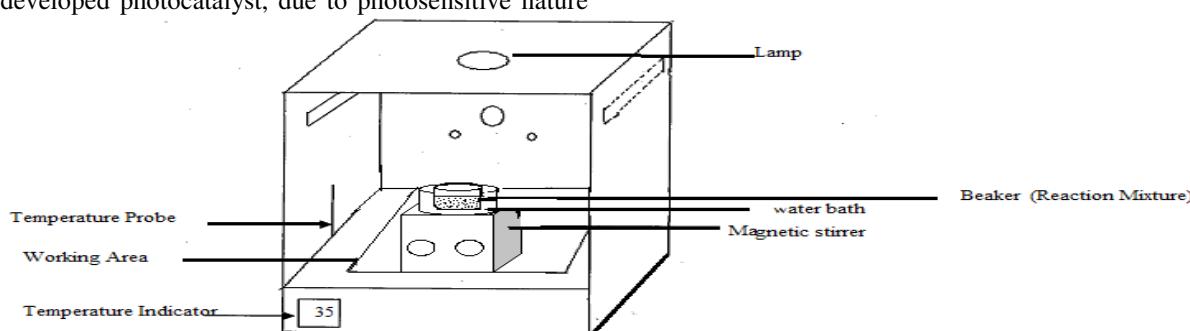


Figure-2
Experimental setup of Photochemical Reaction Chamber

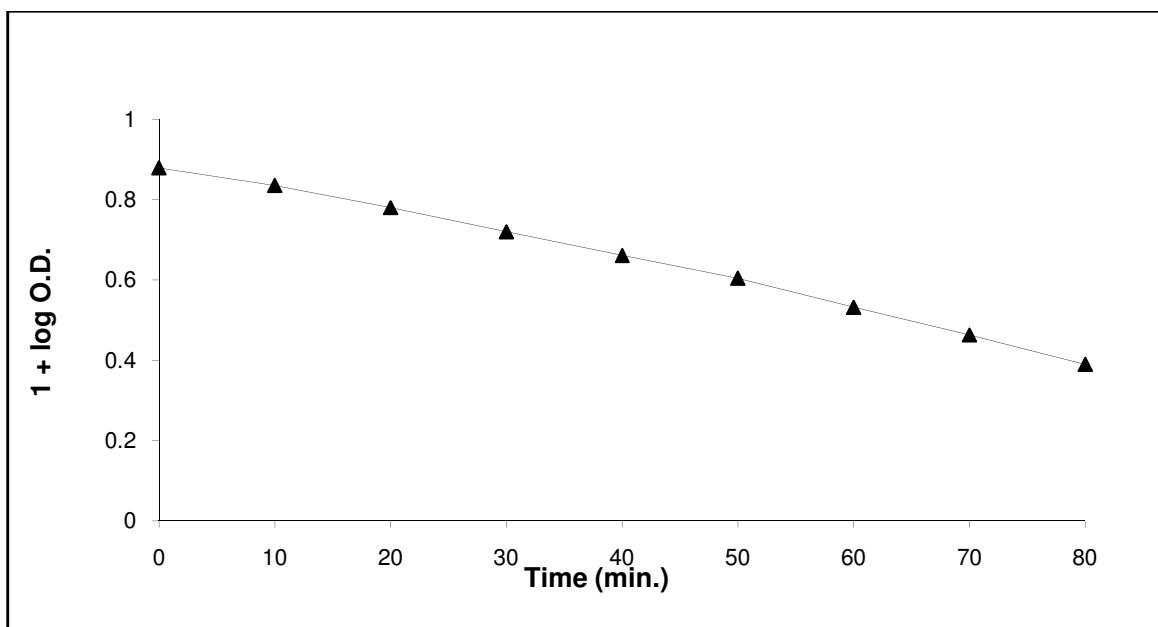


Figure-3

Kinetic Study for Acid red 186- Photocatalyst system (Initial dye concentration 40 mg/L, pH 7.5, catalyst loading 2.0 gm/100 ml and light intensity 10.4 mWcm⁻²)

Results and Discussion

Effect of catalyst loading: Experiments were performed to study the variations in the degradation of Acid Red 186 at different catalyst loading. It can be observed that the bleaching of dye increased with increase in catalyst loading from 1.0gm/100ml to 3.0gm/100ml and all other experimental conditions constant concentration of dye 40 mg/L, at constant pH 7.5 and light intensity 10.4 mWcm⁻². Due to more availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, increase in number of hydroxyl radicals and super oxide ions (O_2^-). These are the principle oxidizing agents in advance oxidation process. A further increase in catalyst loading, however, may prevent the efficient light adsorption in the solution and thus result in the decrease of degradation (figure-4).

Effect of initial dye concentration: The effect of initial concentration of Acid Red 186 on the degradation process was investigated over the concentration range from 10mg/L to 70mg/L with constant catalyst loading 2.0gm. As the dye concentration increased, rate of degradation decreased (figure-5), may be due to following reason: 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 hydroxyl radicals and supra oxide ions (O_2^-) is decreased thereby decreasing rate of degradation. 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 catalyst and remaining dye molecules persist in dye 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. At higher concentration, numbers 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: The effect of pH on the decolorization of Acid Red 186 were investigated by keeping all other experimental conditions constant catalyst amount 2.0gm/100ml, dye concentration 40mg/L and light intensity 10.4 mWcm⁻² and varying the initial pH of dye solutions from 3.5 to 11. It can be observed that the bleaching of dye was increased with increasing pH value from 3.5 to 9.0 (figure-6). On further increasing pH, rate of degradation starts to decrease. Maximum bleaching was obtained at pH 7.5. At this pH dye was reduced by 97% after 160 min. Increase in the rate of photo catalytic degradation may be due to more availability of hydroxyl ions by combining with holes, which are formed due to electronic excitation in catalyst in pH range 7.5 - 9.0. Formations of hydroxyl radicals are responsible more for photo catalytic degradation than super oxide ions (O_2^-).

Effect of light intensity: As light intensity increased, rate of degradation of dye molecules increased up to a certain limit, and after that no changes were observed (figure-7). This is because as light intensity increases, number of photons reaching catalyst surface also increases, so increase in number of excited catalyst molecules result is increase in number of hydroxyl radicals and super oxide ions (O_2^-), and hence rate of degradation of dye molecules also increases.

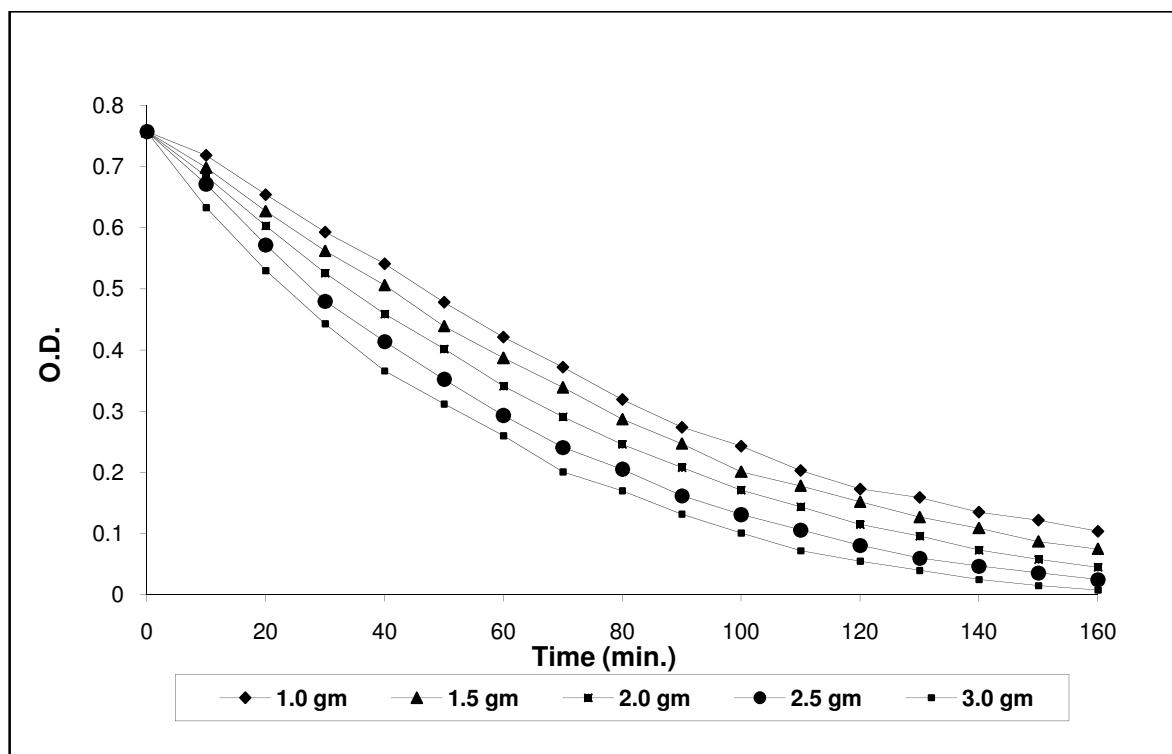


Figure-4
Effect of catalyst loading on optical density (solution volume 100 ml, initial dye concentration 40 mg/L, pH 7.5, light intensity 10.4 mWcm^{-2})

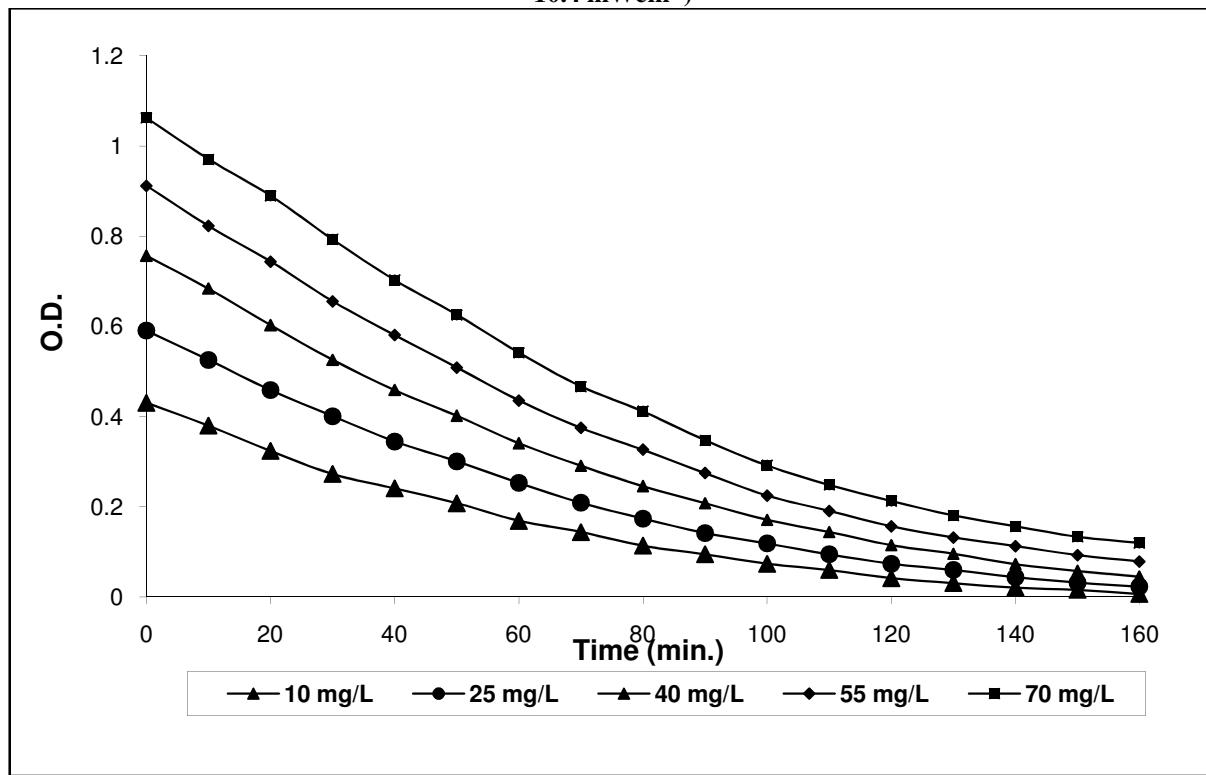


Figure-5
Effect of initial dye concentration on optical density (Catalyst loading 2.0 gm/100 ml, solution volume 100 ml, pH 7.5, and light intensity 10.4 mWcm^{-2})

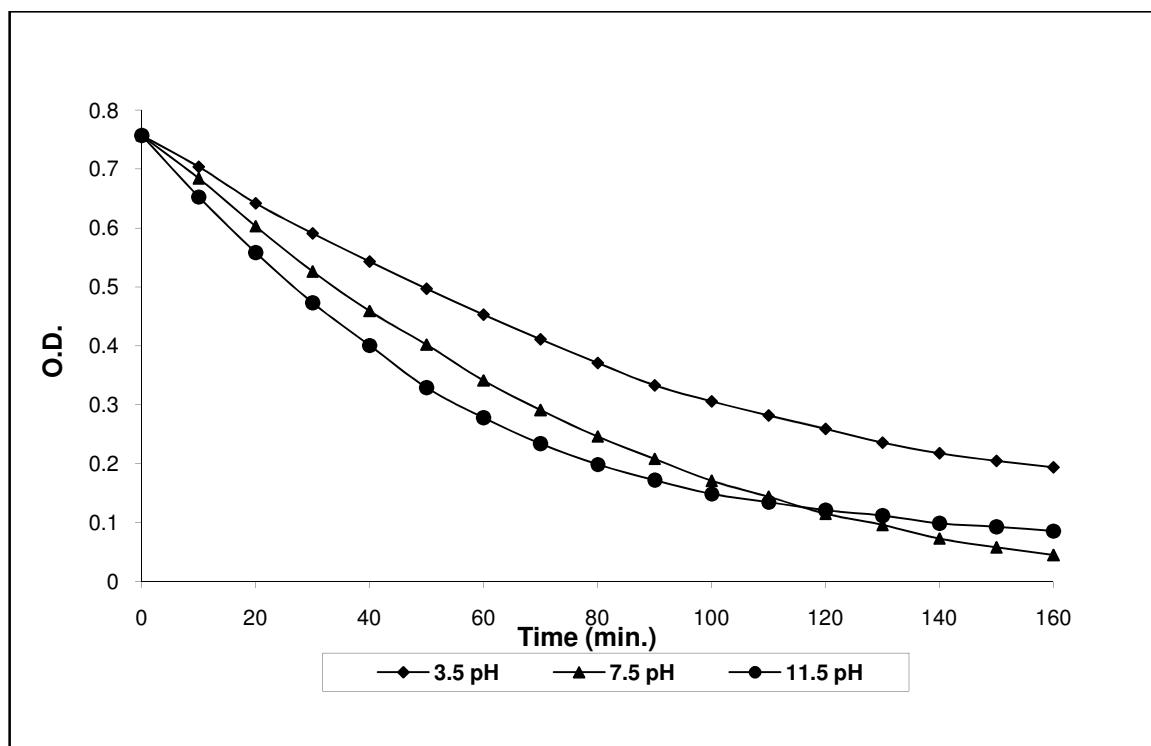


Figure-6
Effect of pH on optical density (Catalyst loading 2.0 gm/100 ml, solution volume 100 ml, initial dye concentration 40 mg/L, and light intensity 10.4 mWcm^{-2})

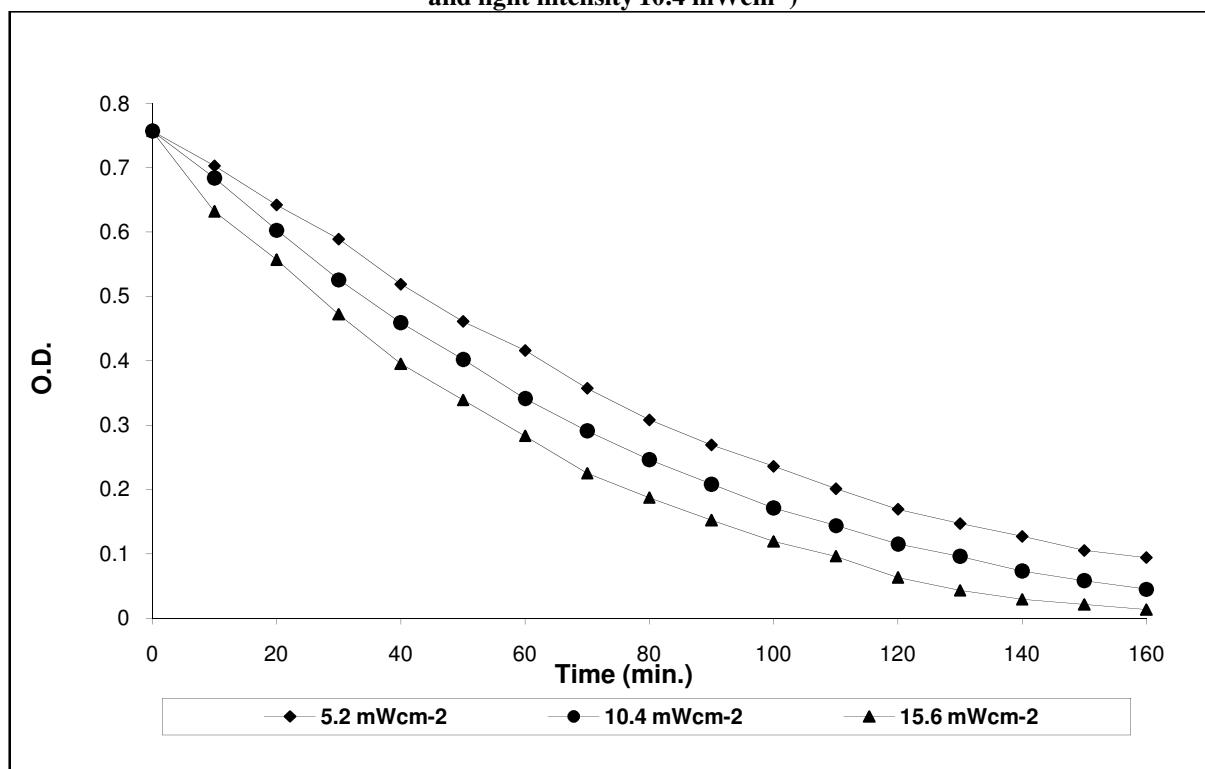


Figure-7
Effect of variation of light intensity on optical density (Catalyst loading 2.0 gm/100 ml, solution volume 100 ml, initial dye concentration 40 mg/L, and pH 7.5)

Effect of dissolved oxygen on rate of degradation: We observed the effect of dissolved oxygen on rate of degradation, as dissolved oxygen increase in dye solution rate of degradation also increase. We observed that when oxygen gas is passed through reaction mixture the rate of degradation also increases when nitrogen or any other non reacting gas is passed through this solution no effect is observed on rate of degradation. This effect may cause due to more availability of oxygen for formation of super oxide ions and hydroxyl radicals. These are highly oxidative in nature and increase the rate of degradation of dye molecules.

Recycling studies: In order to know the stability of the catalyst, the catalyst was recycled five times by using dye solutions at optimum conditions. After each experiment, the catalyst was separated from solution by filtration, washed with deionised water for several times, the catalyst was dried over night and then used for next run. Noticeably, after five cycles of experimentation, the catalysis efficiency was still higher and the catalytic performance was not affected by the times of reuse.

Conclusion

After long observation we conclude that the alternative photocatalyst (MBIR Dowex 11) has very good potential of degradation of azo dyes into simple mineralize products. Photodegradation efficiency of the dye was very less when photolysis was carried out in absence of the catalyst and negligible in absence of light.

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