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Radiation Induced Degradation of Textile Dye from Aqueous Solution by Using Methylene Blue Immobilized Resin Dowex 11 Photocatalyst

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Abstract

Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants in water. The photocatalytic degradation of azo dye Direct Red 81 with UV/Visible/MBIR (Methylene Blue Immobilized Resin) Dowex 11 interface was investigated. Kinetic analysis indicates that the photodegradation rate of azo dye can usually be approximated as pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. The degradation of dye depends on several parameters such as catalyst dose, concentration of dye, pH of the solution, light intensity, radical quencher and dissolved oxygen. The mechanism of the photodegradation process under UV-Visible light illumination involves an electron excitation and generation of very active oxygenated species that attack the dye molecules leading to photodegradation. The dye solution could be completely decolorized and effectively mineralized, with average removal efficiency larger than 95% for a reaction time of 160 min.

Keywords: Photodegradation; Decolorization; Efficiency; Direct Red 81; Dowex-1

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. 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. Recently developed photocatalyst such as methylene blue immobilized resin Dowex-11 have shown to be a relatively cheap and effective way of removing organic compounds and dye pollutants.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 techniques used in treatment of such wastewater. However these methods transfer dyes from liquid to solid phase and produces secondary pollution and requiring further treatment. About 1–20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [1-3]. Recently there has been considerable interest in the utilization of advance oxidation processes (AOPs) for the complete destruction of dyes. AOPs are based on generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non selectively [4-5]. AOPs include photo catalysis systems such as combination of semiconductors and light, and semiconductor and oxidants. Heterogeneous photo catalysis has emerged as an important destructive technology leading to the total mineralization of the organic pollutants including organic reactive dyes [6-9]. AOPs such as Fenton and photo-Fenton catalytic reactions [10-14], H2O2/UV processes [15-16] and TiO2 mediated photo-catalysis [17-20] 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. It is widely accepted that the anatase TiO2 is a more efficient photocatalyst than therutile TiO2 because of the formers relatively high adsorptive affinity for organics and the superior hole-trapping ability [21-26]. Degradation of Acid Green 16 was studied by Sakthivel et al. [27] using ZnO irradiated with sunlight. Here the photo degradation efficiency decreased with an increase in initial dye concentration. Optimum catalyst loading was found to be 250mg in 100 ml. A. Akyol et al. [28] was studied the photo catalytic transformation of Remazol Red by ZnO. Pandurangan et al.[29] carried out the photo catalytic degradation of textile dye, Basic yellow Auramine O by a batch process using ZnO as the catalyst and sunlight as the illuminant. (Poulios and Tsachpinis 1999) [30]. Investigated the photocatalytic degradation of reactive black 5 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 source. Many visible light sensitive photo catalysts have been developed (Meena et al., 2009a; Meena et al., 2009b) [31-32]. The development of visible light photocatalyst is an impressive task in order to utilize the solar energy effectively.The present work investigates the influence of an azo dye Direct Red 81 in presence of visible light induced methylene blue immobilized resin Dowex-11.

Keeping in view the above, the main objective of the present work is to seek attention of researchers towards utilization of visible light for degradation of an azo dye by recently developed methylene blue immobilized resin Dowex-11, for oxidative degradation of dye contaminants. Methylene blue can be act as sensitizer for light induced process. Due to sensitization of photocatalyst, electrons are migrating from valence band (VB) to conduction band (CB) and holes are formed in valence band, these holes can generate hydroxyl radicals (•OH) which are highly oxidizing in nature. Probably hole can react with dye molecules and abstract electrons from dye molecules and process of degradation is start.

Experimental

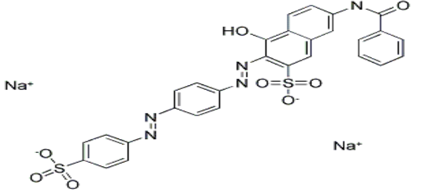
Dye

Direct Red 81 = Loba (Loba Chemicals India)
IUPAC Name =
Molecular Formula = $C_{29}H_{19}N_5Na_2O_8S_2$
Molecular Weight = 675.6
Solubility = Soluble in water
Appearance = Red
λmax = 508 nm
Class = Azo

Structure of dye

Shown in fig.1.

Fig.1. Structure of Dye Direct Red 81



Photocatalytic Studies

We prepared photocatalyst 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). 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. After completing immobilization of methylene blue inside the pores of resin. 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 solution of Direct Red 81 dyes (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. Methylene blue is photosensitized dye. It is use as immobilization of pores of resin. Due to photosensitized properties of dye it becomes exited 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.

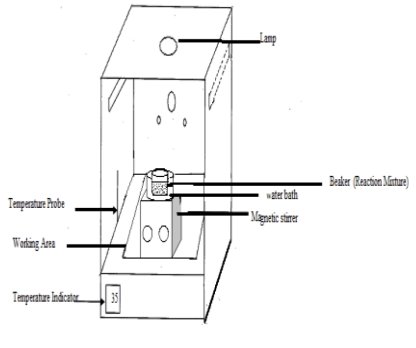
The change in dye concentration is observed simply by Shimadzu-1600 UV/Visible spectro photo meter at λmax 482nm. We shuck out 10 ml of solution by pipette at the 20 minute time interval, Filter the catalyst particles and calculate the degradation (Decolorization) efficiency (X) of dye solution by this equation.

$$X = (C_i - C_t / C_i)$$

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

A schematic diagram of the set-up can be seen in figure.2.

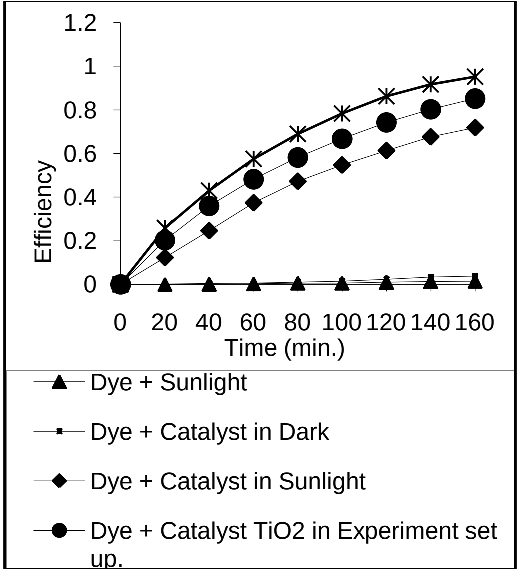
Fig.2. Experimental Set-up of Photochemical Reaction Chamber



Following schedule of observations is follow in all experimental process.

1. In first experiment we observe bio-degradability of dyes (without catalyst). We put dye solution 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. 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 carried out for test action of catalyst with dye solution in sunlight. We observed that the degradation of dye molecules increase with time.
4. In fourth experiment we use catalyst TiO_2 and dye solution in experimental set-up (UV-lamp) and we observe that the degradation rate of dye molecules increase with time compare to the sunlight.
5. In fifth experiment we use catalyst and dye solution 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 for degradation of dye molecules. These observations are shown in fig.3

Fig. 3. Degradation efficiency of Direct Red 81 dyes (40 mg/L) with different parameters.



Mechanism of Degradation

Methylene blue immobilizes resin Dowex-11 is newly developed photocatalyst. Due to photo sensitive 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, Direct Red 81 dye molecules and dissolved oxygen, resultant through chain process, holes, hydroxyl radicals (•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 (O_2^-) on azo dyes, are transformed in simple organic compounds like CO_2, H_2O, etc. The analytical analysis is confirmed the CO_2 and H_2O in products.

On the basis of the observed data, the following tentative mechanism may be proposed

$$\text{Dye} \xrightarrow{\text{Light Radiations}} \text{Dye}^{*1}$$

$$\text{Dye}^{*1} \xrightarrow{\text{ISC}} \text{Dye}^{*3}$$

$$\text{Dye}^{*3} + \text{I-R} \longrightarrow \text{Dye}^{+} + \text{I-R}(e^-)$$

$$\text{I-R}(e^-) + O_2 \longrightarrow \text{I-R} + O_2^{-}$$

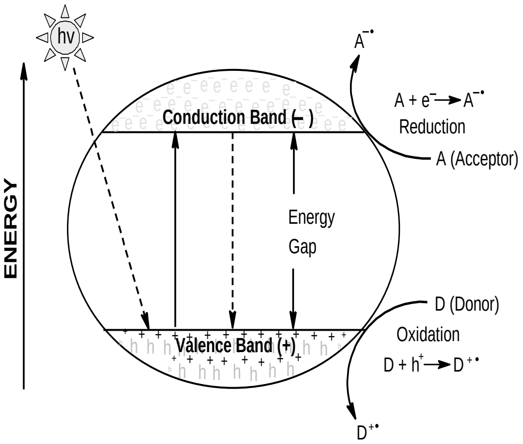
$$\text{Dye}^{+} + {}^{-}\text{OH} \longrightarrow \text{Dye} + {}^{\bullet}\text{OH}$$

$$\text{Dye/Dye}^{+} + {}^{\bullet}\text{OH} \longrightarrow \text{Products}$$

I-R = Immobilized Resin

The generation of holes, hydroxyl radicals and super oxide ions (O_2^-) can explain better with the help of proposed diagram. This proposed diagram shows the action of photocatalyst and process of generation of oxidative intermediates. Photo catalysis shows in fig. 4.

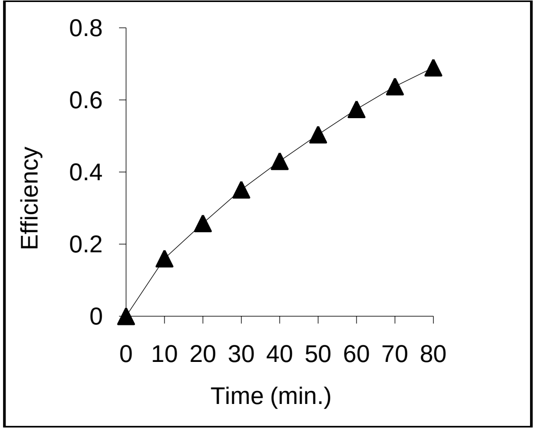
Fig.4. Photocatalytic action: Generation of holes, hydroxyl radicals and super oxide (O_2^-) ions.



Kinetic Study

Photocatalytic degradation of Direct Red 81 was observed at λmax = 508 nm. The optimum condition was obtained at initial dye concentration: 40 mg/L, Catalyst loading: 2gm/100ml, solution volume: 100ml, light intensity: 10.4 $mWcm^{-2}$, pH: 7.5 and Temperature = 303 K. The plot of efficiency versus exposure time is a straight line (Fig. 5). This indicates that the photocatalytic degradation of Direct Red 81 follows pseudo first-order kinetics (Behnajady et al., 2006; Ted Chang et al., 2000; Faisal et al., 2007).[33-35] The rate constant (K) for the reaction was determined using the expression. Rate = K [Direct Red 81] K = 2.303 × slope. The rate constant for this reaction is $K = 2.02 \times 10^{-2}\ \text{min}^{-1}$

Fig.5 Kinetic Study for Direct Red 81-Photocatalyst system (Initial dye concentration: 40 mg/L, pH: 7.5, Catalyst loading: 2gm/100ml, solution volume: 100ml and light intensity: 10.4 mWcm^{2}).

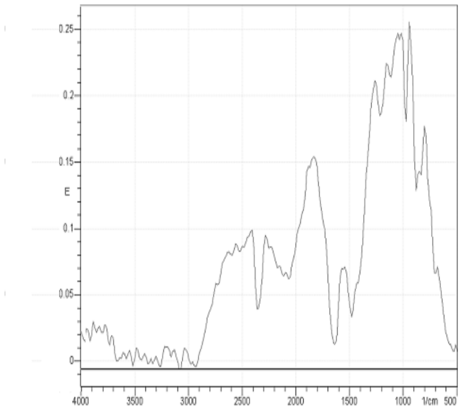


Results and Discussion

IR Characterizations

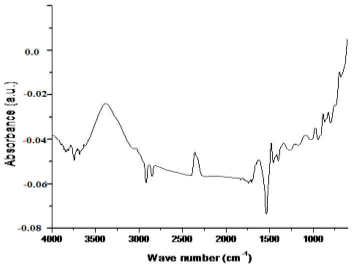
The FTIR spectra analysis was employed by Spectro Jasco Corp. /IR-610 over the range 599.7532 – 4000.605 cm^{-1} FTIR instrument using KBr Pallets. The IR spectrum of Dowex-11 resin (Pure) show peak in the region 3100-3000 cm^{-1} is attribute to =C-H stretching vibration. And two peaks in the region 1600-1450 cm^{-1} show aromatic –C=C- stretching vibration. Following peaks are shown in fig.6.1

Fig. 6.1 FTIR Spectra of Dowex-11 Resin without Immobilization



The FTIR spectra of methylene blue immobilized resin Dowex-11 show a sharp peak in the region 3650-3400 cm^{-1} Due to >N-H stretching vibration, and another strong and sharp peak show in the region 3100-2900 cm^{-1} stretching vibration of =C-H (methylene) group. Due to immobilization another strong and sharp peaks of N-H bending and aromatic – C=C - stretching vibration in the region 1550-1510 cm^{-1} and 1600-1450 cm^{-1}. These peaks are shown in fig. 6.2

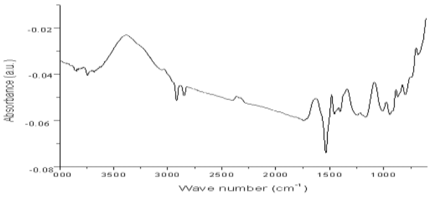
Fig. 6.2 FTIR Spectra of Immobilized Dowex-11 Resin



(b) IR spectra of Dowex-11 resin after immobilization by methylene blue dye

The FTIR spectra of complete experiment (Degradation) of methylene blue immobilized resin Dowex-11 show same peaks in the region 3650-3400 cm^{-1} Due to >N-H stretching vibration and another strong and sharp peak show in the region 3100-2900 cm^{-1} stretching vibration of =C-H (methylene) group due to immobilization. Another strong and sharp peaks of N-H bending and aromatic – C=C - stretching vibration in the region 1550-1510 cm^{-1} and 1600-1450 cm^{-1}. These peaks are shown in fig. 6.3. These same spectra of after complete experiment show that, the dye Direct Red 81 is not present in pores of resin.

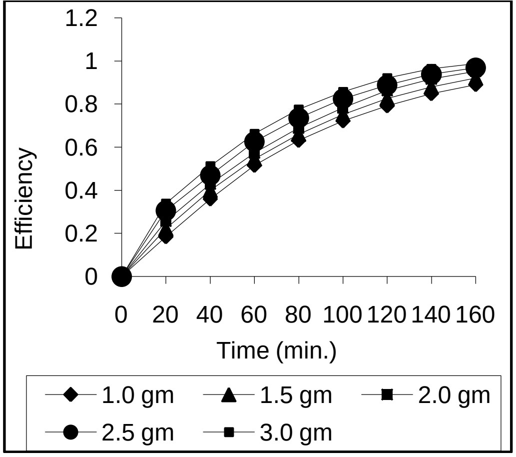
Fig. 6.3 FTIR Spectra of Immobilized Dowex-11 Resin After Complete Experiment



Effect of Catalyst

The amount of the photocatalyst is most important parameter that affects the rate of photo catalytic degradation. We observe effect of variation in amount of photo catalyst from 1.0 to 3.0 gm/100ml and concentration of dye 40 mg/L, at constant pH 7.5 and light intensity 10.4mWcm^{-2}. On the rate of degradation we find out that as concentration of catalyst increases rate of degradation also increases. Increase in the rate of degradation 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 (O_2^-) are increase. These are principle oxidizing intermediate in advance oxidation process resultant increases degradation efficiency. Effect of catalyst loading on degradation efficiency graphically shows in fig. 7.

Fig.7 Effect of Catalyst Loading on Photocatalytic Degradation Efficiency (Temperature: 303 K, Solution Volume: 100 Ml, Initial Dye Concentration: 40 Mg/L, Ph 7.5, UV /Visible Lamp: 10.4 Mwcm^{-2})



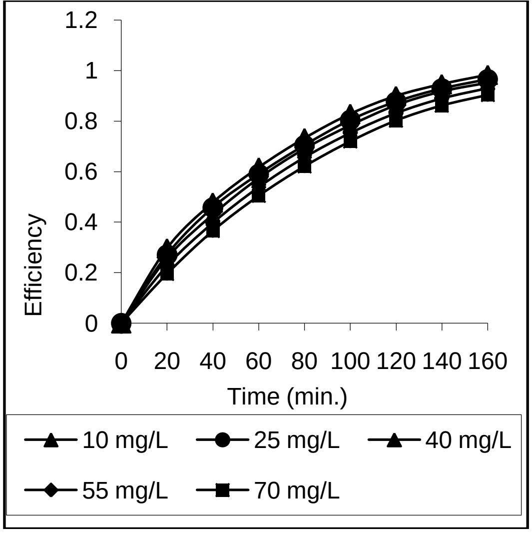
Effect of Initial Dye Concentration

The effect of initial dye concentration on the degradation efficiency was studied by varying the concentration from 10mg/L to 70mg/L at constant photocatalyst (2gm/100ml) the results are shown in (Fig. 8.). The concentration of dye increases the rate of degradation decreases. This effect may be caused by following reason-

The 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 (O_2^-) is decreases so rate of degradation efficiency is also decrease.

The surface area of catalyst is fixed so as the concentration of dye increases rate of degradation decreases because limited number of dye molecules attached at the active site 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 to less availability of photons for excitation of catalyst molecules. Competitions between dye molecules to attach active site also effect rate of degradation. At higher concentration number of dye molecule also high so more will be the competition for attachment to active site of catalyst between the dye molecule and resultant reduce the rate of degradation efficiency. Effect of change in dye concentration is shown graphically in fig.8.

Fig.8 Effect of Initial Dye Concentration on Degradation Efficiency (Temperature: 303 K, Catalyst Loading: 2gm/100ml, Solution Volume: 100 Ml, Ph 7.5, UV/Visible Lamp: 10.4 Mw Cm^{-2})

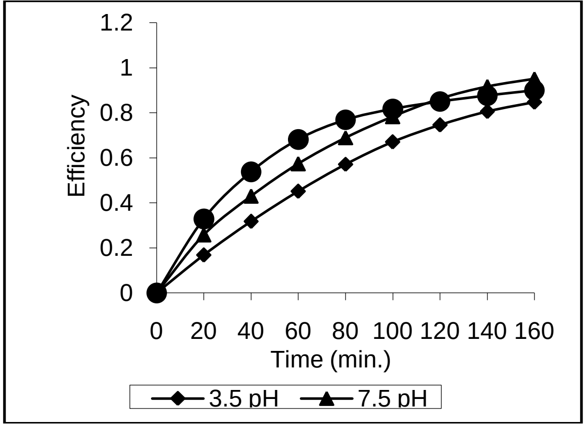


Effect of pH

We observe effect of pH on rate of degradation efficiency of dye molecules is very interesting. The results shows that rate of degradation is very low in high acidic pH range lower then pH 3.5. As well as pH increases rate of degradation also increases when pH reaches to basic range the rate of degradation increases fast, in pH range 7.5 to 9 very good rate of degradation. On further increase pH the rate of degradation also start to decrease after pH range 10 or above rate of degradation is less an continually decreases as pH increases. So we conclude that rate of degradation in basic medium is higher than acidic medium. The increase in rate of photocatalytic degradation may be due to more availability of $^-$OH ions in pH range 7.5 to 9 will generate more $^\bullet$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 photocatalytic degradation than super oxide ions (O_2^-). At higher pH the rate of degradation decreases. This effect may cause due to competition between $^-$OH groups to attach active site of catalyst, so rate of attachment of $^-$OH group decreases. Resultant formation of hydroxyl radicals ($^\cdot$OH) decreases by this reason rate of degradation also decreases. Graphical representation of pH effect is shown in fig. 9.

Fig.9 Effect of Ph on Degradation Efficiency (Temperature: 303 K, Catalyst Loading: 2gm/100ml, Solution Volume: 100 Ml, Initial Dye Concentration: 40 Mg/L, UV Lamp: 10.4 Mwcm^{-2}).

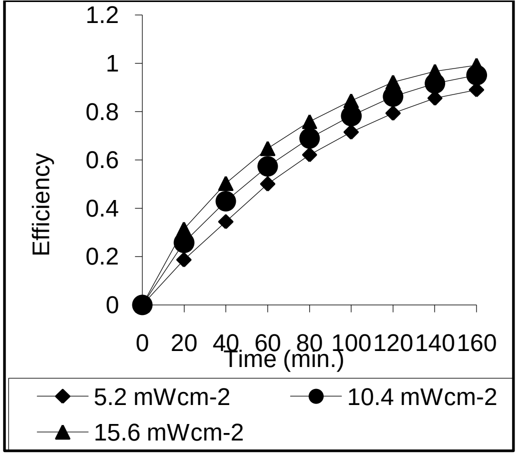
Effect of light intensity



Effect of Light Intensity

Light intensity is most important factor which affects the rate of degradation. We find out that as light intensity increases the rate of degradation of dye molecules also increases up some extant after it no change observe in rate of degradation. This change in rate of degradation 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 (O_2^-) and rate of degradation of dye molecules increase. We observe that after some extant of increase in light intensity there is no effect on rate of degradation 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 no any considerable change observed in rate of degradation 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 degradation remains unchanged. Graphical representation of light intensity variation is shown in fig.10.

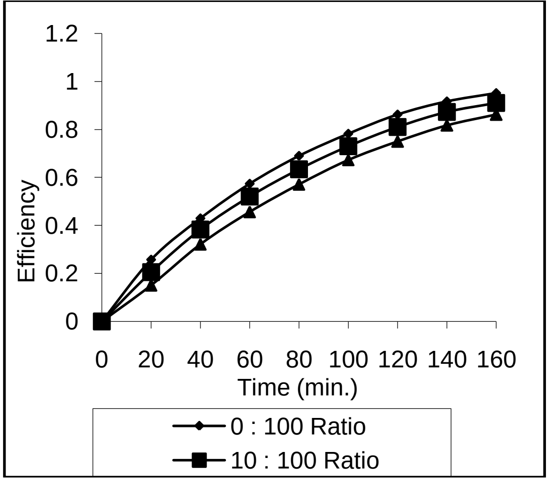
Fig.10 Effect of Variation of Light Intensity on Degradation Efficiency (Temperature: 303 K, Catalyst Loading: 2gm/100ml, Solution Volume: 100 Ml, Initial Dye Concentration: 40 Mg/L, Ph 7.5).



Effect of Variation in Radical Quencher

The oxidative intermediate species such as super oxide and hydroxyl radicals under photocatalytic conditions and their role in the dye degradation process has been investigated indirectly with the use of appropriate quenchers of these species. As it was observed from the experiment that degradation rate of Direct Red 81 were decreases as the ratio of the concentration of propanol increases from 10: 100 to 20:100. Alcohols such as ethanol and propanol are commonly used to quench hydroxyl radicals. So as the ratio of propanol in the dye solution was increases the rate of degradation decreased .This enables us to draw the conclusion that small amount of propanol inhibit the photocatalytic decolorization and hence $^{\bullet}OH$ radicals play a major role in photocatalytic oxidation of Direct Red 81 dyes.The effect of variation in radical quencher (propanol) in photocatalytic activity graphically represented in fig-11.

Fig.11 Effect of Radical Quencher on Degradation Efficiency (Temperature: 303 K, Catalyst Loading: 2gm/100ml, Solution Volume: 100 Ml, Initial Dye Concentration: 40 Mg/L, Ph 7.5, UV Lamp: 10.4 Mwcm^{-2}).



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 (O_2^-) and hydroxyl. These are highly oxidative in nature and increase the rate of degradation of dye molecules.

Conclusion

After long observation we conclude that this photocatalyst (MBIR Dowex-11) has very good potential of degradation of azo dyes into, simple molecules such as CO_2, H_2O etc. and purify wastewater which contains large amount of non fixed dyes mostly azo dyes. Photodegradation efficiency of the dye was very less when photolysis was carried out in absence of the catalyst and negligible in absence of light. The photocatalyst in presence of light successfully decolorizes dye Direct Red 81 solution in to almost completely transparent solution and also the inhibitive effect of propanol has also been studied, and it was concluded that hydroxyl radicals play a major role in oxidation of the dye.

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