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Solar photocatalytic degradation of azo dye ponceau BS through applying alternative developed photocatalyst MBIR Dowex 11

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ABSTRACT

The carcinogenic compounds are major constituent of industrial effluents. Various approaches have been developed to remove organic dyes from the natural environment. An alternate photocatalytic process based on methylene blue immobilized resin (MBIR) Dowex 11 was used to treat Ponceau BS textile azo dye. The effect of operational parameters such as catalyst dose, concentration of dye, pH of the solution, light intensity and dissolved oxygen on dye removal efficiency of Ponceau BS in water has been investigated. Kinetic analysis indicates that the photodegradation rate of azo dye can usually be approximated as pseudo-first-order kinetics. The dye solution could be completely decolorized and effectively mineralized, with average removal efficiency larger than 97% for a photocatalytic reaction time of 2:40 hrs. The mechanism of degradation and FTIR spectra are also discussed.

KEYWORDS

Degradation;
MBIR Dowex 11;
Efficiency;
Immobilization;
Ponceau BS.

INTRODUCTION

The textile processing industry is putting a severe burden on the environment, through the release of heavily polluted wastewaters. Azo dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial pollutants. Photocatalytic degradation of wastewater of textile industries, paper industries, food industries and chemical industries which are generally non biodegradable. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultra filtration can be used for color removal from textile effluents[1-3]. Due to the stability of modern azo dyes advance oxidation process (AOPs) is recently more developed technique in photochemistry and this technique are based on generation of reactive species such as hydroxyl radicals ($^{\cdot}OH$) that oxidized a broad range of organic pollutants quickly and non-selectively[4]. The AOPs include heterogeneous photocatalysis systems such as combination of semiconductors and light, or semiconductor and oxidants[5,6]. The study of works in this area and listed the compounds degraded by photocatalysis by various researchers[7].

The purification of wastewater with TiO_2 photocatalyst in presence of UV radiation has been known to have several advantages, effective removal of organic compounds dissolved or dispersed in water and inexpensive cost[8]. The work on newly developed photocatalyst are alkali and alkaline earth tantalite's TiO_2 and other photocatalyst in different application with new techniques have arisen as a new group of photocatalyst materials for water splitting into H_2 and O_2 and organic molecular degradation under ultra-violet/visible light irradiation[9]. Degradation of methyl orange under UV light (300nm) illumination using ZnO/ZnO_2 as photocatalyst[10]. Anaerobic treatments of azo dye Acid orange 7 under fed batch and continues condition[11].

Decolorization of textile industry wastewater and degradation of C.I. Reactive Orange 4 and its simulated dye bath wastewater by heterogeneous photocatalysis[12,13]. 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[14]. Degradation of Acid Green 16 using ZnO irradiated with sunlight, here the photodegradation efficiency decreased with an increase in initial dye concentration, optimum catalyst loading was found to be 250 mg in 100 ml[15]. Enhanced the photocatalytic activity for methyl orange degradation using $SO_4^{2-}/ZnO/TiO_2$ and aqueous ZnO as photocatalyst for decolorization[16,17]. The degradation is more with solar/ZnO process than with solar/TiO_2 –P25 process at pH 9[18]. The historical perspective of photodegradation of azo dyes ponceau BS by chitosan capped CdS composite nanoparticles and in aqueous phase nanophotocatalysts[19,20]. The study of photodegradation of Ponceau-S, Sudan IV and textile importance dye with methylene blue immobilized resin Dowex 11 photocatalyst[21-23]. The visible light induced photocatalyst MBIR Dowex 11 is an impressive task in order to utilize the solar energy effectively.

EXPERIMENTAL

Photocatalytic studies and design of photoreaction chamber

We prepared photocatalyst by following materials Dowex 11 resin 20-50 mesh (Sisco Chemicals, India Mumbai), and Methylene blue hydrates (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 for immobilization of pores of resin up to 4-5 days. 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 solutions of Ponceau BS dye, Molecular Formula $C_{22}H_{14}N_4Na_2O_7S_2$, λ_{max} 508 nm (Figure 1) and photocatalyst. Solution of reactor is continuously stirred by magnetic stirrer during the experiment and illuminated by halogen lamp (Philips, India) above the reactor which emitted irradiation comparable to visible light (Figure 2). The lamp was surrounded with aluminium reflector in order to avoid loss of irradiation. The intensity was measured by photometer (IL1400A) and pH of the solution was monitored by Fisher Scientific Acumen 50.

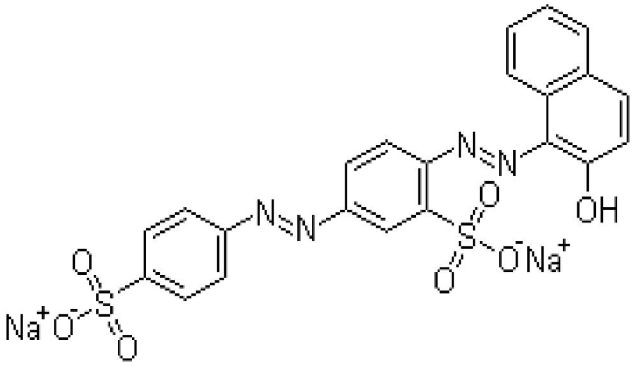

Figure 1 : Structure of dye ponceau BS.

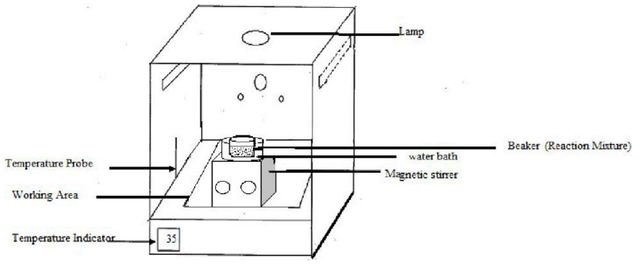

Figure 2 : Experimental setup of photochemical reaction chamber.

Mechanism of degradation

The mechanism of Ponceau BS dye degradation process under UV-Vis/Solar light illumination involves an electron excitation and generation of very active oxygenated species that attack the dye molecules leading to photodegradation. Methylene blue immobilizes resin Dowex-11 is newly developed photocatalyst, due to photosensitive 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, ponceau BS 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 on azo dyes, are transformed in simple organic compounds like CO_2 and H_2O etc.

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

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

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

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

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

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

Im-R = Immobilized Resin

We shuck out 10 ml solution of reaction mixture with the help of a syringe at 10 min time interval, and filtered the catalyst particles through Millipore syringe and change in concentration of dye solution is observed simply by Shimadzu-1600 UV/visible spectrophotometer at λmax_{508nm}. Calculate the dye removal efficiency (X %) of dye solution by this equation.

$$\mathbf{X\% = (C_i - C_t / C_i) \times 100}$$

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

Kinetic study

Photocatalytic degradation of Ponceau BS was observed at λmax = 508 nm. The optimum conditions were obtained at initial dye concentration: 40 mg/L, catalyst loading: 2.0g/100ml, solution volume: 100ml, light intensity: 10.4 $mWcm^{-2}$, pH: 7.5 and temperature 303 K. The plot of 1 + log optical density versus exposure time is a straight line (Figure 3). This indicates that the photocatalytic degradation of Ponceau BS follows pseudo first-order kinetics[24-26]. The rate constant (K) for the reaction was determined using the expression. Rate = K [Ponceau BS], K = 2.303 × Slope. The rate constant for this reaction is $K = 1.62 \times 10^{-2} min^{-1}$.

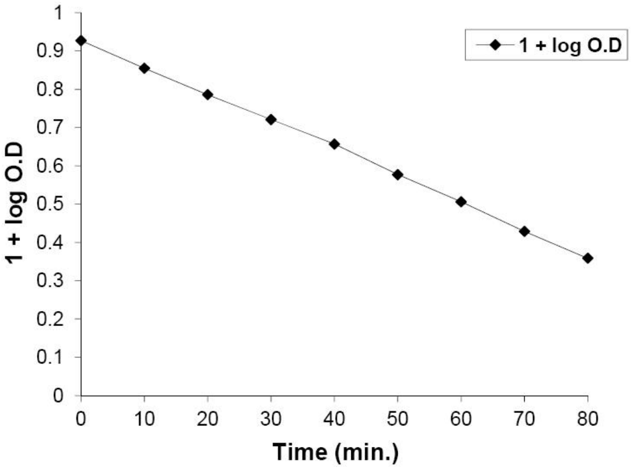

Figure 3 : Kinetic study for ponceau BS - Photocatalyst system (Initial dye concentration 40 mg/L, pH 7.5, catalyst loading 2.0 g/100 ml, solution volume 100 ml and light intensity 10.4 mWc^{m-2}).

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 peaks (Figure 4) in the region 3100-2950 cm^{-1} and 1600-1450 cm^{-1} is attribute to =C-H stretching vibration and aromatic –C=C- stretching vibration.

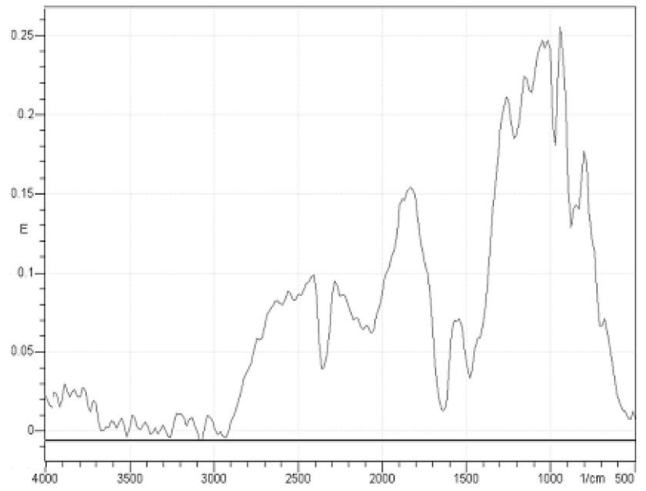

Figure 4 : FTIR spectra of pure resin Dowex 11.

The FTIR spectra of MBIR Dowex-11 show peaks (Figure 5) in the region 3100-2950 cm^{-1} and 1600-1450 cm^{-1} is attribute to =C-H stretching vibration and aromatic –C=C- stretching vibration, and another two peaks in the region 3650-3400 cm^{-1} and 1550-1510 cm^{-1} due to >N-H stretching vibration and N-H bending. These peaks arise due to immobilization of pores of resin with methylene blue dye.

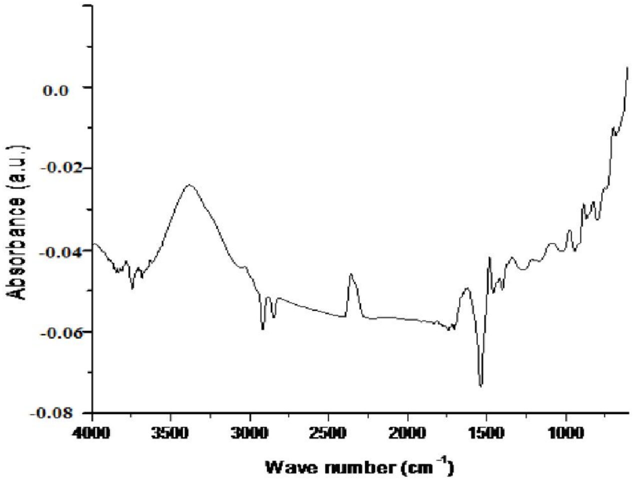

Figure 5 : FTIR spectra of methylene blue immobilized resin Dowex 11.

RESULTS AND DISCUSSION

Effect of catalyst

The amount of the photocatalyst is most important parameter that affects the rate of photocatalytic degradation. We observe effect of variation in amount of photocatalyst from 1.0 to 3.0 g/100 ml, concentration of dye 40 mg/L, at constant pH 7.5 and light intensity 10.4 mWcm^{-2}. We find out that the concentration of catalyst increases rate of degradation also increases, 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 degradation efficiency. Effects of catalyst loading on optical density are shown in Figure 6.

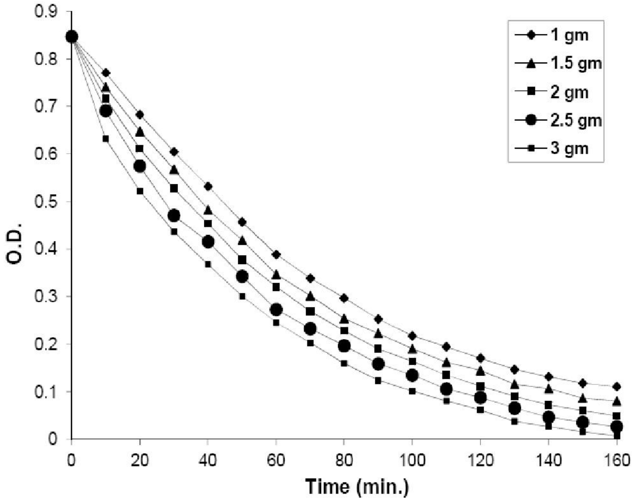

Figure 6 : Effect of catalyst loading on optical density (Temperature 303 K, solution volume 100 ml, Initial dye concentration 40 mg/L, pH 7.5, and light intensity 10.4 mWcm^{-2}).

Effect of initial dye concentration

The effect of initial dye concentration on the degradation efficiency was studied by varying the concentration from 10 mg/L to 70 mg/L at constant photocatalyst (2.0 g/100 ml) the results are shown in Figure 7. 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 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 site of catalyst also decreases due to less availability of photons for excitation of catalyst molecules.

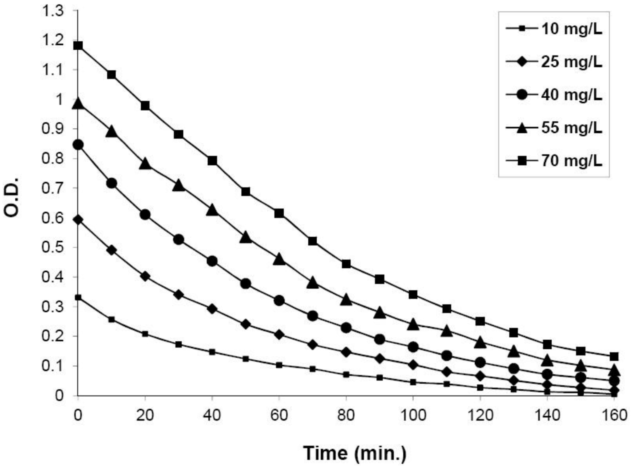

Figure 7 : Effect of initial dye concentration on optical density (Temperature 303K, catalyst loading 2.0 g/100 ml, solution volume 100 ml, pH 7.5, and light intensity 10.4 mWcm^{-2}).

Effect of pH

We observe effect of pH on rate of degradation 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 the rate of degradation is less and continually decreases as pH increases at constant catalyst amount 2.0g/100ml, dye concentration 40mg/L and light intensity 10.4 mWcm^{-2}. 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 •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. 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 (•OH) decreases and rate of degradation also decreases (Figure 8).

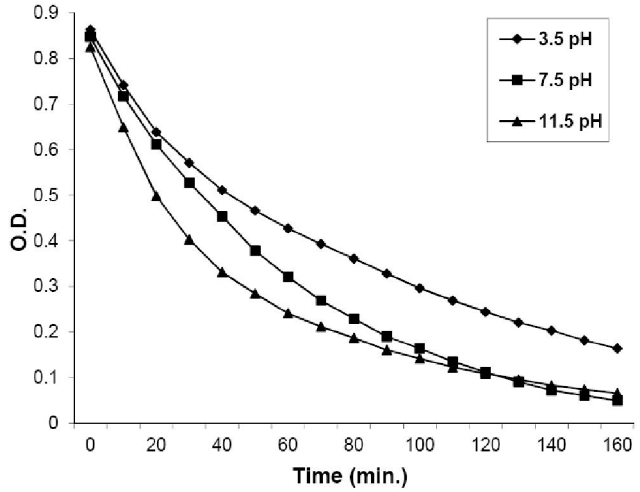

Figure 8 : Effect of pH on optical density (Temperature 303 K, catalyst loading 2.0 g/100 ml, solution volume 100 ml, initial dye concentration 40 mg/L, and light intensity 10.4 mWcm^{-2}).

Effect of light intensity

Light intensity increases the rate of degradation of dye molecules also increases up some extent after it no change observe in rate of degradation. The light intensity increases number of photons increases to reach the catalyst surface, so number of exited catalyst molecules increases and resultant increase the hydroxyl radicals and super oxide ions and rate of degradation of dye molecules increase. After some extent of increase in light intensity there is no effect on rate of degradation. 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 exited in fix light intensity range. Effects of light intensity on optical density are shown in Figure 9.

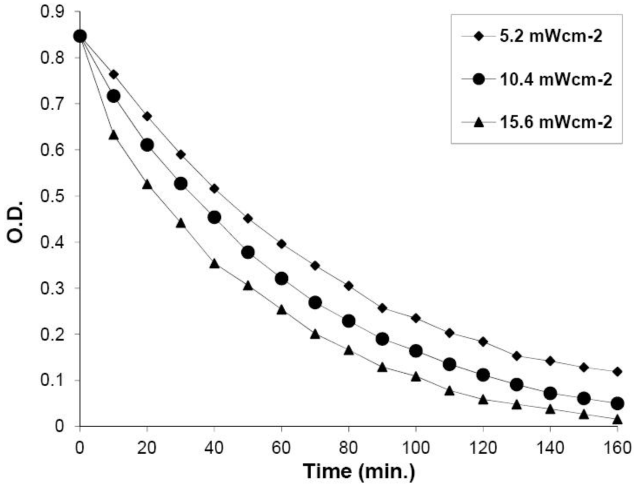

Figure 9 : Effect of variation of light intensity on optical density (Temperature 303 K, catalyst loading 2.0 g/100 ml, solution volume 100 ml, initial dye concentration 40 mg/L, and pH 7.5).

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 ions and hydroxyl radicals. These are highly oxidative in nature and increase the rate of degradation of dye molecules.

CONCLUSIONS

After long observation we conclude that the alternative photocatalyst (MBIR Dowex 11) has very good potential of degradation of azo dyes into simple mineralize products. Photodegradation efficiency of the dye was very less when photolysis was carried out in absence of the catalyst and negligible in absence of light. We observe the effect of different parameters given in order-

- **Variation in dye concentration:** As concentration of dye increase the rate of degradation of dye deceases.
- **Variation in amount of catalyst:** As increase catalyst dose the rate of degradation of dye molecules also increases.
- **Variation in pH:** In acidic range of pH the rate of degradation is very less as pH increases rate of degradation also increases and between pH range 7.5 to 9 rate of degradation is good on further increases in pH the rate of degradation again after to decreases.
- **Variation in light intensity:** On increase light intensity the rate of degradation of dye molecules also increases up to limit after certain light intensity there is no further change
- **Effect of dissolved oxygen:** Rate of degradation increases up to some extent on increases the dissolves oxygen in dye solution.

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