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STUDIES OF METHYLENE BLUE IMMOBILIZED RESIN (DOWEX-11) FOR DEGZRADATION OF AZO DYE (SIRIUS LIGHT YELLOW R)

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***Abstract**: The present study involves the degradation of an azo dye Sirius light yellow R (Direct- yellow 50) with methylene blue immobilized resin (MBIR) Dowex 11 as photo catalyst using natural solar light in aqueous solution has been investigated under different conditions. Photo degradation Efficiency was small when the photolysis was carried out in the absence of MBIR Dowex11 and it was also negligible in the absence of UV light. The influence of operational parameters such as the amount of photo catalyst, dye concentration and initial pH on photo degradation by MBIR Dowex 11 has been analyzed. The degradation of Sirius light yellow R follows pseudo first order kinetics.*

***Key words:** - Photo catalysis, Sirius light yellow R, photo degradation, MBIR Dowex 11.*

1. INTRODUCTION

Photo catalytic technology is becoming more and more attractive to industry today because global environmental pollution has come to be recognized as a serious problem. Photo catalytic process to degrade organic pollutants in water has been the subject of recent research. Heterogeneous photo catalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants organic reactive dye [1]-[4]. Michael & Bartosz [5], [6] examined the possibilities of using TiO_2 to decompose cyanide in water. But this technology has not yet been successfully commercialized in past because of problems connected to separation of TiO_2 particles from suspension. To solve this problem, supported catalyst has been developed [7], [8]. Photo degradation of azo dyes by chitosan capped CdS composite nano particles and in aqueous phase nano photo catalyst[9], [10]. Poulios et al. studied photo catalytic degradation of Auramine O in aqueous suspension using ZnO and TiO_2 separately in a batch reactor. They found that the rate of degradation of pollutants is faster with Zno than with TiO_2 (Deussa P25). The biggest advantage of ZnO is that it absorbs a larger function of solar spectrum than TiO_2 [11. Therefore it is a great interest to use the freely available and inexhaustible solar light for photocatalysis [12], [13]. Earlier, Grzechulska and Morawski" reported the photo catalytic decomposition of azo dye using TiO_2 with UV light. Visible light sensitive photo catalyst have been developed by Meena et al.[14]-[18]. The development of visible light photo catalyst is an impressive task in order to utilize the solar energy effectively. The main objective of the present work is to seek attention of researchers towards utilization of visible light for degradation of azo dye Sirius light yellow R by recently developed photo catalyst (MBIR) Dowex 11.

2. EXPERIMENT

The commercial azo dye Sirius light yellow R (Direct yellow 50) (80% of dye) obtain from Loba chemicals (India) was used as such (λ_{max}= 390 nm). The photocatalyst MBIR Dowex 11 20-50 mesh purchased from sisco chemicals (Mumbai India). Methylene blue hydrates for microscopy Loba (India). The reagent oxalic acids, phenopthalein, zinc oxide, were used as received. The pH of solutions was adjusted using H_2SO_4 or NaOH, Double distilled water was used to prepare the experimental solutions. For immobilization prepare a 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. All the process carried out in the dark place then filter prepared resin from solution wash this resin by double distilled water twice and used it as photo catalyst. Photochemical degradation experiments were carried out in glass reactor which containing solution of Sirius light yellow R dye (Fig:-1) and photo catalyst stirred by magnetic stirrer during the experiment. The solution is illuminated by halogen lamp (Philips India) above the reactor which emitted irradiation comparable to visible light. The intensity was measured by photometer (IL1400A).The lamp was surrounded with aluminium reflection in order to avoid less of irradiation pH of the solution was monitored by Fisher scientific Acumen 50. The mechanism of the photo degradation process under UV-visible light illumination involves an electronexcitation and generation of very active oxygenated species that attack the dye molecule leading to photo degradation.

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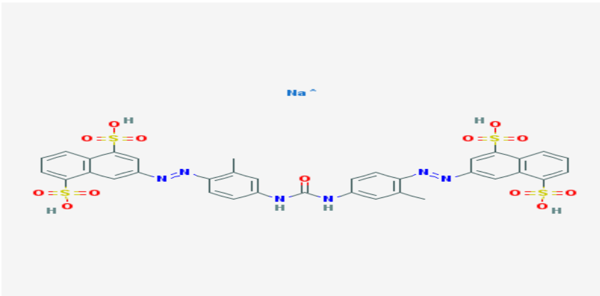

Figure 1: Sirius Light Yellow R (Direct yellow 50)

Dye $\xrightarrow{\text{light radiation}}$ Dye*[1]		(1)
Dye*[1] $\xrightarrow{\text{ISC}}$ Dye*[3]		(2)
Dye*[3] + I-R $\longrightarrow$ Dye*+ I-R (e^-)		(3)
I-R (e^-) + O_2 $\longrightarrow$ I-R + O_2^-		(4)
Dye^+ + OH^- $\longrightarrow$ Dye + OH		(5)˙
Dye/Dye^++OH^- $\longrightarrow$ Products		(6)

Im-R=Immobilizedresin

10ml solution of reaction mixture suck out in time interval and filtered the catalyst particle through Millipore syringe and change in concentration of dye solution is measured simply by Shimadzu-1600UV/visible Spectrometer at λ max = 390 nm. Calculated the removal efficiency(x) of dye solution by this equation; X = (Ci – Ct / Ci) Where Ci and Ct are optical densities of dye solution at initial time and at time t respectively.

3. RESULT AND DISCUSSION

Effect of dye concentration-

The effect was investigated by varying the initial concentration of dye Sirius light yellow R from 10mg/l to 70mg/l at constant catalyst loading, optimum pH 7.5 and at 10.4mW cm^{-2} light intensity. Degradation efficiency is inversely affected by the dye concentration that is photo catalytic degradation decreases with increasing initial concentration of the dye solution shown in fig 2.

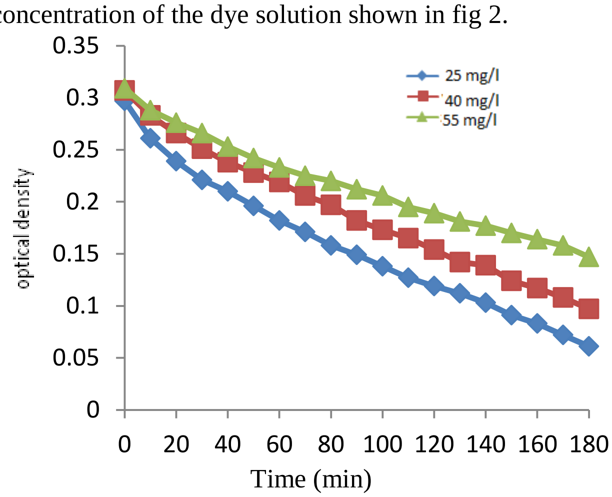

Figure 2: Effect of Variation in dye concentration for Sirius Light yellow R immobilized resin System (catalyst loading: 2gm, pH: 7.5, solution volume: 200ml and light intensity: 10.4mWcm^{-2})

This inverse effect can be commented as the dye concentration is increased the equilibrium adsorption of dye on the catalyst surface active sites increases and hence competitive adsorption of OH^- on the same sites decreases which means a lower formation of rate OH radical it is responsible for high degradation efficiency.

Effect of Catalyst:-

The amount of the photo catalyst is most important parameter that affects the rate of photo catalytic degradation. We observe the effect of variation in the amount of photo catalyst from 1.0 to 3.0g/100 ml and concentration of dye 40mg/l at constant pH 7.5 and light intensity 10.4mW cm^{-2}. Increase the amount of catalyst rate of degradation also increase due to availability of more catalyst surface area for absorption of quanta and in interaction of molecules of reaction mixture with catalyst but this increase was up to a unit. On further increase in concentration of catalyst a decrease in the photo catalytic degradation was observed. Effect of catalyst loading on removal efficiency shown in fig 3.

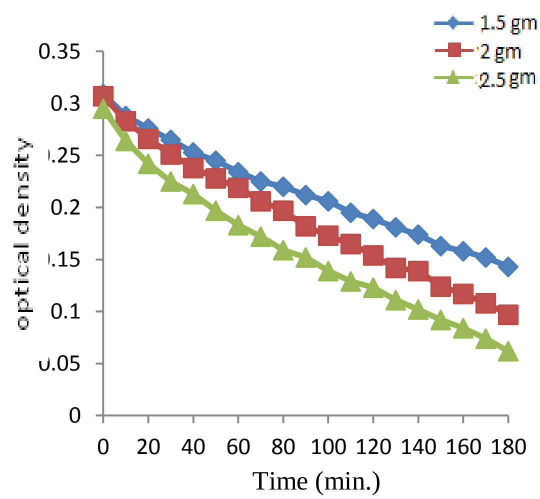

Figure 3: Effect of Variation in catalyst loading for Sirius Light Yellow R-immobilized resin system
(Initial dye concentration: 40mg/l,pH 7.5,solution volume: 200ml and light intensitymWcm^{-2})

Effect of pH:-

PH plays important role in degradation of dye. It was observed that the rate of degradation is very low in high acidic pH range lower than pH 3.5. As well as pH increase rate of degradation also increase. Maximum degradation was observed at pH . On further increase pH the rate of photo catalytic degradation also start to decrease. So we conclude that the rate of degradation in basic medium is higher than acidic medium formation of hydroxyl radicals is more responsible for the photo catalytic degradation than super oxide (O_2). Graphical representation of pH effect or removal efficiency shown in fig 4.

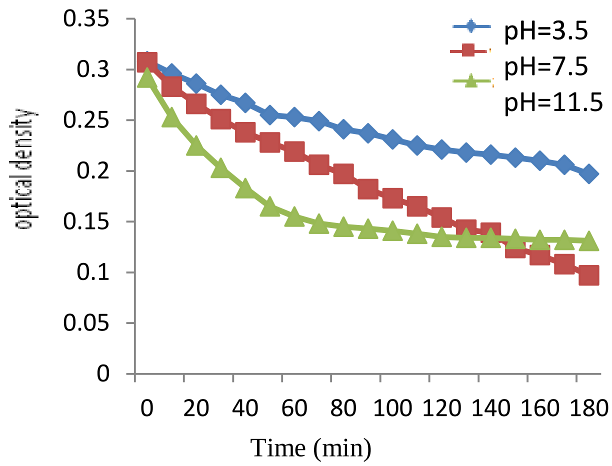

Figure 4: Effect of Variation in pH for Sirius Light Yellow R-immobilized resin system
(Initial dye concentration: 40mg/l, catalyst loading: 2gm, solution volume: 200ml and light intensity: 10.4mWcm-2)

Effect of light intensity:-

The light intensity is one of the main parameter for the degradation studies. It was found that light intensity increase the rate of degradation of dye molecules. The light intensity increase number of photons increases to reach to catalytic surface so number of excited catalytic molecule increase and resultant increase the hydroxyl radicals and super oxide (O_2) the rate of degradation of dye molecule increase. But after some extant of increase in light intensity there is no effect on the rate of degradation on further increase in light intensity because there is no requirement of more photons for excitation. So after a range we increase light intensity to any range the rate of degradation remains unchanged. Effect of light intensity on removal efficiency shown in fig 5.

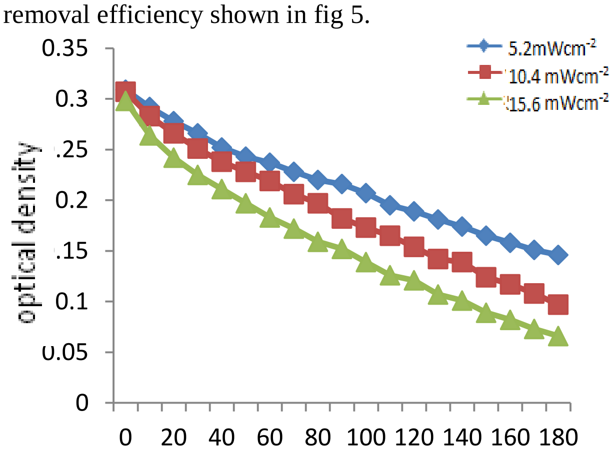

Figure 5: Effect of Variation in light intensity for Sirius Light Yellow R-immobilized resin system (Initial dye concentration:-40mg/l, catalyst loading: 2gm, solution: 200mland pH 7.5

Kinetic study:-

Photo catalytic degradation of dye Sirius light yellow R was observed at λ max = 390nm. The optimum condition was obtained at initial dye concentration: 40mg/l, catalyst loading: 2g/100ml, light intensity: 10.4mW cm^{-2}, pH: 7.5 and temperature: 303K. The plot of removal efficiency versus exposure time (Fig:-6) is indicate that the photo catalytic degradation of dye follows pseudo first order kinetics according to Langumiur-Hinshelwood model. The rate constant (K) for reaction was determined using the expression K = 2.303slope.The rate constant for this reaction is K = 9.38×10^{-5} sec^{-1}.

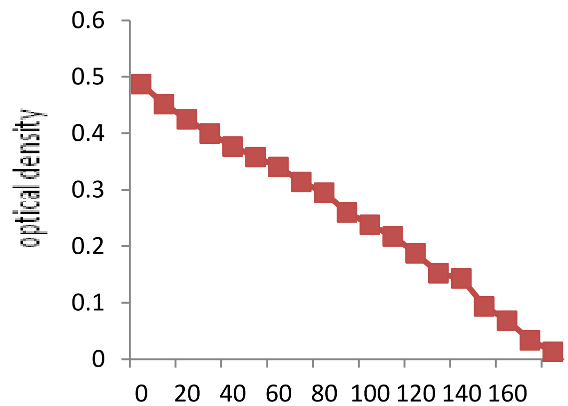

Figure 6: Kinetics for Sirius light Yellow R-immobilized Resin system

4. CONCLUSION

Aim of the present work is to gain attention of researcher's conserved utilization of solar energy for degradation of dye pollutants by photo catalyst. And find out new photo catalyst for different applications as compared to solar photo catalytic systems with other catalyst, methylene blue Immobilized Resin Dowex 11 used as solar photo catalyst gives very good results and successfully improved the degradation rate of organic dyes. The photo catalytic degradation of Sirius light yellow R has been studied using MBIR Dowex11 as photo catalyst. The photo catalytic degradation of the dyes follows pseudo first order kinetics for the system. The photo catalytic degradation efficiency has been generally found to increase in catalyst loading. the photo catalytic degradation decrease with increase in initial dye concentration, with the increase in the concentration of a dye solution , the photons get intercepted before they can reach the catalytic surface decreasing of the catalyst and all the degradation occur at an optimal pH 7.5 value. Therefore this technology has the potential to improve the quality of the waste water from textile industries and many others.

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