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A Study on Effect of Various Parameters on Rate of Photocatalytic Transformation of Azo Dye Direct Yellow 9

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Abstract: *The removal of the non-biodegradable organic chemicals is a crucial ecological problem. Transformation of Azo dyes is challenging for researchers and environmentalists. Transformation of these azo dyes by recently developed photo catalyst Methylene Blue immobilized Resin Dowex-11 is better alternate to replace costly traditional treatment technologies for industrial application. Batch experiments were carried out for the transformation of azo dye Direct Yellow 9 (DY 9) in aqueous solution. The effect of different reaction parameters like catalyst loading 1gm-3.0gm/50ml, pH 3.5-11.5, temperature 303k, dye concentration10mg/50ml-70mg/50ml, light intensity 5.2-15.6 mWcm^{-2} and also the inhibiting effect of propanol on the transformation rate of DY 9 has been studied. Activity of photo catalyst MBIR-11 remains impervious on continuous use.*

Keywords:- *Photo catalyst; Transformation; Azo dyes; Direct Yellow 9; Methylene Blue immobilized-Resin; Dowex-11*

1. INTRODUCTION

Azo Dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial pollutants. Due to the stability of modern Azo dyes, mostly azo dyes conventional biological treatment methods for industrial wastewater are ineffective resulting often in an intensively colored discharge from the treatment facilities.

Heterogeneous photo catalysis, by semiconductor particles is a promising technology for the reduction of global environmental pollutants[1-4]. Recently developed photo catalyst such as Methylene blue immobilized Resin Dowex-11 have shown to be a relatively cheap and effective way of removing organic compounds and pollutant dye pollutants[5-9]. Purification of wastewater of textile industries, paper industries, food industries, chemical industries, contain residual dyes which are not readily bio degradable is challenging for researchers and environmentalists. Adsorption and chemical coagulation are common technique used in treatment of such wastewater. However these methods transfer dyes from liquid to solid phase and produces secondary pollution and requiring further treatment.

Advance oxidation process (AOP) is recently more developed technique in photochemistry and this technique is best for treatment of textile industries effluent (wastewater) [11-13]. We use Methylene Blue Immobilized Resin Dowex-11 for oxidative transformation of dye contaminants. Methylene Blue Immobilized resin is a newly developed photo catalyst and has vast potential of transformation of azo dyes. Methylene Blue can be act as sensitizer for light induced process. Due sensitization of photo catalyst, electron are migrate from balance band (VB) to conduction band (CB) and holes are formed in balance band; these holes can generate hydroxyl radicals which are highly oxidizing in nature. Probably hole can react with dye molecule and abstract electron from dye molecule and process of transformation start.

Aim of the presence work is to attention of researchers toward utilization of solar energy for transformation of dye pollutants by Photo catalyst and fined out new photo catalyst for different applications. A new developed cheap and better photo catalyst ant its applicability. The potential of transformation of (Direct Yellow 9, is an Azo dye used as model compound for experiment) dyes by (Methylene immobilized Resin Dowex-11) catalyst is better and this catalyst work well in dim light also.

2. MATERIALS AND METHODS

Dye: Direct Yellow-9

Synonyms	=	Clayton yellow, Thiazole yellow G
Molecular Formula	=	$C_{28}H_{19}Na_2N_5O_6S_4$
Appearance	=	Yellowish brown powder
Solubility in water	=	Soluble in water

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Molecular weight = 695.71 gm/mol
λ_{max} = 402 nm

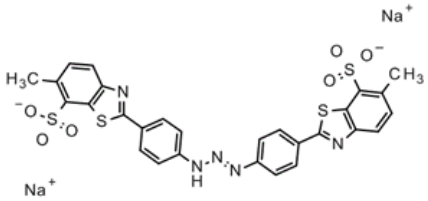


Photo catalyst:

Photo catalyst prepared by following materials Dowex-11 Resin 20-50 mesh (Sisco Chemicals India Mumbai), Methylene Blue Hydrate for Microscopy, (C. I. No. 52015, Loba Chemicals India). We prepare approximately M/1000 concentration solution of Methylene Blue in Double distilled water and add Dowex-11 resin in this solution and shack well. Put this mixture for 3 days for complete immobilization of Methylene Blue inside the pores of resin. All the process carried out in dark place. After three days we can filter prepared resin from solution, wash this resin by double distilled water twice and used it as photo catalyst.

Experimental set up and procedure:

The photo reaction is carried out in glass reactor which containing mixture of Dye (DY 9) and photo catalyst. Solution of reactor is continuously stirred by magnetic stirrer during the experiment. The solution is illuminated by 500W halogen lamp above the reactor. The change in dye concentration is observed simply by Shimadzu-160 UV/Visible spectrophotometer. Shuck out 10 ml of solution by pipette at the 10 minute time interval and observe change in percentage transparency of dye solution. A schematic diagram of the setup can be seen in figure1.

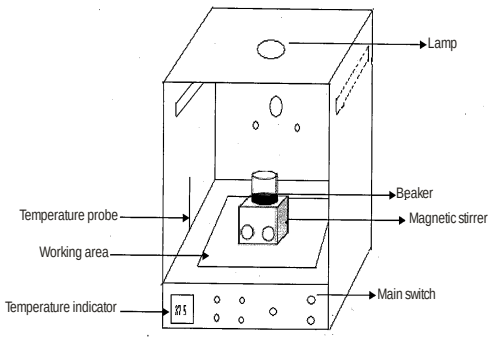
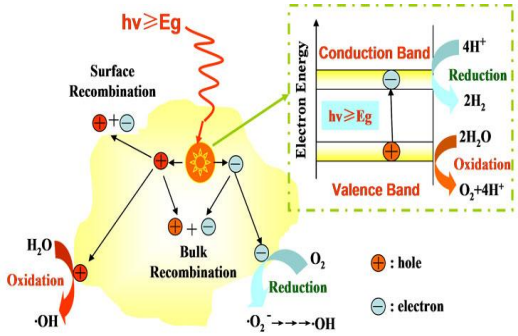


Fig-1: Schematic diagram of the experimental setup

3. RESULT AND DISCUSSION

The main factors influencing the photo catalytic transformation of Azo-dyes are catalyst loading, concentration of dye, pH of the solution, light intensity and propanol as quencher. The generation of holes, hydroxyl radicals and Super oxide ions can explain better with the help of proposed diagram. This proposed diagram (fig-2) shows the action of photo catalyst and process of generation of oxidative intermediates.



Photocatalysis mechanism scheme of semiconductor

Fig-2: Shows the Process of generation of holes, hydroxyl radicals and Super oxide ions

Effect of catalyst:

The amount of the photo catalyst affects the rate of photo catalytic transformation. Effect of variation in amount of photo catalyst on the rate of transformation at constant pH 7.5 is observed. It is found that as the concentration of catalyst increases rate of transformation also increases (fig-3). Increase in the rate of transformation with increase in amount of catalyst is due to availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, resultant number of holes, hydroxyl radicals and super oxide ions are increase. These are principle oxidizing intermediate in advance oxidation process resultant increases the rate of transformation.

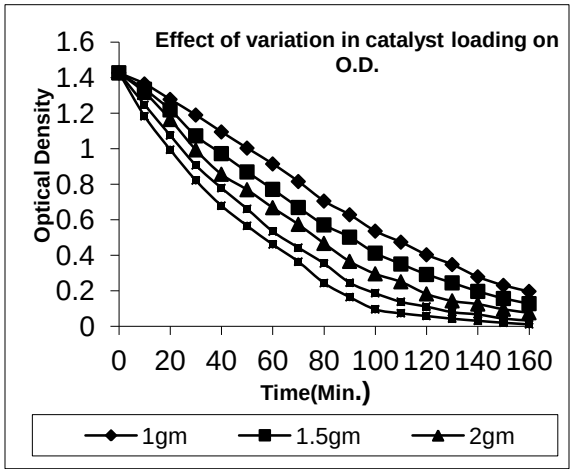


Fig-3: Effect of catalyst loading on photo catalytic transformation (Temperature: 303 K, solution volume: 50 ml, initial dye concentration: 40 mg/l, pH 7.5, UV /visible lamp: 10.4 $mWcm^{-2}$.)

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Effect of initial dye concentration:

The effect of change in dye concentration on photo catalytic transformation observed and found that as concentration of dye increases the rate of transformation decreases (fig-4). This effect may be caused by following reason - (1) As dye concentration increase number of photons reach to catalyst surface decrease resultant less number of catalyst molecules undergoes excitation and due to this effect rate of formation of holes, hydroxyl radicals and super oxide ions is decreases so rate of transformation is also decrease. (2) Catalyst surface area is fixed so as the concentration of dye increases rate of transformation decreases because limited number of dye molecules attached at the active side of the catalyst and remaining dye molecules persist in solution until earlier attached molecule is degraded and number of active side of catalyst also decreases due less availability of photons for excitation of catalyst molecules. Competitions between dye molecules to attach active side also effect rate of transformation. At higher concentration number of dye molecule also high so more will be the competition for attachment to active side of catalyst between the dye molecule and resultant reduce the rate of transformation.

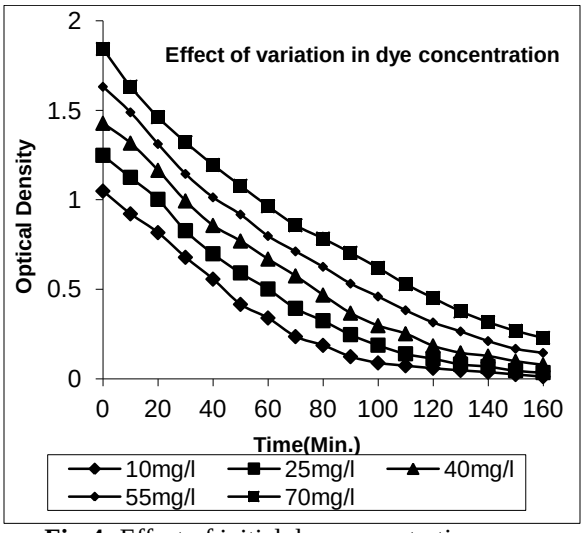

Fig-4: Effect of initial dye concentration on transformation (Temperature: 303 K, solution volume: 50 ml, pH 7.5, UV/visible lamp: 10.4 mWcm^{-2}.)

Effect of pH:

Effect of pH on rate of transformation of dye molecules is very interesting. The results shows that rate of transformation is very low in high acidic pH range lower then pH 3.5 rate of transformation is very less, as pH increases rate of transformation also increases when pH reaches to basic range the rate of transformation increases fast, in pH range 7.5 to 9 very good rate of transformation (fig-5). On further increase pH the rate of transformation also start to decrease after pH range 10 or above rate of transformation is less an continually decreases as pH increases. So it concluded that rate of transformation in basic medium is higher than acidic medium.

The increase in rate of photo catalytic transformation may be due to more availability of ^{-}OH ions in pH range 7.5 to 9 will generate more $^{\cdot}OH$ radicals by combining with the holes which are formed due to electronic excitation in catalyst. Formation of hydroxyl radicals is more responsible for the photo catalytic transformation than super oxide. At higher pH the rate of transformation decreases. This effect may cause due to competition between ^{-}OH groups to attach active side of catalyst, so rate of attachment of ^{-}OH group decreases. Resultant formation of hydroxyl radicals ($^{\cdot}OH$) decreases by this reason rate of transformation also decreases.

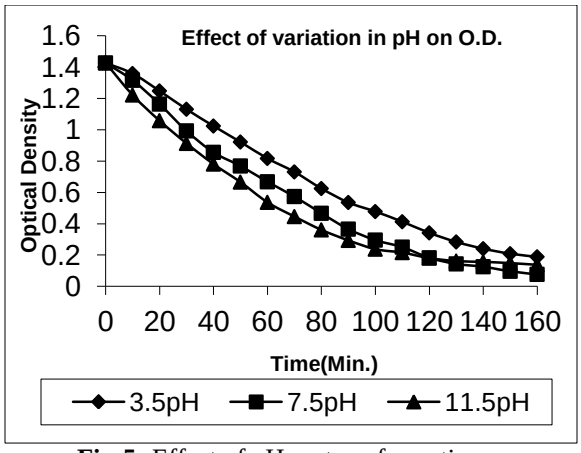

Fig-5: Effect of pH on transformation (Temperature: 303 K, solution volume: 50 ml, initial dye concentration: 40 mg/l, UV lamp: 10.4 mW cm^{-2}.)

Effect of light intensity:

The effect of light intensity on rate of transformation observe and find out that as light intensity increases the rate of transformation of dye molecules also increases up some extant after it no change observe in rate of transformation (fig-6). This change in rate of transformation of dye molecules by variation in light intensity as light intensity increases number of photons increases to reach the catalyst surface so number exited catalyst molecules increases and resultant increase the number of holes, hydroxyl radicals and Super oxide ions and rate of transformation of dye molecules increase.

After some extant of increase in light intensity there is no effect on rate of transformation on further increases in light intensity. This may cause that maximum number of photons which required for excitation are available in fix range irradiating light intensity after it if we further increase light intensity

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no any considerable change observed in rate of transformation because there is no requirement of more photons for excitation. Because all catalyst molecules become active (exited) in fix light intensity range after it we increase light intensity to any range, the rate of transformation remains unchanged.

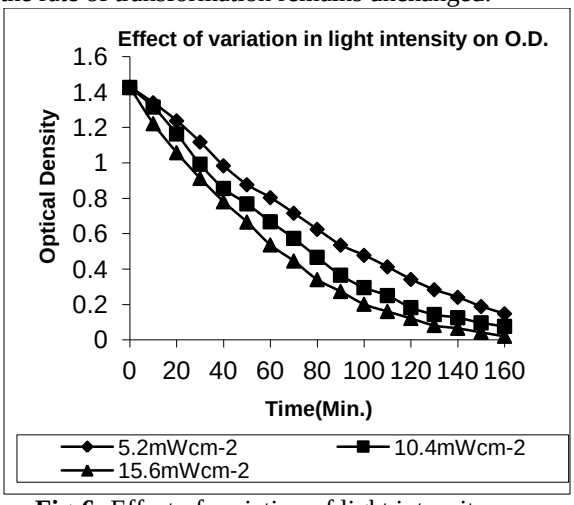

Fig-6: Effect of variation of light intensity on transformation (Temperature: 303 K, solution volume: 50 ml, initial dye concentration: 40 mg/l, pH 7.5.)

Effect of quencher:

Alcohols such as ethanol & propanol are commonly used to quench hydroxyl radicals. As it was observed from the experiment (fig-7) that transformation efficiency of dye was decreases in presence of propanol in comparison to dye solution in absence of propanol. This enables us to draw the conclusion that small amount of propanol inhibit the photocatalytic transformation & hence OH radicals also play a major role in photo catalytic oxidation of dye.

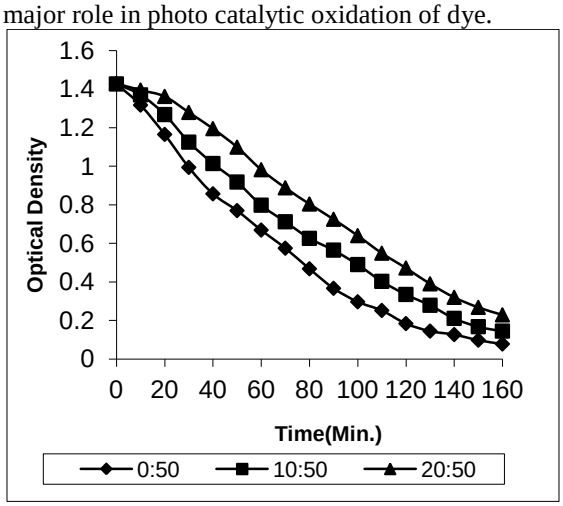

Fig-7: Effect of variation of quencher on transformation (Temperature: 303 K, solution volume: 50 ml, initial dye concentration: 40 mg/l, pH 7.5.)

4. CONCLUSION

After long observation it concluded that this photo catalyst (Methylene Blue immobilized Resin Dowex-11) has very good potential of transformation of Azo dyes into simple molecules such as CO_2 H_2O,N_2 etc and purify textile effluent (wastewater) which contains large amount of non fixed dyes mostly Azo dyes. These Azo dyes are non bio degradable. The effect of different parameters given in order-

1. Variation in dye concentration: - As concentration of dye increase the rate of transformation of dye deceases.
2. Variation in amount of catalyst: - As concentration of catalyst increase the rate of transformation of dye molecules also increases.
3. Variation in pH:- In acidic range of pH the rate of transformation is very less as pH increases rate of transformation also increases and between pH range 7.5 to 9 rate of transformation is good on further increases in pH the rate f transformation again after to decreases.
4. Variation in light intensity: - On increase light intensity the rate of transformation of dye molecules also increases up to limit after certain light intensity there is no further change occurs in rate of transformation.
5. Variation in quencher: - As concentration of quencher increase the rate of transformation of dye deceases.

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