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Visible Light Induced and Newly Developed Photo catalyst Methyelene Blue Immobilized Resin Dowex-11 Assisted Decolorization of Azo Dye Acid Orange-7

Disha, Pratibha Yadav and R C Meena*

Department of Chemistry, Jai Narain Vyas University, Jodhpur, India

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ABSTRACT

Batch experiments were carried out for the decolorization of azo dye AO7 in aqueous solution using methylene blue immobilized resin Dowex-11, under artificial irradiation. The present experimental methodology was applied to assess the individual & interaction effects of several operational variables (dye concentration, catalyst loading, pH & light flux) and also the inhibiting effect of propanol on the decolorization rate has been studied. Based on the optimal experimental data the decolorization kinetic study, the rate constant was found to be $2.50x10^{-2}$ min^{-1} & graphically the semi log plot of dye concentration verses time was linear, suggesting pseudo first order kinetics. The present work demonstrates easy & approachable experimental modeling for the treatment of an azo dye (AO7).

Keywords: Decolorization, AO7 (Acid Orange-7), Methyelene blue immobilized resin Dowex-11.

INTRODUCTION

Modern world is associated with industrialization because it serves as a vehicle for the development as well as for the economic growth. However this industrialization brings a lot of industrial wastes in to the environment. These products contain both organic & inorganic contamination which is persistent in nature (non biodegradable & highly aromatic toxic compounds).The application of different dyes like acidic, basic, reactive & direct dyes by textile industries creates water contamination. The kind of textile waste discharge in water bodies alter the pH, increase the BOD & COD & gives intense color to the water[1] .This diminishes the water quality make it unhealthy & undesirable to aquatic as well as for human consumption there by limiting utilization of the water bodies.

Presently over 100000 different dyes are manufactured processed & formulized in textile industries. Dyes varies by their chemical nature among them azo dyes are the most widely used, further acidic azo dyes which are anionic containing acidic groups along with one or more azo groups get easily dissolve in water & enrich it with high levels of organic matter phosphorous & nitrogen. From research it has been revealed that the dye consumption by the textile industries worldwide is in excess of 10^7 kg/year of dyes are discharged by textile industries [2] .since these dyes are water soluble they easily incorporated in to the body metabolism & are split in to toxic aromatic amines which produces problems like irritation ulcers, cancer etc & respiratory problems [3-4]

Regarding above mentioned health problems by these pollutants a lot of research & studies has been done for the adequate treatment of industrial & textile wastes various methods like coagulation & flocculation [5], membrane [6]

& bio films technologies [7], adsorption [8] & chemical oxidation [9]. However there are problems related with complete destruction & further treatment of wastewater with these physicochemical & biological methods, because the post treatment dye wastes may contain some components or moieties that could be toxic & mutagenic to aquatic life. Therefore, the degradation of azo dyes under alternative AOP (Advance Oxidation Processes) technologies as for example- Photo catalytic processes has been employed, which are capable of almost complete mineralization & for effective treatment of wide range of organic pollutants.AOP is a catalytic process based on the generation of very reactive species such as hydroxyl radicals that non-selectively, oxidizes wide range of organic pollutants[10] .To utilize visible light or solar light among AOPs photochemical oxidation[11] & photo catalytic oxidation[12-13] methods have been paid more attention in the recent years .AOPs seems to be very promising way of treatment of wastewater from textile industry. In AOPs heterogeneous photo catalysis's found as an emerging destruction technology leading to complete mineralization of organic pollutants [14-20].

Many visible light &UV light sensitive photocatalyst [21-25] have been developed. The development of visible light photo catalyst is an impressive task in order to utilize the solar energy effectively. The present work investigates the influence of an azo dye, (AO7) in presence of visible light induced methylene blue immobilized resin Dowex-11. The inhibitive influence of propanol has also been studied.The main objective of the present work is to seek attention of researchers towards the efficiently better &cheap photocatalyst. Since Dowex-11 is an ion exchange resin has been specially engineered with unique porosity to optimize organic removal. Here immobilization technique is applied just to fill porosity with photosensitized dye methylene blue so that the visible light photocatalyst can be developed. Since methylene blue is a photosensitized dye so, as it absorbs photon of suitable wavelength it get excited& the ejected e- transfers in to singlet state & through inter system crossing(ISC) e-transfer to triplet state of methyelene blue. Further electronic interaction occurs between resin, methyelene blue & solution mixture & resultant is formation of holes, very reactive hydroxyl radicals & super oxide ions (O-) that rapidly oxidizes the organic pollutants. The predicted tentative mechanism of decolorization has been given as follows:

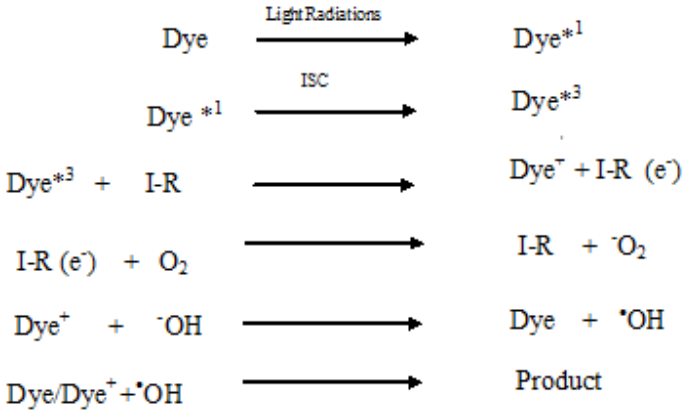
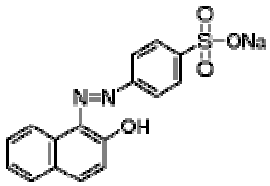


Table-1

Chemical Structure	
C.I Number	15510
Synonym	Orange II
Molecular formula	$NaC_{16}H_{11}SN_2O_4$
Molecular Weight	350.32
λ_{max}	483nm

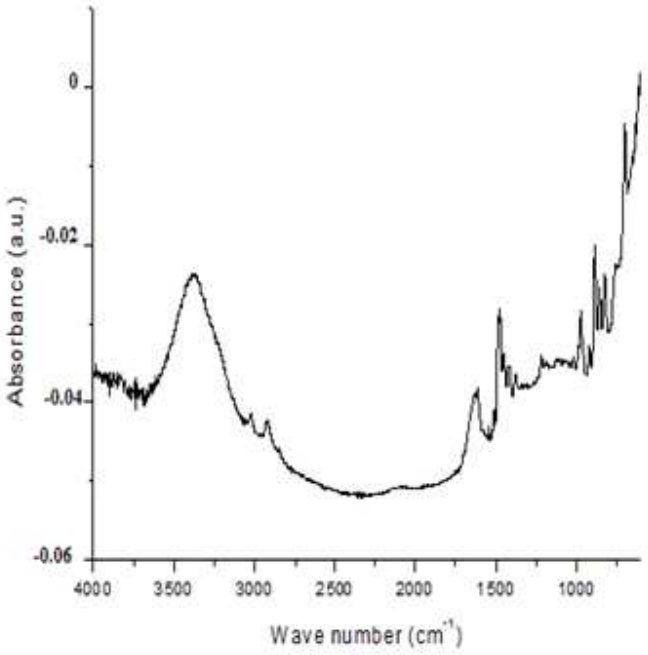


Fig.1. The IR spectra of Dowex-11 resin without grafting

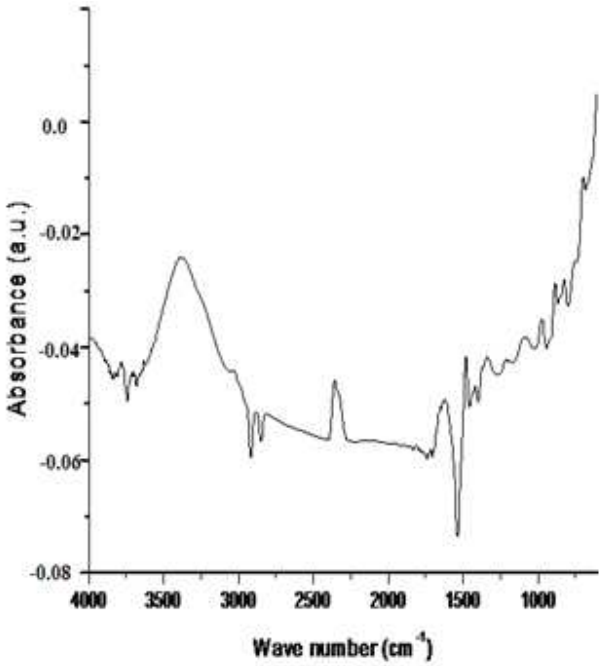


Fig.2. The IR spectra of Dowex-11 resin after immobilization by methylene blue dye.

since operating capacity is a critical feature of an anion exchange resin, here the new uniform particle size methylene blue immobilized resin Dowex-11 consistently offers 90-95% removal of organic material when new; 80-85% removal after extended services, this was proved by repeating the same experiment under optimal conditions (40mg/L dye concentration,2g/L catalyst loading, pH 7.5, and 10.4 $mWcm^{-2}$ light intensity).Also the homogeneous mixture separation can be done easily because of the beads like structure of the catalyst. Therefore post treatment processes is not a tedious task. This catalyst is also very good alternative to traditional technologies for industrial application.

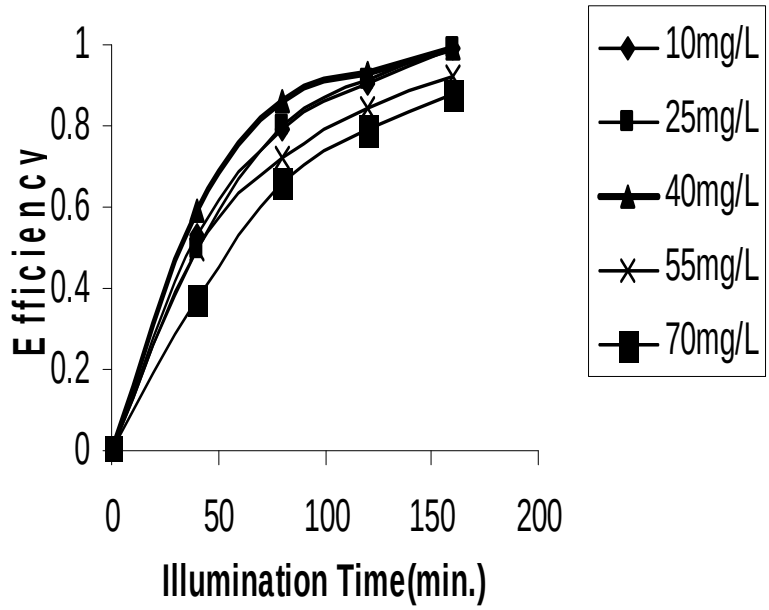


Fig.3. Influence of variation in dye concentration on the decolorization efficiency in presence of 2g/L catalyst, 10.4mWcm^{-2} light intensity, pH-7.5.

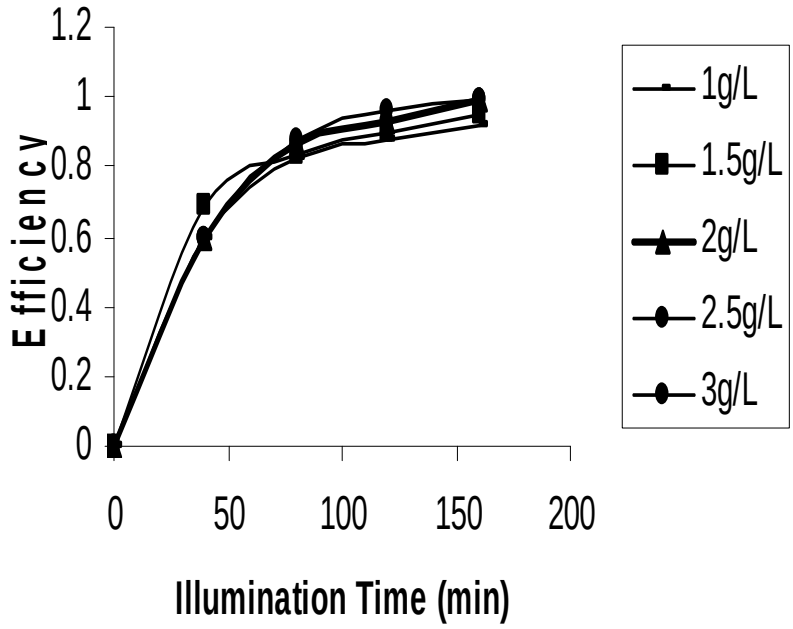


Fig.4. Influence of variation in catalyst loading on the decolorization efficiency in presence of 40mg/L dye concentration, 10.4mWcm^{-2} light intensity, pH-7.5.

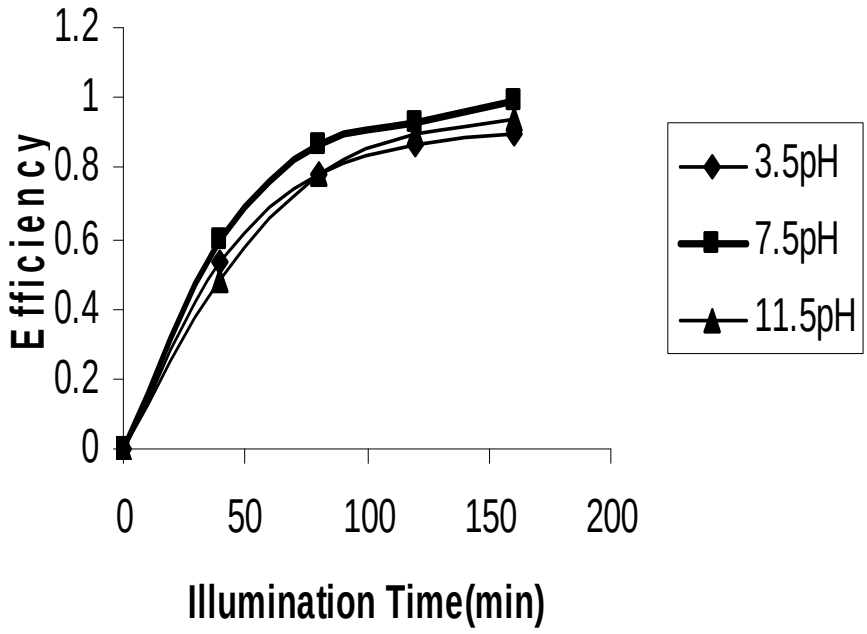


Fig.5. Influence of variation in pH on the decolorization efficiency in presence of 40mg/L dye concentration, 2g/L catalyst, 10.4mWcm^{-2} light intensity

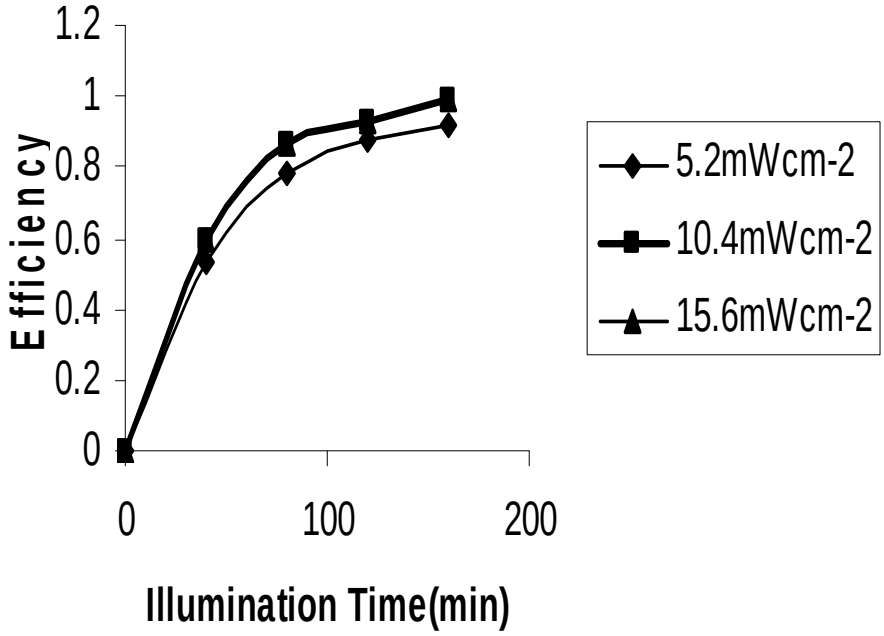


Fig.6. Influence of variation in light flux on the decolorization efficiency in presence of 40mg/L dye concentration, 2g/L catalyst, 7.5pH

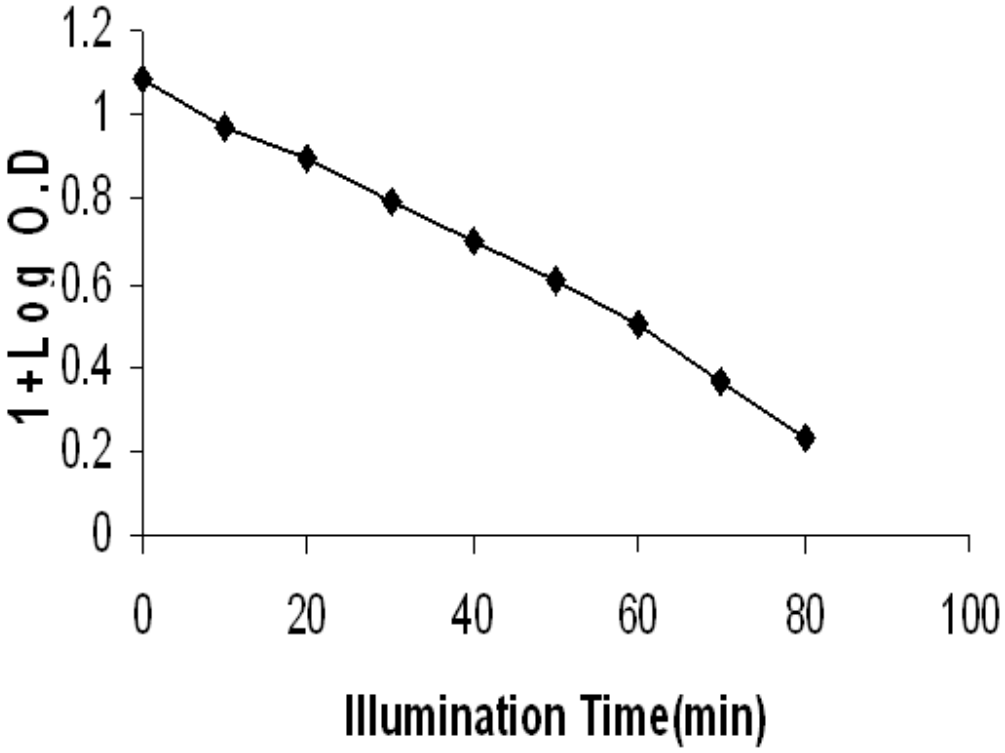


Fig.7. Relationship between 1+log Optical Density (AO7) and illumination time on photocatalytic decolorization of AO7. $[AO7]_0$=40mg/L, 2g/L catalyst loading, pH-7.5, 10.4mWcm^{-2} light intensity

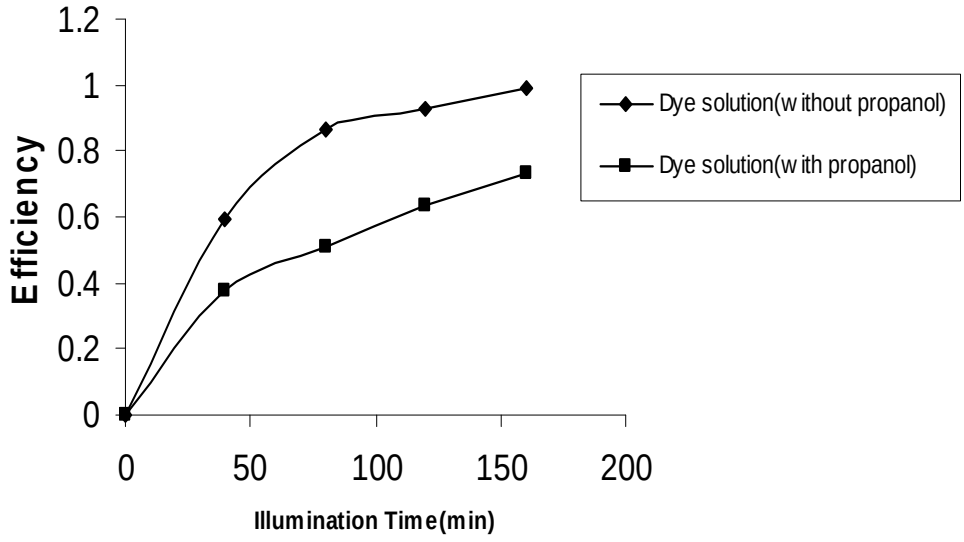


Fig.8. Plot showing difference in photodecolorization efficiency of AO7 in presence & absence of propanol at 40mg/L dye concentration, 2g/L catalyst loading, pH-7.5, 10.4mWcm^{-2} light intensity

MATERIALS AND METHODS

The dye AO7 was collected from local dye suppliers & was used without further purification .The main characteristics of the dye is given in table-1.Photo catalysts prepared from Dowex-11 resin 20-50 mesh (Sisco

Chemicals India, Mumbai), Methylene blue hydrated for microscopy (Loba Chemicals India), pH of the solution was maintained by NaOH & H_2SO_4 of AR grade. Dye solution of the desired concentration was prepared using doubly distilled water.

Process of Immobilization

Immobilization was done by preparing M/1000 concentration of methylene blue in double distilled water after that the resin Dowex-11 has added to the solution, the mixture was shaken & placed in dark for 3 days to get complete immobilization of methyelene blue inside the pores of the resin. On fourth day the resin was filter from the solution & washed with double distilled water twice & used as photo catalyst. The immobilization takes place it can be identified by its characteristic IR spectrum (Figure-1) shows the peaks of the resin (without grafting) before immobilization and Figure-2 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. These peak shows that the immobilization of the photo sensitized dye (methylene blue) in the resin has been taken place.

Experimental setup and procedure of study

The photo decolorization reaction was carried in a batch photo reactor containing 50 ml of a model solution of AO7 & a defined amount of photo catalysts. The concentration of model dye was equal to 10 mg/L to 70 mg/L & the catalyst concentration ranged from 1 g/L to 3 g/L. The solution in the reactor was continuously stirred during the experiment. After 15 minute in dark to set equilibrium, the reaction was illuminated with 10.4 $mWcm^{-2}$ tungsten lamp (philips). The lamp was positioned 10 cm above the reactor. The irradiation intensity was measured using a photometer (1L1400A). The experiment was performed at ambient (30^oC) temperature. The reaction was carried out with 3 different pHs (Fisher scientific Acumen) 3.5, 7.5& 11.5 corresponding to initial dye concentration (40 mg/L).The solution was aerated throughout the experiment. At specific time interval the samples of solution were withdrawn & analyzed. The decolorization rate of AO7 was estimated on the basis of changes by Shimadzu-160 Spectrophotometer. The FT-IR spectra of the resin before and after immobilization were recorded by Spectro Jasco Corp. /IR-610 over the range 599.7532 – 4000.605 cm^{-1}

RESULTS AND DISCUSSION

Initially the experiment was carried out in light only (without catalyst) in order to determine the photo stability of AO7. The solution was placed in the same batch photo reactor that was applied in the photocatalysis experiment. It was found that after 160 minute of illumination of the dye solution the measured optical density of the solution was almost constant, that means no degradation of the dye AO7 took place. Therefore, it can be stated that in the presence of methyelene blue immobilized resin Dowex-11 the decolorization stated. To determine the effect of the initial dye concentration, catalyst loading, pH variation & light flux variation on the effectiveness of photo degradation of AO7 the photo decolorization of model dye was performed.

The degradation efficiency(X) was given by formula given in equation (1):

$$X = \frac{C_o - C}{C_o}$$

C_o = Initial Concentration

C = Concentration of AO7 at time t

Effect of initial dye concentration

The effect of initial AO7 concentration on photo degradation efficiency is shown in figure-3 when initial concentration exceeds optimum level degradation decreased. The presumed reason is that lower concentration (up to 40mg/L) hydroxyl radical, super oxide ions were sufficient to attack dye molecules, but with increase in concentration (above 40 mg/L) of the dye, more & more dye molecules are adsorbed on the surface of the catalyst as a result of which catalyst surface available to generate hydroxyl radicals, super oxide ions were not sufficient enough to attack dye molecules, thereby photo degradation efficiency decreases.

Effect of catalyst loading

A series of experiments were performed to assess optimum catalyst loading by variation in amount of catalyst dosage (1g/L to 3 g/L) at pH-7.5 with dye concentration (40mg/L). From figure-4 it can be conclude that photo degradation efficiency increases by increasing catalyst loading. Increase in degradation with increase in catalyst loading was due to increase in number of active sites, which in turn increased hydroxyl radical, holes & super oxide ions but when we keep on increasing catalyst loading above 3gm no change has been observed, this may be due to increase in catalyst loading above optimum level resulted in decrease in light penetration & aggregation of particles may also reduce effective surface area of catalyst for absorption of reactant.

Effect of pH

pH value is one of an important factors influencing the rate of degradation, in the photo catalytic processes. It is also an important operational variable in actual waste water treatment.Figure-5 shows that when pH range 7.5-9.0 the photo degradation efficiency was very good, & it is low in acidic pH range increase in rate of photocatalytic decolorization in 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 photocatalytic bleaching.

Effect of light flux

The effect of light intensity on rate of photodegradation efficiency is shown in figure-6 from experiment it has been found that as light intensity increases the rate of degradation of dye molecules also increases this may be due to 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 super oxide ions (o^-) but this increase in degradation rate was up to certain extent & after it no change are observed in rate of degradation this is because maximum number of photons which are required for excitation are available in fix range irradiating light intensity &after it if further increase in light intensity no considerable changes are observed in rate of degradation ,because all catalyst molecules become active (excited) in fix light intensity range after it if we increase light intensity to any range the rate of degradation remains unchanged.

Kinetics of photocatalytic degradation.

From figure-7, the semi log plot of dye concentration verse time was linear suggesting that the photo degradation reaction follows pseudo first order kinetics ($2.50x10^{-2}min^{-1}$). When initial concentration exceeded optimum level, degradation decreased. Moreover, as initial dye concentration increased, path length of photons entering solution decreased & at low concentration, number of photons absorption by catalyst increased, hence rate of degradation is proportional to substrate concentration in accordance with apparent Pseudo First order kinetics.

The rate constant was determined using the expression K=2.303x Slope.

Addition of propanol

Alcohols such as ethanol & propanol are commonly used to quench hydroxyl radicals. As it was observed from the experiment (figure-8) that decolorization efficiency of AO7 was decreases in presence of propanol(in the ratio 2:5) in comparison to dye solution in absence of propanol . This enables us to draw the conclusion that small amount of propanol inhibit the photocatalytic decolorization & hence OH radicals also play a major role in photo catalytic oxidation of AO7 dye.

CONCLUSION

The result of our study showed that recently developed photo catalyst MB immobilized resin Dowex-11 could be efficiently used to decolorize carcinogenic organic pollutants like azo dyes (AO7) present in wastewater. The results revealed that the degree of degradation of AO7 was obviously affected by the initial dye concentration, pH, catalyst loading & light flux. From optimal condition 40mg/L, 7.5 pH, 2g/L catalyst loading & 10.4 $mWcm^{-2}$ light intensity the inhibitive effect of propanol has also been studied, & it was concluded that hydroxyl radicals play a major role in oxidation of the dye (AO7). The degradation of the dye, follow the pseudo-first order kinetics with respect to the concentration of AO7. 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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