

Methylene Blue Immobilized Resin Dowex-11 as Photo Catalyst for UV Light Irradiation Assisted Degradation of Acid Yellow 36

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Abstract

A novel and efficient photo catalyst Methylene blue immobilized Dowex-11 was prepared to investigate its catalytic activity for the degradation of acid yellow 36 (Acid Metanil yellow) in the presence of UV light irradiation. The effect of different reaction parameters on the photo catalytic oxidation of Acid Yellow 36 was assessed the optimal operational parameters were found as photons: pH 7.5, temperature 333K catalyst loading 3.0gm/50ml and 2.5 hrs light irradiation. Stability and reused of the catalyst were tested. The possible reaction mechanism was also discussed.

Keywords: Metylene blue immobilized resin Dowex -11, photo catalytic oxidation, acid Yellow36

Introduction

A wide variety of textile dyes, detergents, pesticides and other organic compounds which are toxic and stable to natural decomposition are nowadays introduced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills and their persistence in the environment is a subject of concern [1]. Color removal from the textile wastewater has become an issue of interest during the last few years because of toxicity of dyes and colored wastewater from the textile industries also decreases the visibility of the receiving waters.

Dyes and dye intermediates with high degree of aromaticity and low biodegradability are introduced into the aquatic system resulting in increase of environmental risk. Dye pollutants from the textile industry are an important source of environmental contamination.

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 [2-3]. 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 [4-7].

Degradation of Acid Green 16 was studied by Sakthivel et al. [8] 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. [9] was studied the photo catalytic transformation of Remazol Red by ZnO. Patricia A. Carneiro et al. [10] using TiO₂ thin film electrode prepared by the sol-gel method, investigate the photo bleaching of a textile azo dye Reactive orange 16 in aqueous solution mainly because of its photo stability, non-toxicity, low cost and water insolubility under most environmental conditions. D. Mendez-Pezet et al [11] carried out anaerobic treatment of azo dyes Acid orange 7 under fed batch and continues condition. The removal rate of dye pollutant is increased at high rate when some glucose is added to reaction mixture. Pandurangan et. al. [12] 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. Rambabu Pachwarya and R. C. Meena [13] have been studied the degradation of azo dye Amido Black 10B by recently developed photo catalyst (Methylene Blue immobilized Resin Dowex-11).

Acid yellow 36 is an example of persistent organic contaminants, which show low biodegradability and pose serious risks to human health and the environment. Therefore, the removal of acid yellow 36 from aqueous effluents is a significant environment issue. Considering that acid yellow 36 is resistant to biological degradation and can be hardly destroyed in conventional wastewater water treatment technologies, there is a pressing need to provide a method for the degradation and bleaching of acid yellow 36 from the environment which is of low cost and little time consuming. Photo catalysis processes have been the efficient available technologies to destroy a wide variety of persistent organic pollutants in aqueous solution [14]. These processes base on the formation of very active hydroxyl radicals which react quickly with the pollutants. The generation of hydroxyl radicals in the photo catalytic transformation is described in Eq. below



These hydroxyl radicals are the principle oxidizing agents in advance oxidation process and lead to increase the rate of transformation [15].

Aim of present work is to gain attention of researchers towards utilization of solar energy for degradation of dye pollutants by photo catalyst and find out new photo catalyst for different applications. This is a newly developed cheap and better photo

catalyst that can be reused without losing its efficiency. We apply it in different conditions and find out the effect of different parameters on the rate of degradation.

Experimental

Materials and chemicals

Acid yellow 36 (C₁₈H₁₄N₃NaO₃S; mol.wt. 375.370; λ_{max} – 414nm) was obtained from LOBA Chemicals India. Photo catalyst was prepared by using Dowex-11 resin (particle size, 20-50 mesh) (Sisco Chemicals India, Mumbai) and Methylene Blue hydrate (LOBA Chemicals India). For immobilization DOWEX-11 resin was added to the solution of Methylene Blue (10⁻³ M). Put the solution in dark for 3 days for complete immobilization of MB inside resin pores. After this filtered, the solution to get immobilized resin and washed it by double distilled water twice and used as photo catalyst in further experiments.

Analytical Methods

Photoreaction was carried out in a glass reactor, which contains a mixture of dye (Acid Yellow 36) and photo catalyst. Solution was continuously stirred by magnetic stirrer during the experiment. Solution was illuminated by 200W halogen lamp placed above reactor. At 10 min time interval, 10ml solution was taken out from reaction mixture and filtered the catalyst particles. In all cases, 50ml. of the Acid Yellow 36 dye solution containing appropriate quantity of the Methylene blue immobilized resin Dowex-11 catalyst were used. After stirring continuously in the dark for 2min the suspension was irradiated by UV irradiation and it was treated as the starting point (t=0) of the reaction, where the optical density of dye solution was designated as C₀ at specific time interval, optical density of the solution was designated as C. Change in dye concentration was recorded by UV/Vis spectrophotometer (Shimadzu-160). The dye removal was calculated by using the equation given below:

$$CR\% = \frac{C_0 - C}{C_0} \times 100$$

Where, C₀ and C are optical densities of dye solution at initial time and at time t respectively.

Results and Discussion

Chemical Reaction of Dye Degradation

Methylene Blue is a photosensitive dye; when irradiated with light radiations; electronic transition occurs from VB to CB and through intersystem crossing (ISC) electron reach in to triplet state of MB. Intermolecular electronic transition starts between photo catalyst, Methylene Blue dye molecules, water molecules and Metanil Yellow dye molecules resulting into highly oxidizing agents holes, hydroxyl radicals and super oxide ions (Fig. 1), which transfer azo dye in simple organic compounds. Main factors influencing photo catalytic degradation of azo dye are pH of the

solution, variation in catalyst loading, concentration of dye and light intensity. Methylene Blue becomes excited by absorbing photons of light radiation from ground state to singlet state. Through ISC electron can transfer to triplet state of MB. Further intermolecular electronic transition occurs between photo catalyst, MB and dye solution and resultant is formation of holes, hydroxyl radicals and super oxide ions which are main oxidative agents in the photo catalytic reaction.

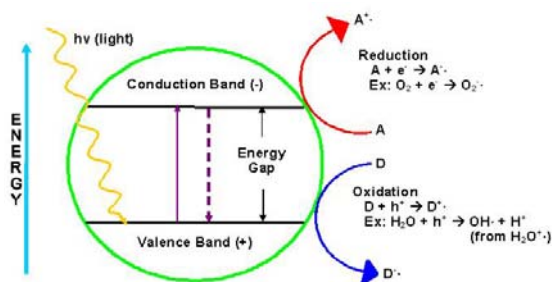


Fig. 1 Photo catalytic action: Generation of holes, hydroxyl radicals and super oxide ions

Effect of pH

The effect of pH on the decolorization of acid yellow 36 was investigated by keeping all other experimental conditions constant and varying the initial pH of acid yellow 36 from 3.5 to 11. It can be observed that the bleaching of acid yellow 36 was increased with increasing pH value from 3.5 to 9.0 (Fig. 2). On further increasing pH, rate of degradation starts to decrease. Maximum bleaching was obtained at pH 7.5. At this pH acid yellow 36 was reduced by 97% after 2.5 hrs. Increase in the rate of photo catalytic degradation may be due to more availability of hydroxyl ions by combining with holes, which are formed due to electronic excitation in catalyst in pH range 7.5-9.0. Formations of hydroxyl radicals are responsible more for photo catalytic degradation than super oxide ions (O^{-•}).

Effect of catalyst loading

Experiments were performed to study the variations in the transformation of acid yellow 36 at different catalyst loading. It can be observed that the bleaching of acid yellow 36 increased with increase in catalyst loading from 1.0gm/50ml to 3.0gm/50ml. due to more availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, increase in number of holes, hydroxyl radicals and super oxide ions (O^{-•}). These are the principle oxidizing agents in advance oxidation process. A further increase in catalyst loading, however, may prevent the efficient light adsorption in the solution and thus result in the decrease of degradation (Fig. 3).

Effect of initial dye concentration

The effect of initial concentration of acid yellow 36 on the transformation process was

investigated over the concentration range from 10mg/l to 70mg/l with constant catalyst loading 2.0gm. As the dye concentration increased, rate of degradation decreased (Fig. 4), may be due to following reason: i)As dye concentration increases, number of photons reaching to catalyst surface decreases because less number of catalyst molecules undergo excitation and hence rate of formation of holes, hydroxyl radicals and supra oxide ions (O⁻) is decreased thereby decreasing rate of degradation; ii)Since catalyst surface area is fixed, so as concentration of dye increases rate of degradation decreases because limited number of dye molecules attach at active site of catalyst and remaining dye molecules persist in dye solution until earlier attached molecules are degraded and number of active site of catalyst also decreases due less availability of photons for excitation of catalyst molecules; and iii)At higher concentration, number of dye molecules are also high so there will be more competition for attachment to active site of catalyst between dye molecules, resulting in reduction in rate of degradation .

Effect of light intensity

As light intensity increased, rate of degradation of dye molecules increased up to a certain limit, and after that no changes were observed (Fig.5). This is because as light intensity increases, number of photons reaching catalyst surface also increases, so increase in number of excited catalyst molecules result is increase in number of holes, hydroxyl radicals and super oxide ions (O⁻), and hence rate of degradation of dye molecules also increases.

Recycling studies

In order to know the stability of the catalyst, the catalyst was recycled five times by using acid yellow 36 solutions at optimum conditions. After each experiment, the catalyst was separated from solution by filtration, washed with deionised water for several times, the catalyst was dried over night and then used for next run .noticeably, after five cycles of experimentation, the catalysis efficiency was still higher and the catalytic performance was not affected by the times of reuse.

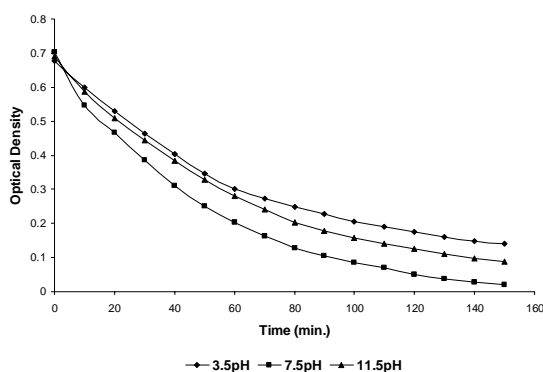


Fig. 2 Effect of pH on degradation (Temp. 303K, dye solution 50ml, initial dye conc. 40mg/l, catalyst loading 2gm, light intensity 10.4mW/cm²).

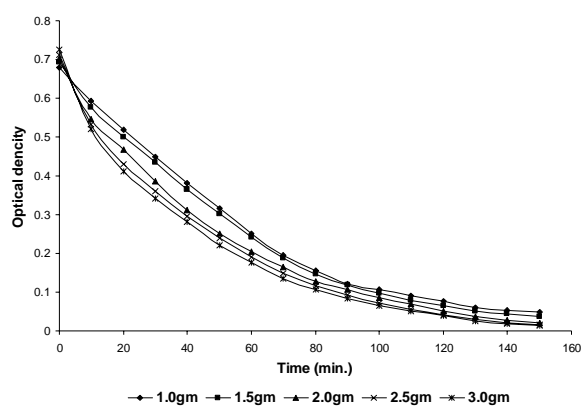


Fig. 3 Effect of catalyst loading on degradation (Temp. 303K, dye solution 50ml, initial dye conc. 40mg/l, pH 7.5, light intensity 10.4mW/cm²).

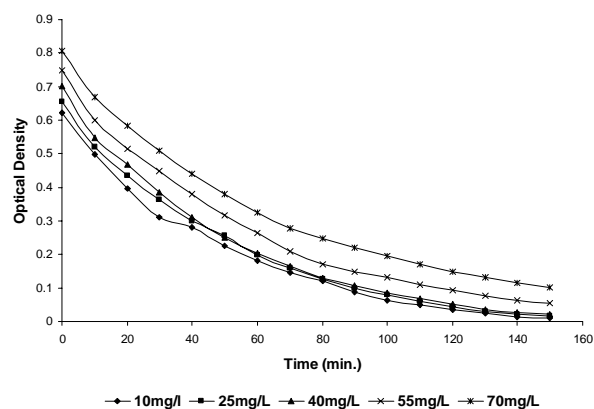


Fig. 4 Effect of dye conc. on degradation (Temp. 303K, dye solution 50ml, pH 7.5, catalyst loading 2gm, light intensity 10.4mW/cm²).

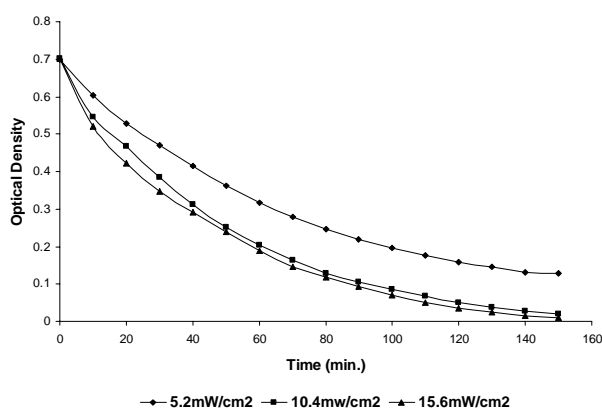
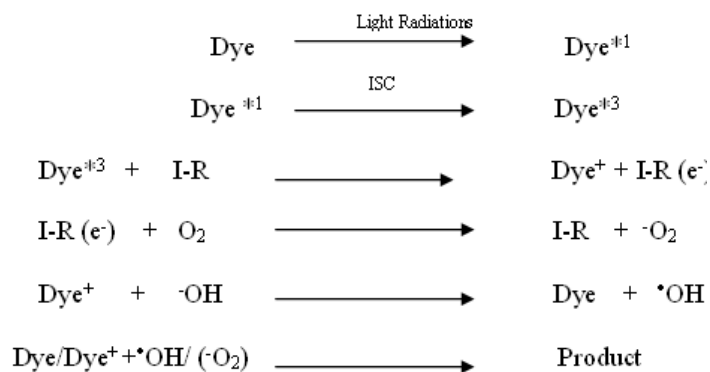


Fig. 5 Effect of light intensity on degradation (Temp. 303K, dye solution 50ml, initial dye conc. 40mg/l, catalyst loading 2gm, pH 7.5)

Postulated Reaction Mechanism

On the basis of results a tentative mechanism has been proposed for photo catalytic decolorization of Acid yellow -23 with catalyst Methylene Blue immobilized Resin Dowex -11 in the presence of light -:



The dye molecule absorbs photons and electrons become excited and its 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.

Conclusion

In conclusion, this study has proved that Methylene Blue immobilized resin Dowex - 11 is an efficient catalyst for degradation of azo dyes in to simple molecules in presence of ultraviolet radiations. As dye concentration increases, rate of degradation decreases. As concentration of catalyst increases, rate of degradation of dye molecules also increases. Degradation rate is optimum at pH 7.5-9.0. On increasing light intensity, degradation rate is increased up to a certain extant, after that no further changes are observed. The degradation of Acid Yellow 36 by Methylene Blue immobilized resin Dowex-11 followed pseudo first order kinetics with respect to the concentration of Acid Yellow 36. No obvious decline in efficiency of the catalyst was observed after 5 repeated cycles and this demonstrated the stability and reusability of the catalyst.

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