



Research Article

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**Effect of Operational Parameters on Photocatalytic Transformation of
Azo Dye Sunset Yellow in Water**
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Abstract

Photocatalytic transformation of Sunset Yellow, commonly used as textile dye, has been investigated. Optimum degradation (90.76%) of Sunset Yellow (40 mg/L) was observed in around 160 min. (minutes) at room temperature at pH 7.5 and catalyst loading was 2.0 g/L. The semi log plot of $1 + \log \text{O.D}$ (optical density) of dye verses time was linear, suggesting pseudo first order kinetics ($K = 0.0119 \text{ min}^{-1}$). The effects of some parameters such as pH, light intensity amount of catalyst loading and initial dye concentration were also examined. The heterogeneous photocatalyst methylene blue immobilized resin 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. This catalyst has potential to degrade all dye molecules and we recover 100% transparent water from dark color textile effluent wastewater within few hour treatments. In addition, the recycle and reuse of the catalyst were also observed. The present work demonstrates easy & approachable experimental modeling for the treatment of an azo dye (Sunset Yellow).

Keywords: Advanced Oxidation Process, Dowex-11, Photocatalyst, Photo Transformation

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1. Introduction

Azo dyes constitute an important class of synthetic, colored, organic compounds, which are characterized by the presence of one or more azo bonds ($-\text{N}=\text{N}-$). They represent about 50% of the worldwide dye production and are widely used in a number of industries, such as textile dyeing, food, cosmetics, paper printing, with the textile industry as the largest consumer (Ollgaard et al., 1999) (Stolz, 2001). During dye production and textile manufacturing process, a large quantity of wastewater containing dye stuffs with intensive color and toxicity are introduced into the aquatic systems (Brown and De Vito, 1993). In such cases, it is important to remove color from wastes, because the presence of even small amounts of dye (below 1 ppm) is clearly visible and influences water environment considerably. The degradation of azo dyes have been reported in many papers (Bizani et al., 2006) (Ibhadon et al., 2008) (Sahoo and Gupta, 2005) (Sobana et al., 2006) (Songa et al., 2008). Traditional techniques

such as biodegradation, adsorption, coagulation, reverse osmosis, and the others are ineffective for complete destruction of dyes (Sohrabi and Ghavami, 2008). Biodegradation, for instance, does not work efficiently because of a high resistance of dye molecules. Therefore, it can lead to the generation of hazardous aromatic amines (Habibi et al., 2005). Most of above-mentioned methods are nondestructive. They only transfer contaminations from solution to another phase, thus producing a large amount of sludge with a secondary pollution, which is difficult to remove (Mahmoodi et al., 2006). Therefore, it is essential to consider other, more efficient and less invasive methods (Kansal et al., 2007).

One of the wastewater treatment methods is advanced oxidation process (AOP) defined by Glaze et al., which present a suitable alternative to remove color from water (Neamtu et al., 2004) (Rathi et al., 2003). Common AOP involves Fenton, Fenton-like, photo-Fenton process, ozonation, photochemical and electrochemical oxidation, photolysis with H_2O_2 and O_3 , high voltage electrical discharge (corona) process, semiconductor photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams (El-Desoky et al., 2010) (Gogate and Pandit, 2004a, 2004b) (Huang et al., 2009) (Serra et al., 2009). The principle of AOP is the generation of very reactive species such as hydroxyl radicals ($\cdot OH$) (Wu et al., 1999), which have a high oxidation potential ($E_0=+2.80V$). Hydroxyl radicals rapidly oxidize a wide range of organic pollutants (Daneshvar et al., 2003). Many researchers consider TiO_2 as the best photocatalyst that has the ability to treat water from a number of organic pollutants (Ahmed et al., 2011) (Tang and An, 1995) (Wahi et al., 2005). On the other hand, it has been proven similar efficiency of photocatalytic between MBIRD-11 and TiO_2 .

Here the main objective of the present work is to seek attention of researchers towards utilization of visible light for degradation of an azo dye Sunset Yellow (also known as Orange Yellow S, FD&C Yellow 6 or C.I. 15985) which is synthetic yellow azo dye and sulfonated version of Sudan I and a possible carcinogen, by recently developed Methylene Blue Immobilized Resin Dowex-11 (Meena et al., 2009, 2013) (Meena and Meena, 2010, 2011) (Meena and Pachwarya, 2009, 2011). The influence of different parameters (pH, catalyst loading, dye concentration and light intensity) has been studied and find out that potential of transformation of Sunset Yellow dye by newly developed photo catalyst is efficiently better, cheap and the homogeneous mixture separation is not a tedious task because of the beads like structure of the catalyst. Therefore further treatment can be done easily.

2. Materials and Methods

2.1 Dye

Sunset Yellow	= Loba (Loba Chemicals, India)
IUPAC Name	= Disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate
Molecular Formula	= $C_{16}H_{10}N_2Na_2O_7S_2$
Molecular Weight	= 452.37 g mol ⁻¹
Solubility	= Soluble in water
Appearance	= Red powder
λ_{max}	= 482 nm
Class	= Azo

Structure of dye Shown in Fig- 1.

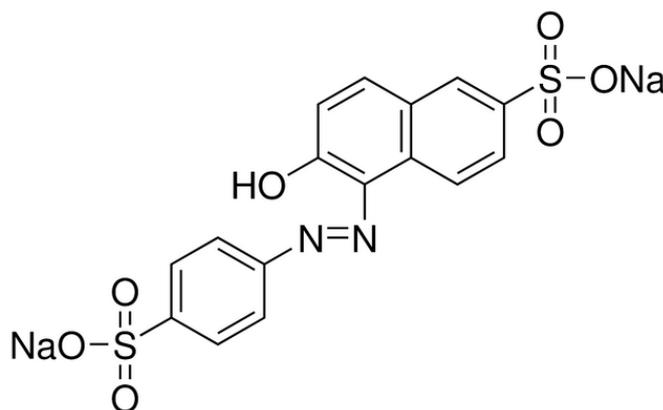


Fig1. Structure of dye Sunset yellow

2.2 Photocatalyst:

We prepared photocatalyst by Dowex-11 Resin 20-50 mesh (Sisco Chemicals, India Mumbai) and methylene blue hydrate for Microscopy (C.I. No. 52015) (Loba Chemicals India).

2.3 Preparation of Photocatalyst:

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. All the process carried out in dark place. After completing immobilization of methylene blue inside the pores of resin, filter prepared resin from solution. Then wash by double distilled water twice and used it as photocatalyst.

2.4 Role of methylene blue

Methylene blue is photosensitized dye. It is use as immobilization of pores of resin. Due to photosensitized properties of dye it becomes excited by absorbs photons of light radiations. In first electronic excitation, electron transfers into singlet state and through inter system crossing (ISC) electron can transferred to triplet state of methylene blue. Further inter molecule electronic interaction occurs between resin, methylene blue and solution mixture are resultant the formed holes, hydroxyl radicals and super oxide ions (O_2^-), these are highly oxidative in nature (Fig-2).

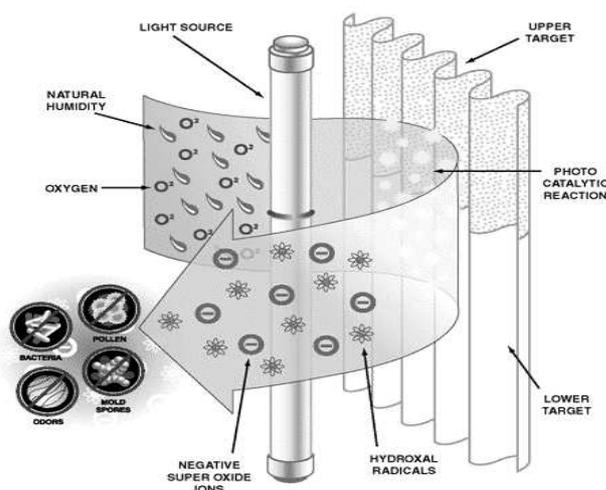


Fig 2. Process of generation of holes, hydroxyl radicals and super oxide (O_2^-) ions

2.5 Analytical method:

The change in dye concentration is observed simply by Shimadzu-160 UV/Visible spectrophotometer at λ_{max} 482nm. We shuck out 10 ml of solution by pipette at the 10 minute time interval, Filter the catalyst particles and calculate the removal efficiency (X%) of dye solution by this equation.

$$X \% = [(C_0 - C / C_0) \times 100]$$

Where, C_0 and C are optical densities of dye solution at initial time and at time t respectively.

2.6 Experimental set up and Experimental procedure

The photo reaction is carried out in glass reactor which containing solution of Sunset Yellow dye (40 mg/L) and photocatalyst. Solution of reactor is continuously 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 aluminum reflector in order to avoid loss of irradiation. pH of the solution was monitored by Fisher Scientific Acumen 50. A schematic diagram of the setup can be seen in Fig-3.

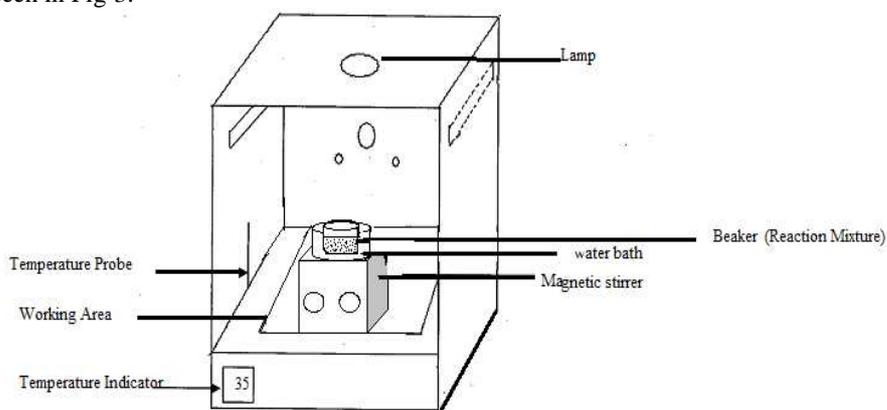


Fig 3. Experimental Set-up of Photochemical Reaction Chamber

Following observation is follow in all experimental process.

1. In first experiment, we observe bio degradability of dye (without catalyst). We put dye solution (40 mg/L) in sunlight for 160 min. and after 160 min. we observe no change found in dye concentration then we carried out next experimental step.
2. In second experiment, we carried out in dark for test action of catalyst in dark. We put reaction mixture (dye solution and catalyst) in dark chamber there is no any change observed in dye concentration.
3. In third experiment, we add pure resin (catalyst) with immobilization of methylene blue. This experiment carried out in sunlight for test action of catalyst. We observed that the transformation of dye increase with time.
4. In fourth experiment, we use methylene blue immobilized resin in experimental set-up (UV lamp) and we observe that capable for complete mineralization of dye contaminate of textile industries. This catalyst used many times there is no effect on efficiency of transformation of dye molecules. These observations are shown in Fig- 4.

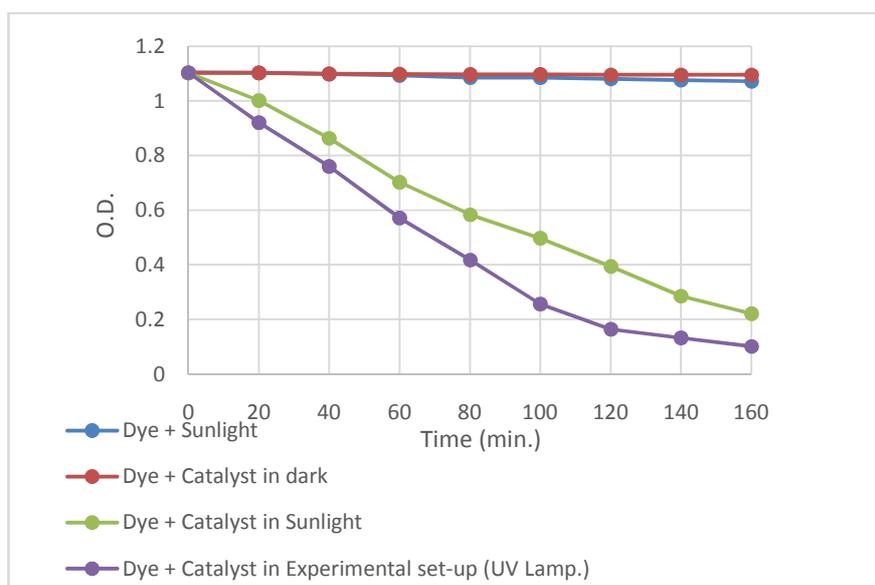


Fig4. Effect of different parameters on photocatalytic transformation of dye

3. Results and Discussion

The photo catalytic transformation of azo dye (Sunset Yellow) was observed at λ_{\max} 482nm. The optimum condition for the removal of the dye is, dye concentration at 40mg/L, pH-7.5, catalyst loading 2.0gm, light intensity 200 watt. Rate of the reaction (k) was determined using the expression, Rate (k) = 2.303 * slope. Fig-5 shows the semi logarithmic plot of 1+log O.D versus exposure time was found to be straight line suggesting the transformation of the dye follows pseudo first order kinetics and rate constant is $1.19 \times 10^{-2} \text{ min}^{-1}$.

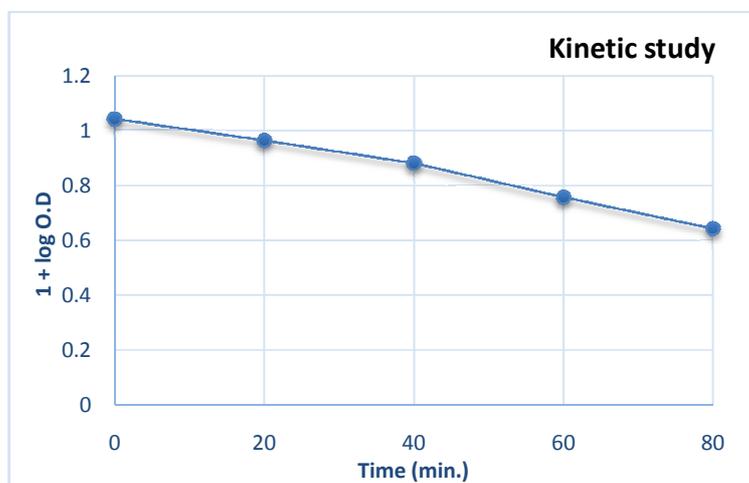


Fig 5. Kinetic study of photocatalytic transformation of Sunset Yellow

Effect of variation in pH

The photo transformation of the dye was studied at different pH values ranges from 3.5 to 11.5 .Transformation rate of the dye is very low in acidic pH range As pH range increases, transformation rate increases. In pH range 7.5-9.0 rate of transformation was very good (Fig-6). On further increasing pH, rate of transformation starts to decrease. Increase in rate of photo catalytic transformation in the 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 photo catalytic transformation.

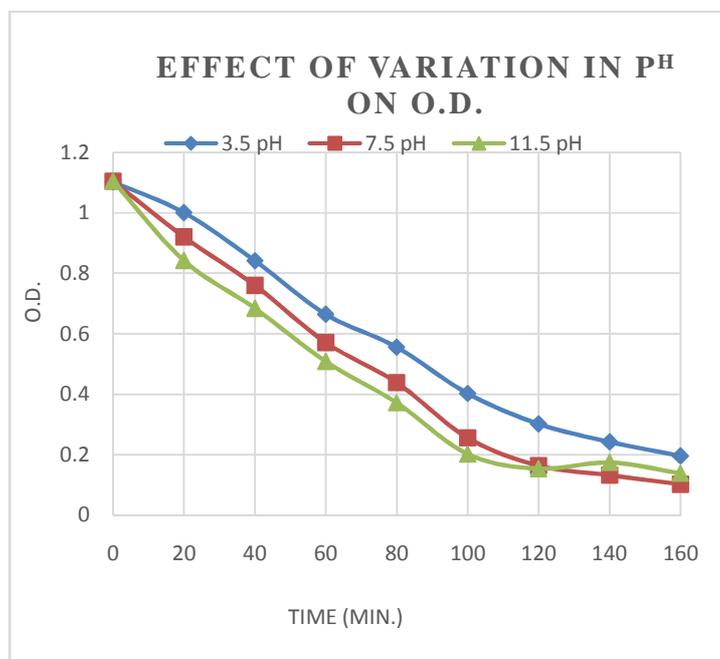


Fig6. Effect of pH on photocatalytic transformation of the dye

Effect of catalyst loading

As catalyst loading increase the rate constant increases from 1.0gm to 3.0gm, by taking other parameters constant. This can be due to more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst , resulted increase in number of holes, hydroxyl radicals and supra oxide ions. Since these are principle oxidizing intermediates in AOP and rate of transformation increases (Fig-7).

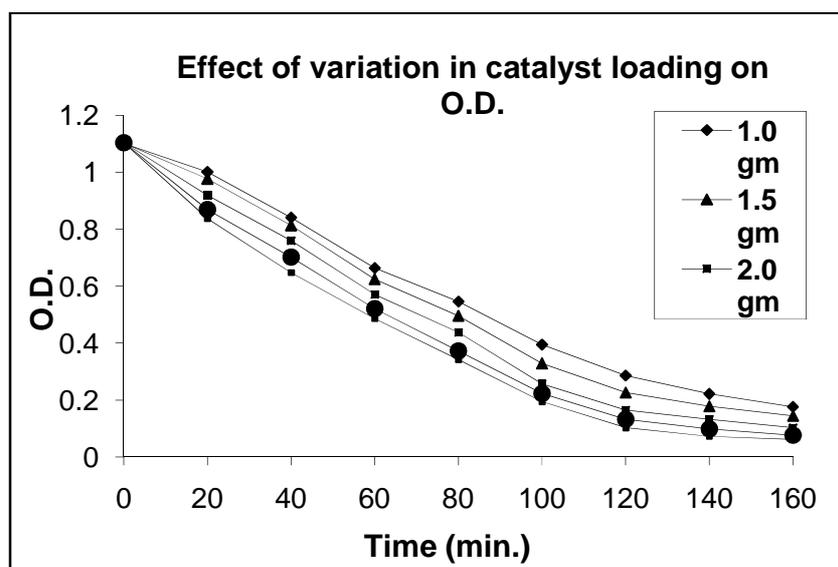


Fig7: Effect of catalyst loading on photocatalytic transformation of the dye

Effect of concentration of dye

Transformation rate of the dye decrease with increase in concentration of the dye from 10mg/L to 70mg/L. As shown in Fig-8, the rate constant revealed that the maximum transformation observed at low concentration of the dye. As concentration increases the rate constant decreases above the optimal value. At high concentration the decrease in transformation phenomenon can be explained in terms of the increased concentration of the dye. However, the irradiation time and amount of catalyst have been kept constant hence the production of hydroxyl radicals and supra oxide radicals was limited.

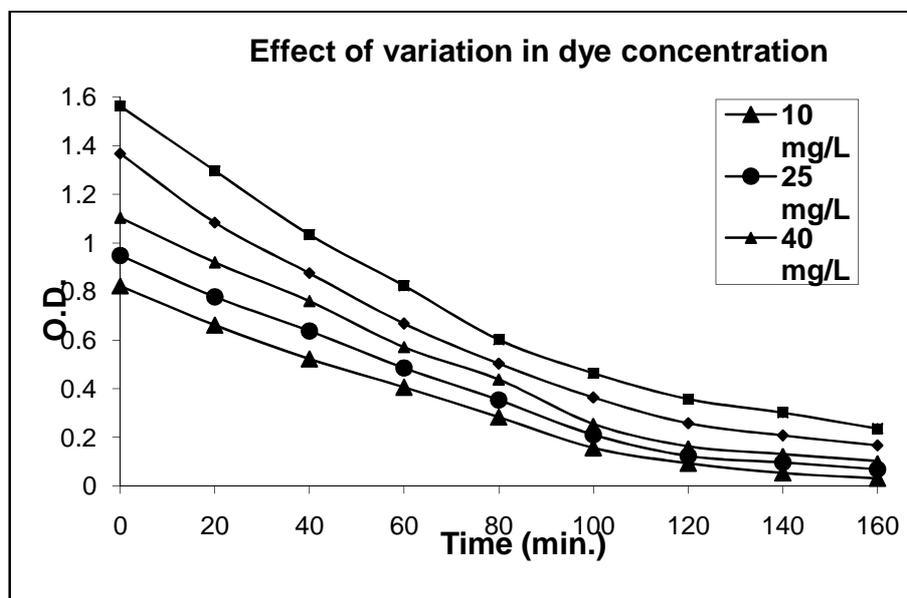


Fig8. Effect of concentration of dye on photocatalytic transformation of the dye

Effect of light intensity

The influence of light intensity was studied in the range 60 to 500 watt an almost linear plot between the rate constant and light intensity was observed, that indicates an increase in the light intensity will increase the rate of reaction (Fig -9). This may be 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 supra oxide ions(O⁻). As a consequence ,an overall increase in the rate of transformation of dye molecules has been observed.

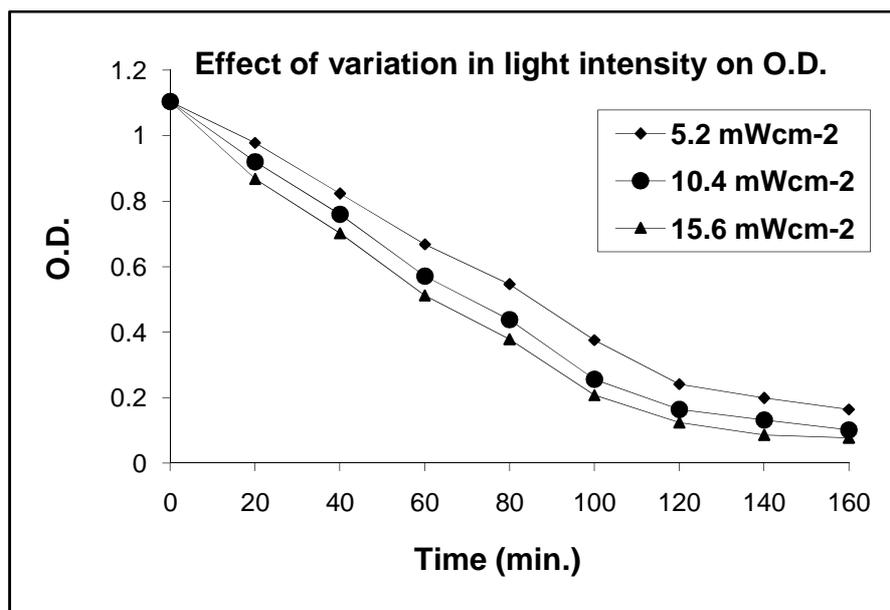
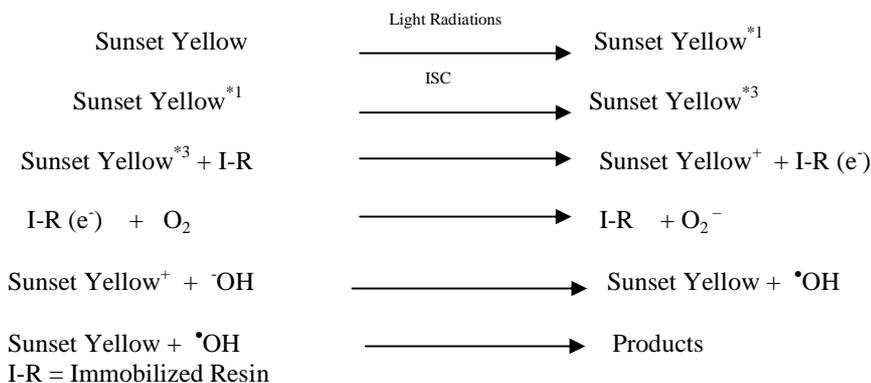


Fig9. Effect of light intensity on photocatalytic transformation of the dye

Mechanism

Tentative mechanism has been proposed on the basis of above experimental observation.

On irradiation the dye molecules absorb photons and get excited, resulted electrons jump to singlet state. Then these excited singlet state molecule is convert into triplet state through intersystem crossing. The triplet dye may donate its electron to the photo catalyst and the dye becomes positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of photo catalyst. The positively charged molecules of the dye will immediately react with hydroxyl ion to form hydroxyl radicals and these hydroxyl radicals will oxidize the dye molecule in to the product.



4. Conclusion

After long observation we conclude that this photocatalyst (MBIR 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-biodegradable.

We observe the effect of different parameters given in order-Effect of variation in dye concentration: - As concentration of dye increase the rate of transformation of dye decreases.

Variation in amount of catalyst: As concentration of catalyst increase the rate of transformation of dye molecules also increases.

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 of transformation again after to decreases.

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.

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