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Photocatalytic degradation of textile dye through an alternative photocatalyst methylene blue immobilized resin dowex 11 in presence of solar light

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ABSTRACT

The photocatalytic degradation of azo dye which is generally used in textile industry, acid red 73 in presence of methylene blue immobilized resin (MBIR) Dowex 11 with solar light in aqueous solution has been studied. The operational parameters such as dye concentration, catalyst loading, pH and light intensity were investigated during the process. The experiment was carried out by irradiation the aqueous solution of dyes containing photocatalyst with solar light and UV. The results showed that the optimum degradation larger than 92% of acid red 73 was observed in around 160 min. at room temperature at 7.5 pH and catalyst loading in around 2.0 gm.

Keywords: Photocatalyst, Dowex-11, Acid red 73, Degradation, Solar light.

INTRODUCTION

Dyes are used mostly in the textile (fabric used in clothing) industry and paper industry. These industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. The annually world production of textile industry is about 30 million tones requiring 700,000 tones of different type dyes which causes considerable environmental pollution problems [1]. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Various chemical and physical processes such as adsorption, air stripping, flocculation, precipitation, reverse osmosis and ultra-filtration can be used for color removal textile effluents [2-5]. Many textile manufacturers use dyes that release aromatic amines (e.g. banzidine, toluidine). Dye bath effluents may contain heavy metals ammonia, alkali salts, toxic solids & large amounts of pigments many of which are also toxic. Treatment of dye-based effluents is considered to be one of the challenging tasks in environmental fraternity. Dyes are complex aromatic compounds

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which are normally used for coloration of various substrates like leather, textiles, papers etc. They are sometimes fused with heavy metals on the structural interface and are considered to have relatively bad consequence on the surrounding environment due to their toxic and inhibitory nature [6,7].

In recent years an alternative to conventional methods, is “advanced oxidation processes” (AOPs), based on the generation of very reactive species such as hydroxyl radicals, that oxidizes a broad range of organic pollutants quickly and non-selectively [8,9]. The formation of very active hydroxyl radical ($^{\bullet}OH$) which react with the pollutants. The generation of hydroxyl radicals in to the photo catalytic transformation is described in following equation

$$Dye^{*3} + Im\text{-}R \rightarrow Dye^{+} + Im\text{-}R\ (e^{-})$$
$$Dye^{+} + OH^{-} \rightarrow Dye + {}^{\bullet}OH$$

(Im-R:- Immobilized Resin)

These hydroxyl radicals are the oxidizing agents in advance oxidation process and lead to enhance the rate of transformation [10]. Tang and An [11] investigated the treatment of five commercial dyes with suspended UV/TiO_2 photo catalytic process and showed the color removal ratio varied at different pH values. The photo catalytic transformation of many dyes (Crystal Violet, Orange G, Malachite Green, Rhomazole Blue, Indigo Carmine, Congo Red, Methyl Yellow). The subject of research work related to dye transformation has been excellently reviewed by Yashodharam et al. [12], Kamat [13] and Frewd and Gomes [14].

Titanium dioxide (TiO_2) is generally considered to be the best photo catalyst and has the ability to detoxification water from a number of organic pollutants [15-17]. ZnO was reported that it is more efficient than TiO_2 in UV light photocatalytic degradation of some organic compounds in aqueous solution [18,19]. Earlier, Grzechulska and Morawski [20] reported the photocatalytic decomposition of azo dye AB 1 using TiO_2 with UV light. Shu et al. [21] reported the decolorization of AB 1 by UV/H_2O_2 process. So far the degradation of AB 1 by ZnO had not been investigated under solar light. Mendez-Pezet et al. [22] carried out anaerobic treatment of azo dyes like Acid Orange 7 under fed batch and continues condition. The removal rate of above dye pollutant is increased at high rate when some glucose is added to reaction mixture. Degradation of Amaranth with methylene blue immobilized resin Dowex 11 photocatalyst is carried out by Pratibha Yadav and R. C. Meena [23].

Aim of the presence work is to attention of researchers toward utilization of solar energy for photo degradation of azo dye pollutants by photocatalyst and fined out new photo catalyst for different parameters. A newly developed photocatalyst is cheap and better. The degradation of dye by photo catalyst (MBIR Dowex-11) is better and this catalyst work in presence of dim light and sun light also.

MATERIALS AND METHODS

The experiment was carried in a photo catalytic reactor to examine the degradation of Acid Red 73 $\lambda_{max\ 507nm}$, mol. wt. 556.49 shown in Fig. 1 has been obtained from nearby textile industry and has been used as such. All chemicals used were of AR grade. We prepare photo catalyst from Dowex-11 resin 20-50 mesh (Sisco Chemicals India Mumbai), methylene blue hydrate for microscopy, (Loba chemicals India). Solution was prepared by dissolving a defined quantity of the dye in double distilled water. For the preparation of catalyst a resin which is insoluble, cross-linked, long chain organic polymer with a micro porous structure is used i.e., Dowex-11 resin and a photosensitized dye Methylene Blue C.I. 52015 also called Swiss blue is used. The wastewater was monitored spectrophotometrically with an UV/Vis spectrophotometer. Adding .01 N NaOH or .01 N H_2SO_4 adjusted the pH initially.

The photocatalytic transformation reactions were carried out in glass reactors containing a model solution of acid red 73 and a fixed amount of a photo catalyst. The solution in the reactor was continuously magnetically stirred during the experiment. The solution was illuminated with a 200W halogen lamp. The lamp was positioned above the reactor. A schematic diagram of the setup can be seen in following figure 2.

At a regular time interval, the change in dye concentration is observed simply by Shimadzu-160 UV/Visible spectrophotometer at λmax_{507nm}. We shuck out 10 ml of solution by pipette at the 10 min time interval and calculate the decolorization efficiency (X) 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.

RESULTS AND DISCUSSION

Effect of catalyst

The quantity of the photocatalyst is most essential parameter that affects the rate of photocatalytic degradation. It can be observed that the variation in amount of photocatalyst from 1.0 to 3.0 gm and concentration of dye 40 mg/l, at constant pH 7.5 and intensity10.4 $mWcm^{-2}$. On the rate of degradation, we find out that as amount of catalyst increases rate of degradation also increases. The rate of degradation continuously increases with increasing in the 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 hydroxyl radicals and super oxide ions (O_2^-) are increase. These are principle oxidizing intermediate in advance oxidation process resulting increases degradation. Effect of catalyst loading on rate of degradation graphically shows in fig. 3.

Effect of initial dye concentration

The effect of initial dye concentration on the rate of the degradation was investigated by varying the initial concentration from 10mg/l to 70mg/l at constant photocatalyst loading (2.0gm) and results are shown in (Fig. 4). As seen in the figure the concentration of dye increases the rate of degradation decreases. This effect may be caused by following reason-

As the dye concentration increase the number of photons which is approach to the catalyst surface active site also 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 active site of catalyst surface area is fixed so as the concentration of dye increases then 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. Competitions between dye molecules to attach active site also affect the rate of degradation. Effect of change in dye concentration is shown graphically in Fig. 4.

Effect of pH

The 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 rate of degradation is less and 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 photo catalytic degradation 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 degradation than super oxide (O_2^-). This effect may cause due to competition between $^{-}$OH groups to attach the 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. 5.

Effect of light intensity

Light intensity is most important factor which affects the rate of degradation. We observed that as light intensity increases the rate of degradation of dye molecules also increases but after some extant of increase in light intensity there is no change observed 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 active site of catalyst so number of exited catalyst molecules increases and resultant increase the number of hydroxyl radicals and super oxide ions (O_2^-) and rate of degradation of dye molecules also increase. 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 substantial change observed in rate of degradation because there is no requirement of more photons for excitation. Graphical representation of light intensity variation is shown in fig. 6.

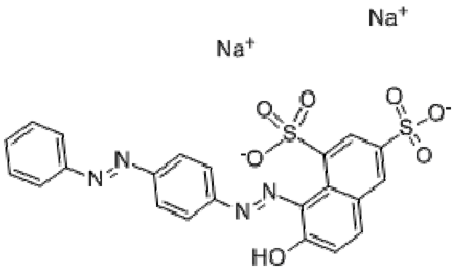

Fig. 1. Structure of Acid Red 73

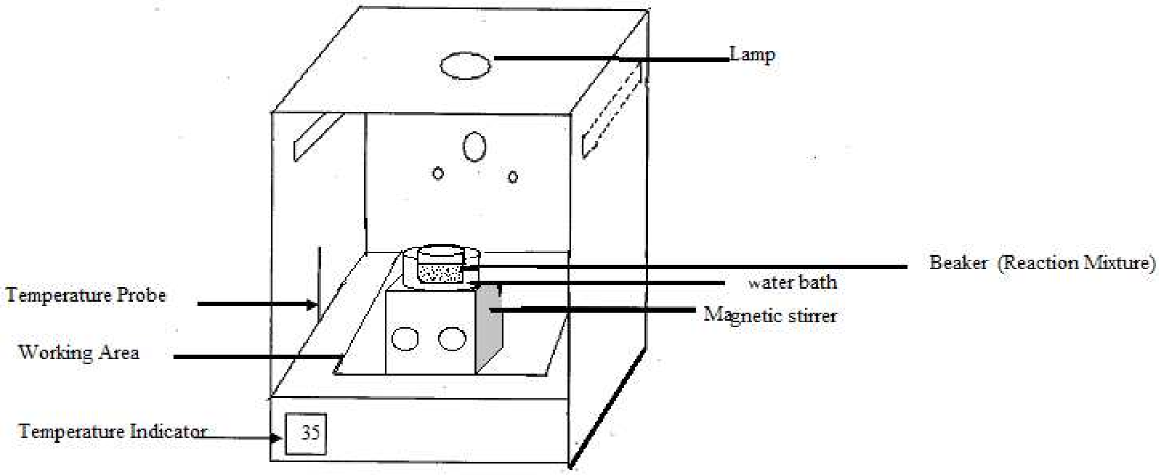

Fig. 2. Schematic diagram of the experimental setup

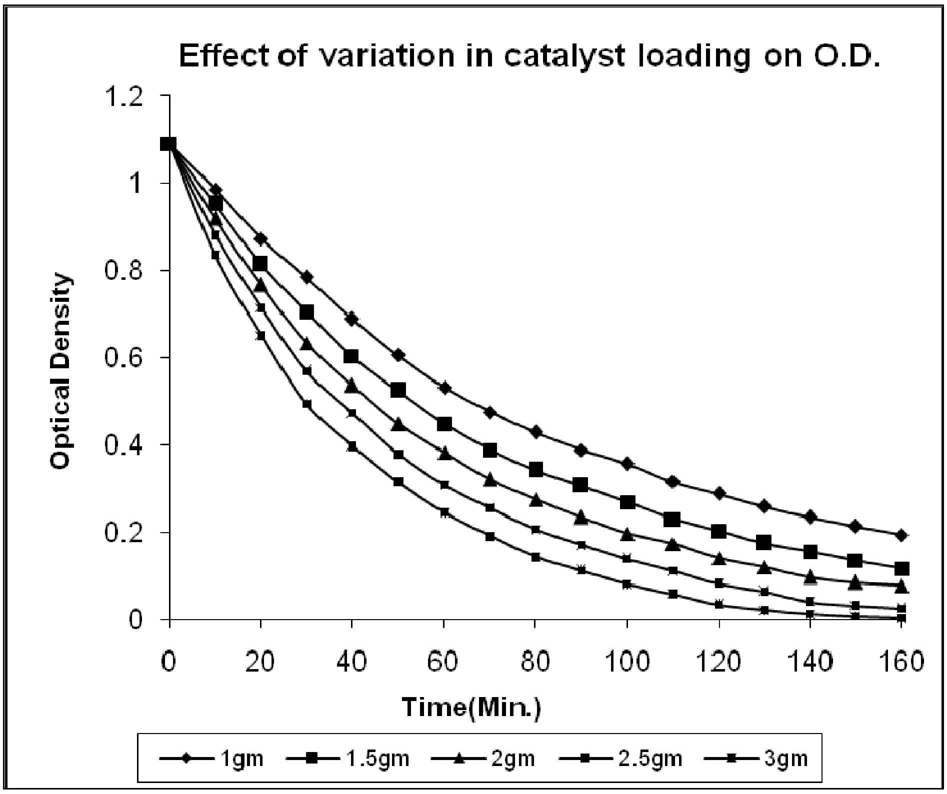

Fig. 3. Effect of catalyst loading on photo catalytic degradation
(Temperature= 303 K, dye solution= 50 ml, Initial dye concentration= 40 mg/l, pH= 7.5, light intensity= 10.4mWcm^{-2}*)*

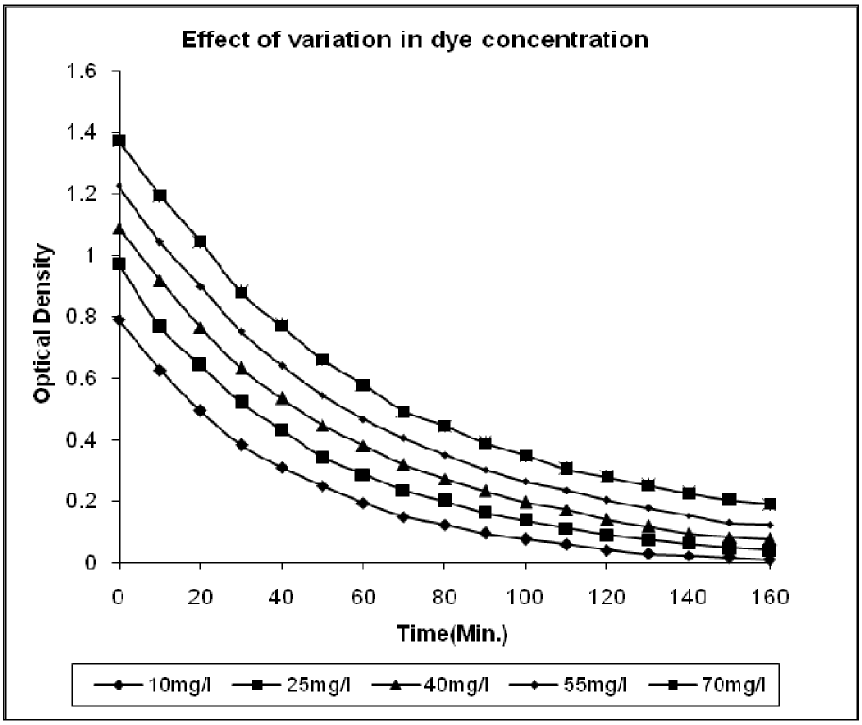

Fig. 4. Effect of Initial dye concentration on degradation
(Temperature= 303 K, dye solution= 50 ml, pH= 7.5, catalyst loading= 2.0gm, light intensity= 10.4mWcm^{-2})

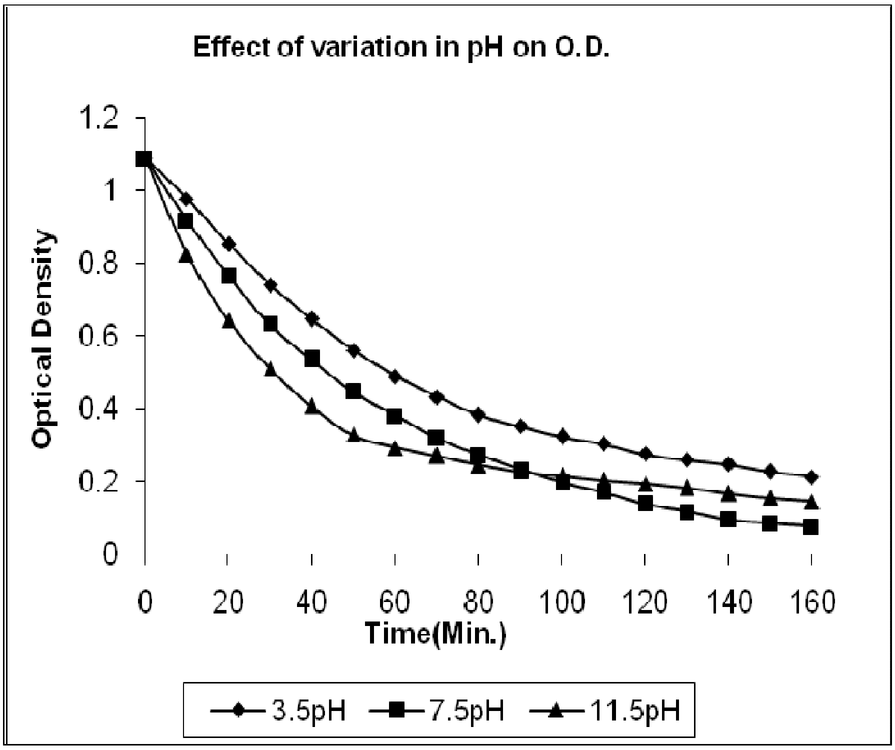

Fig. 5. Effect of pH on degradation
(Temperature= 303 K, dye solution= 50 ml, Initial dye concentration= 40 mg/l, catalyst loading= 2.0gm, light intensity= 10.4mWcm^{-2})

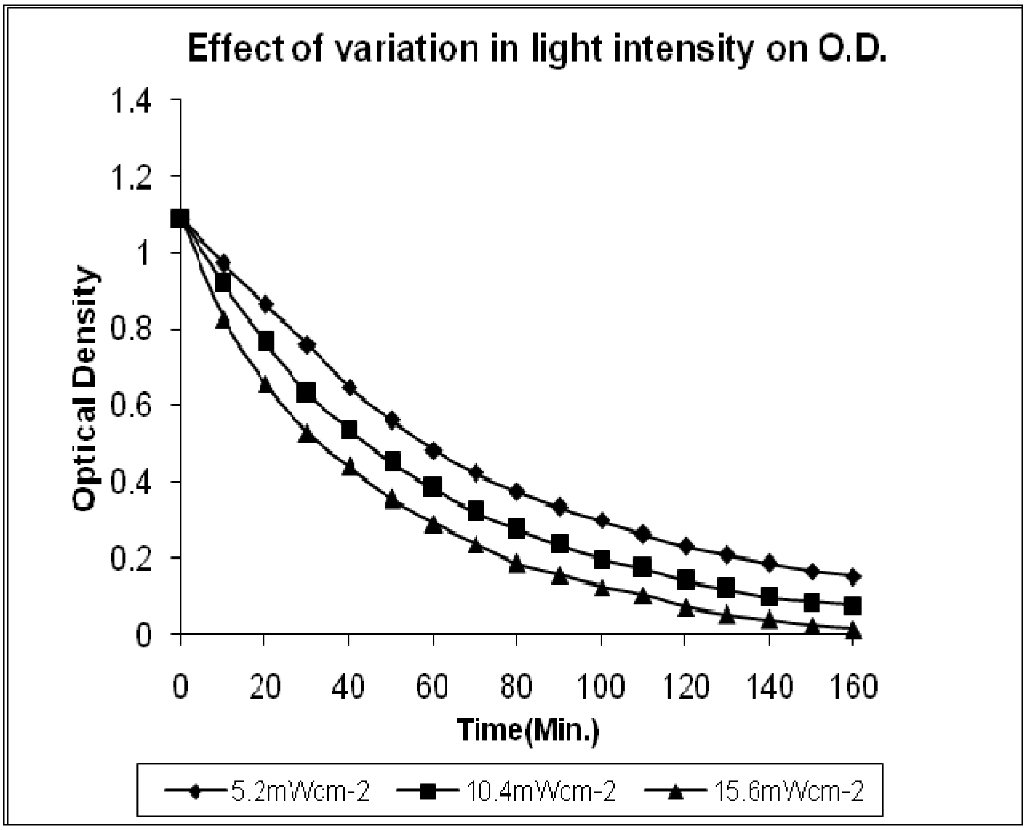

Fig. 6. Effect of variation of light intensity on degradation

(Temperature= 303 K, dye solution= 50 ml, Initial dye concentration: 40 mg/l, pH = 7.5)

CONCLUSION

After examination we conclude that this photo catalyst (methylene blue immobilized resin Dowex-11) has very good potential of degradation of azo dyes into simple molecules such as CO_2 and H_2O and purify textile effluent (wastewater) which contains large amount of non fixed dyes mostly azo dyes.

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