

UV Irradiation Assisted Photocatalytic Decolorization of Direct Red 23 in Aqueous Solution

Swati and R. C. Meena

Department of Chemistry, Jai Narain Vyas University, Jodhpur (Rajasthan), INDIA.

Abstract- Study on the photocatalytic decolorization of aqueous solution of Direct Red 23, a commercial azo-reactive textile dye, in the presence of UV light radiation. The effect of different reaction parameters on the photo catalyst of DR 23 was assessed best operational parameters were observed as photons: catalyst loading 1gm-3.0gm/50ml, pH 3.5-11.5, temperature 303k, dye concentration 10mg/50ml-70mg/50ml and 2.30hrs light irradiation on photo decolorization. FTIR is employed successfully to study the behavior of dowex-11 Resin and after the immobilized by Methylene blue dye. FTIR spectrum is recorded in the range 400-4000cm⁻¹. Activity of photo catalyst MBIR-11 remains impervious on continuous use.

Index Terms- Photocatalytic decolorization process, Methylene blue immobilized resin dowex-11, operational parameters, Direct Red 23, UV radiation.

I. INTRODUCTION

Now days, industrial waste water, detergents and a wide variety of textile dyes and other industrial dyestuffs constitutes one of the largest group of organic compounds that represent an continuously increasing the environmental dangers. This waste water causes damages to the ecological system of the receiving surface water capacity and certain a lot of disturbance to the ground water resources. Many dyes are used in the textile industries are stable to light and are not biodegradable. In order to reduce the risk of environmental pollution from such waste water¹. Among these biodegradation, chlorination, ozonation and adsorption are the most commonly used conventional process. Effluents dyes are usually resistant to aerobic degradation and carcinogenic compounds may be generated during the anaerobic treatment, for example: - aromatic amines from azo dyes; in these respects, bio-treatment alone has been found to be ineffective for the treatment of dye effluents².

Decolorization of azo dye effluents has therefore received increasing attention for the removal of dye pollutants, traditional physical technique (adsorption on activated carbon, reverse osmosis, ion exchange on synthetic adsorbent resins, ultra filtration, coagulation by chemical agents, etc.) can generally be used efficiently³⁻⁶. Decolorization is a result of two mechanisms: adsorption and ion exchange (Slokar and Le Marechal(1998), and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, adsorbent surface area, particle size, contact time, pH, and temperature (Kumar et al., 1998). Adsorption also does not end result in the formation of harmful substance^{7,8}.

Photocatalytic oxidation of azo dyes and other dyes have been investigated by a number of researchers. Photocatalytic oxidation processes can oxidize a wide variety of toxic and persistent organic compounds to harmless inorganics such as mineral acids, carbon dioxide and water (Dominguez et al., 1998)⁹. Also, in this process form several byproducts such as halides, inorganic acids, metals and organic aldehydes depending on the initial materials and the extent of decolorization (Robinson et al., 2001)¹⁰.

In order to remove hazardous materials like dyes, adsorption is a method which has gain considerable attention in the recent few years adsorption is such and simple technique¹¹. Recently developments of advanced oxidation processes (AOPs) have led to new improvements of the oxidative degradation of the organic compounds. UV radiation in the presence of H₂O₂ has yielded encouraging results of color removal from azo reactive dye containing water¹². Advanced oxidation processes such as catalytic oxidation using photon Fenton, Fenton and visible/solar light system^{13,14} H₂O₂/UV processes and titanium oxide photocatalysis^{15,16}.

Rate of degradation of acid green 16 was studied by Sakthivel et al¹⁷ using ZnO irradiated with sun light. Yingma and Jian Nian Yao prepared a thin film on TiO₂ and used it to study photodegradation of Rh-B. Ciping et al. observed that the formation of free radical intermediates in photoreactions with ZnO dispersion. Richard *et al.* reported that the oxidizing species involved in photocatalytic transformation on ZnO are either hydroxyl radicals or holes¹⁸⁻²⁰.

Lizamaet al²¹ reported the photocatalytic decolorization of reactive blue 19(RB 19) in aqueous solution in the presence of TiO₂ or ZnO as catalyst and concluded that ZnO is a more efficient photocatalyst than TiO₂ in the removal of RB-19. Rambabu Pachwarya and R.C. Meena²² have been investigated the degradation of textile azo dye Amido black- 10 B by newly developed photocatalyst (Methylene blue immobilized resin Dowex 11).

Direct Red 23 is the commercial textile azo dye which is caused some harmful effects. Therefore the removals of such type of dyes from effluents become environmentally important. So in this paper we studied, photocatalyst (MBIR-11) was observed for the decolorization efficiency of aqueous solution of a textile dye, Direct Red 23 in different conditions and observe the effect of many parameters on the rate removal efficiency.

II. MATERIALS AND METHODS

Molecular Formula = C₃₅H₂₅N₇Na₂O₁₀S₂
Molecular Weight = 813.72

Solubility = Soluble in water
 Appearance = Red
 Class = Azo
 λ_{max} = 508 nm
 And double distilled water was used for preparation of various solutions.

Structure of dye

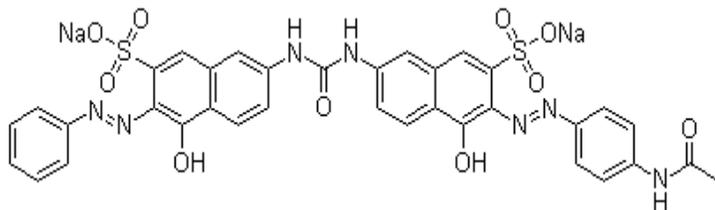


Fig.1 Structure of Direct Red 23

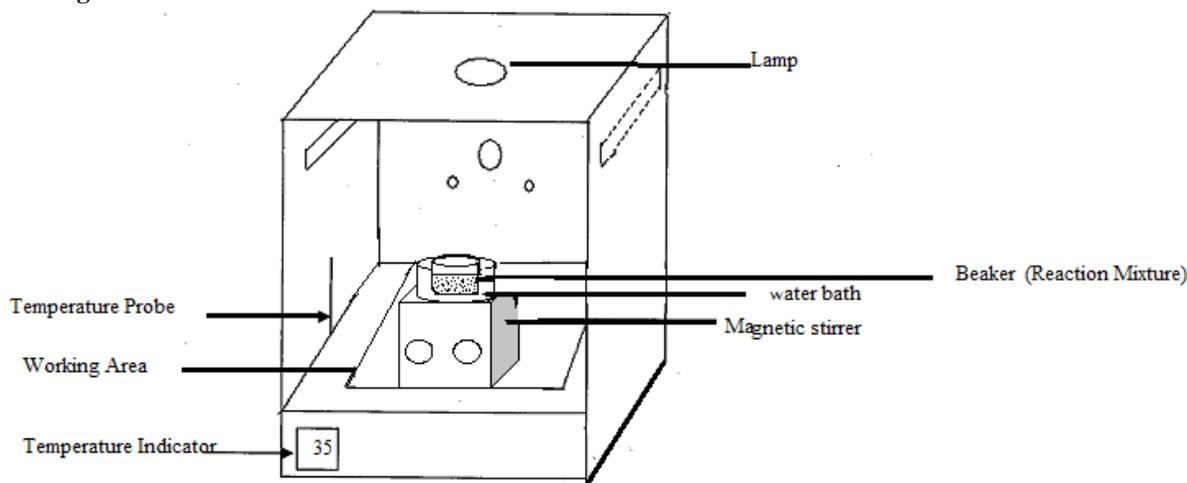


Fig.2 Experimental Setup of Photocatalytic process

Photocatalytic Experiments

To 50ml of dye solution, photocatalyst such as MBIR 11 was added to irradiation. Observation were finding out under solar light as well as UV light. The aqueous solution of dye was magnetically stirred throughout the experiment. After 10 min. intervals aliquot was taken out with the help of a pipette and then filtered the solution. Then rate of decolorization efficiency was investigated. The decolorization efficiency (%) has been calculated as:

$$\text{Efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

Where C_0 is the initial concentration of dye and C is the concentration of dye after photo irradiation.

Similar experiments were carried out by varying the concentration of dye (10 mg- 70 mg/l), radical quencher, pH of the solution (pH 3-11), catalyst loading (1- 3gm) and light intensity.

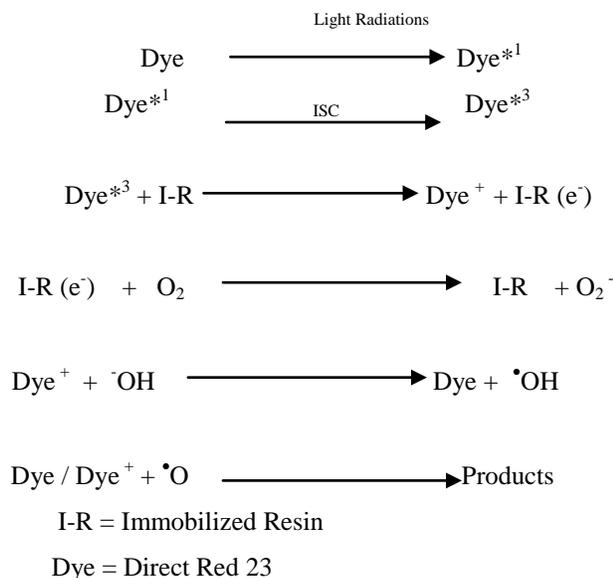
Apparatus

For the decolorization, the photocatalytic degradation was carried out in specially designed glass reactor containing an azo dye solution (volume 50 ml) and a defined amount of a photo catalyst and the reactor solution was illuminated with a 200W mercury lamp having wavelength 510nm. Constant stirring of solution in the reactor was insured by using magnetic stirrers. The temperature was maintained constant throughout the reaction time and we used borosilicate glass reactors. Solution was illuminated by 200W mercury lamp placed above reactor. At 10 min interval, 10 ml solution was taken out from reaction mixture. Filtered the catalyst particles and investigated the transparency of colored water with the help of 160UV/Visible spectrophotometer and lamp was positioned above the reactor.

III. RESULTS AND DISCUSSION

Mechanism of degradation of azo dye

We used Methylene blue immobilized resin Dowex-11 is newly developed photocatalyst. Due to its photosensitive nature, when light radiation is irradiated on its then 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 create between resin, methylene blue dye molecules, Direct red 23 dye molecules, water molecules and dissolved oxygen, consequential through chain process, hydroxyl radicals ($\cdot\text{OH}$) and super oxide ions (O_2^-) are formed and these are highly oxidizing in nature, by the action of 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 are present in products. On the basis of the experimental data, the following tentative mechanism may be proposed



The generation of hydroxyl radicals and Super oxide ions (O_2^-) can explain better with the assist of proposed diagram. This proposed diagram shows the action of photocatalyst and process of generation of oxidative intermediates. Photocatalytic action shows in fig.3

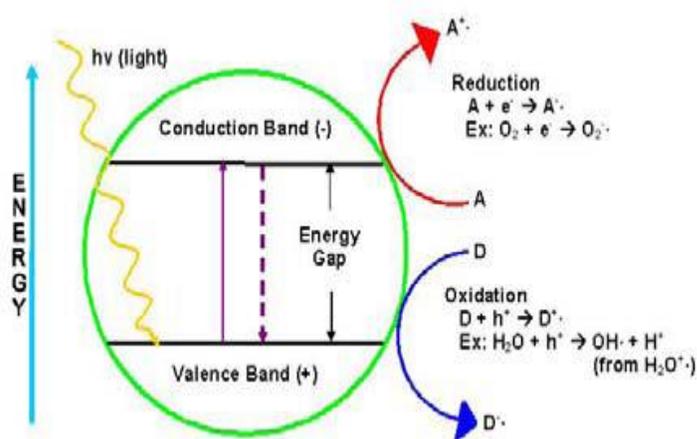
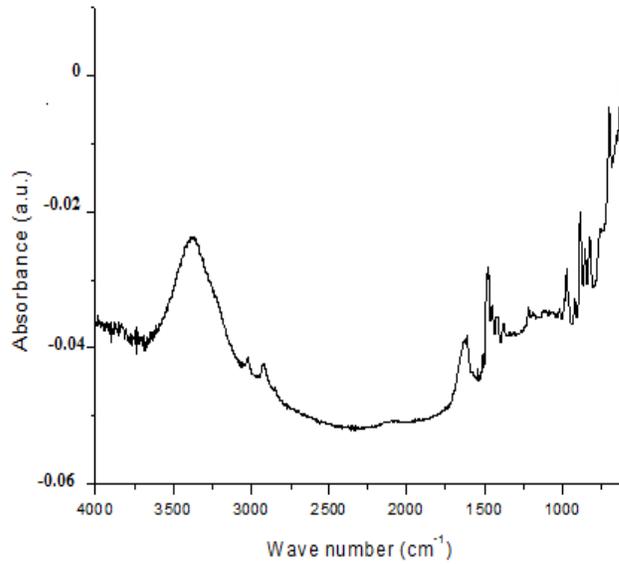


Fig.3 Photocatalytic Action

FTIR spectra of photocatalyst(MBIR-11)

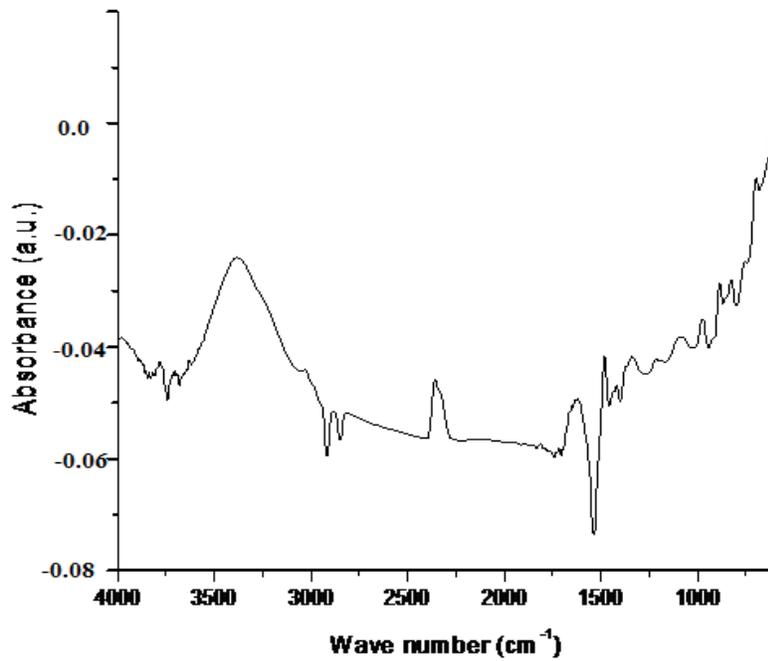
The IR spectrum of Dowex-11 resin (Pure) show peak in the region $3100-3000 \text{ cm}^{-1}$ is attribute to $=\text{C-H}$ stretching vibration. Another strong and sharp peak show in the region $1650-1600 \text{ cm}^{-1}$ is denote $-\text{C}=\text{C}-$ stretching vibration. And two peak in the region $1600-1450 \text{ cm}^{-1}$ show aromatic $-\text{C}=\text{C}-$ stretching vibration. Following peak is shown in fig. 4(a).

In order to examine the differences between immobilized Resin Dowex-11 and pure resin Dowex 11, the FT-IR spectra were applied to the study. The FTIR spectrum of immobilized Resin Dowex-11 exhibited many alterations from that of pure Resin Dowex-11. The major differences where $3650-3400 \text{ cm}^{-1}$ to $>\text{N-H}$ stretching vibration and $3100-2900 \text{ cm}^{-1}$ stretching vibration of $=\text{C-H}$ (Methylene) group. Due to immobilization and another strong and sharp peak of N-H bending in the region $1550-1510 \text{ cm}^{-1}$, these peaks are shown in fig. 4(b). These same spectra of after complete experiment show that, the dye Acid red 73 is not present in pores of resin.



(a) IR spectra of Dowex-11 resin without grafting

Fig. 4 (a) FTIR spectra of Dowex-11 resin without immobilization



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

Fig. 4 (b) FTIR spectra of immobilized Dowex-11 resin

Factors influencing the photocatalytic decolorization

Effect of initial dye concentration

It is important to study of the photocatalytic reaction rate on the substrate concentration. It is generally noted that the decolorization efficiency increases with the increases in dye concentration to a certain level and a further increases in the dye concentration leads to degradation rate of the dye. Due to the probability of $\cdot\text{OH}$ radical's formation on the catalyst surface and to the probability of $\cdot\text{OH}$ radicals reacting with dye molecules. The presumed reason is that at high dye concentrations the generation of $\cdot\text{OH}$ radicals on the surface of catalyst is reduce

since the active sites are covered of dye ions. The major portion of degradation occurs in the region near to the irradiated side (termed as reaction zone) where the irradiation intensity is much higher than in the other side²³. Thus at higher dye concentration, decolorization decreases at sufficiently long distance from the light source or the reaction zone due to the retardation in the penetration of light. Hence, it is concluded that as initial concentration of the dye increases the requirement of catalyst surface needed for the decolorization also increases (Fig. 5).

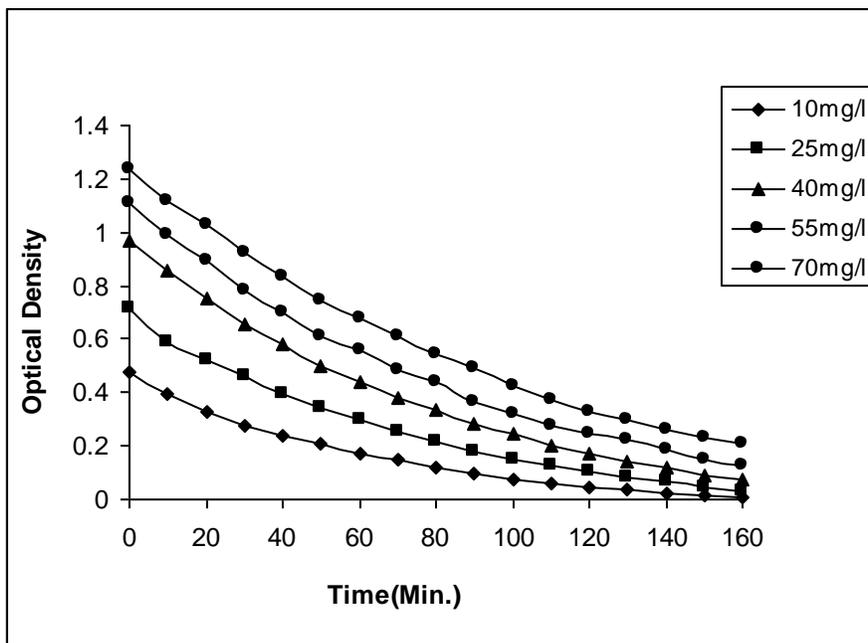


Fig.5 Effect of variation in dye concentration

Effect of pH

The results shows that rate of degradation is very low in high acidic pH range lower than 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. The increase in rate of Photocatalytic degradation may be due to more availability of $\cdot\text{OH}$ ions (Fig.6).

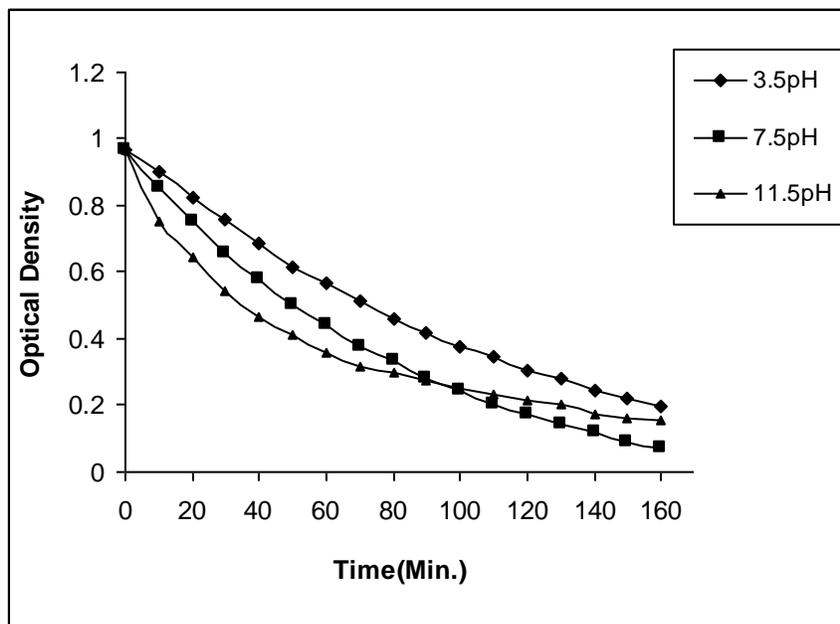


Fig.6 Effect of variation in pH on O.D.

Effect of variation in 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 extent 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 extent 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 in fix light intensity range after it we increase light intensity to any range, the rate of degradation remains unchanged (fig.7).

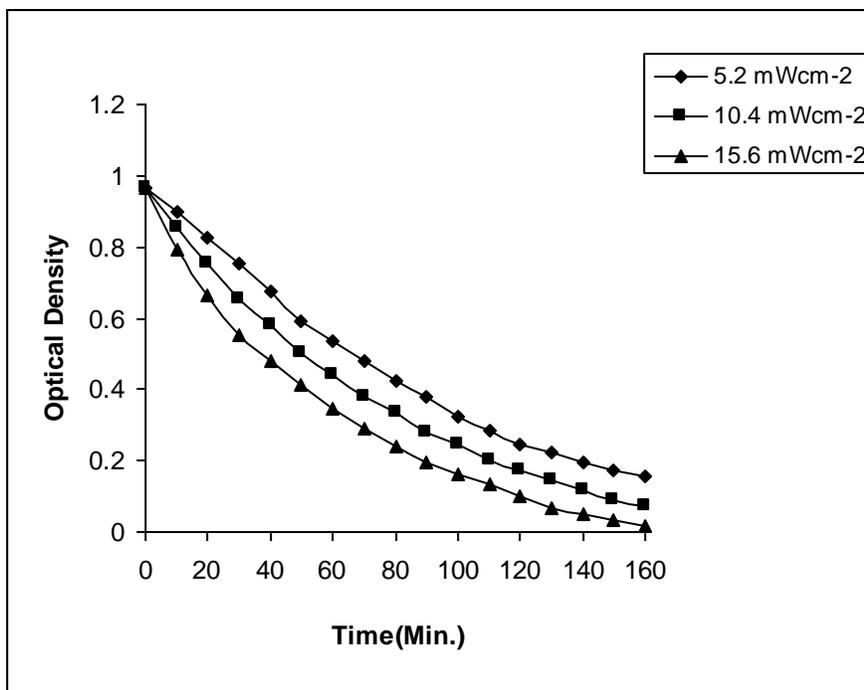


Fig.7 Effect of Variation in Light Intensity on O.D.

Effect of variation in catalyst loading

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 then hydroxyl radicals and super oxide ions (O_2^-) are increase. These are principle oxidizing intermediate in advance oxidation process resultant increases degradation of dye solution (Fig.8).

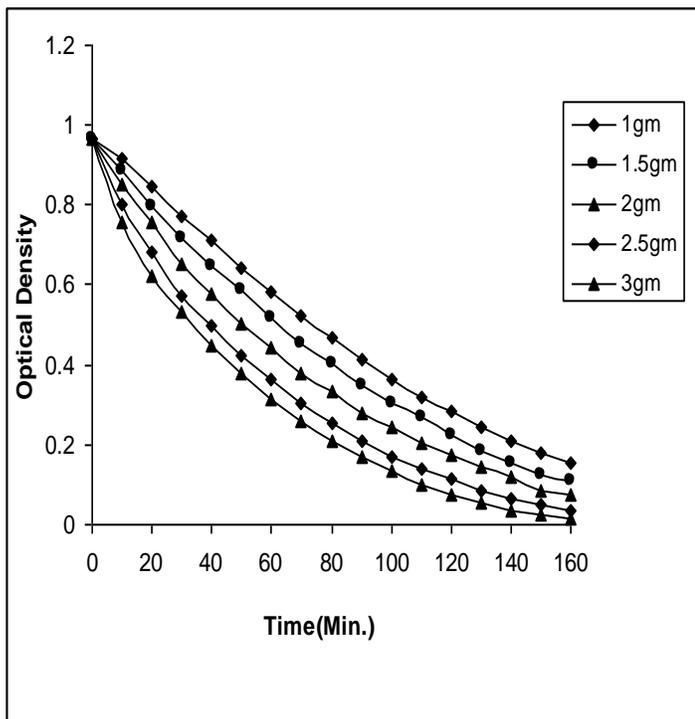


Fig.8 Effect of variation in catalyst loading on O.D.

IV. CONCLUSION

After long examination we conclude that the photo catalyst (MBIR Dowex 11) has very good potential of degradation of azo dyes into simple mineralize products. Photo degradation of the dye was very less when photolysis was carried out in absence of the catalyst and negligible in absence of light.

ACKNOWLEDGEMANTS

The authors are thankful to the UGC, New Delhi for financial assistance and Head of the department for providing necessary laboratory facilities.

REFERENCES

- [1] Arami, M, Limaee N. Y. Mahmoodi. N.M. Tabrizi. N.S. Removal of dyes from colored textile waste water by adsorbent: equilibrium and kinetic studies. *Journal of colloid and interface Science*, 2005, 288.371-376.
- [2] S. Ladakowicz, M. Solecka, R. Zylla, *J. Biotechnol.* 89(2001) 175.
- [3] W.Z. Tang, H.An, *Chemosphere* 31 (1995) 4157.
- [4] V. Meshko, L. Markovska, M. Mincheva, A. E. Rodrigres, *Wat. Res.* 35 (2001) 3357.
- [5] W. S. Kuo, P. H. Ho, *Chemosphere* 45(2001) 77.
- [6] C. Galindo, P. Jacques, A. Kalt, *Chemosphere* 45(2001) 997.
- [7] Y. M. Slokar and A. Majcen Le Marechal, *Methods of decoloration of textile wastewaters, Dyes and Pigments*, 37 (1998) 335-356.
- [8] V. Kumar, L. Wati, P. Nigam, I. M. Banat, B. S. Yadav, D. Singh and R. Marchant, *Decolorization and biodegradation of anaerobically digested sugarcane molasses spent wash effluent from biomethanation plants by white-rot fungi*, *Process Biochemistry*, 33 (1998) 83-88.
- [9] C Dominguez, J Garcia, M A Pedraz, A Torres and M A Galan (1998) Photocatalytic oxidation of organic pollutants in water. *Catalysis Today* 40 85-101.
- [10] T Robinson, G MC Mullan, R Marchant and P Nigam (2001) Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* 77 247-255
- [11] S.A. Saad, S. Daud, F.H. Kasim, M.N. Saleh, Methylene blue removal from simulated waste water by adsorption using treated oil palm empty fruit bunch, *ICOSM.*, 2007, 293.
- [12] D Georgiou, P Melidis, A Aivasidis, K Gimouhopoulos. *Dyes Pigments*, 2002, 52, 69.
- [13] M S Lucas and J A Peres, 2006 *Dyes Pigm.*, 71, 235.
- [14] M Muruganandham & M Swaminathan, 2007 *Dyes Pigm.* 72 137.
- [15] H Zheng & X Xiang 2004 *spectroscopie spectro anal.* 24 (2004) 687.
- [16] S Wang, 2008, 'A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater', *Dyes and Pigments* 76: 714.
- [17] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, *Solar Energy Materials and Solar Cells*, 77 (2003) 65.
- [18] Yingma and J.N. Yao, *J. Photochem. Photobiol.*, 116A (1998), p. 167.
- [19] R. Ciping, L. Xinmin, Dauhui, and Z.Y. Kang, *GanguangKexue Yu Kung*, 9 (1991), p. 137.
- [20] C. Richard, P. Boule, and J.M. Aubry, *J. Photochem. Photobiol.*, 60A (1991), p. 235.
- [21] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Optimized photodegradation of Reactive Blue 19 on TiO_2 and ZnO suspensions, *Catal. Today* 76 (2002) 235.
- [22] R. C. Meena & Ram babu Pachwarya 2009 *J. Scient. Ind. Res.* 68 730.
- [23] L. Zhang, C.Y. Liu, K.M. Ren, *J Photochem. Photobiol. A* 85 (1995) 239.

AUTHORS

First Author – Swati, Research scholar M.sc, Ph.D, Department of Chemistry, Jai Narain Vyas University, Jodhpur (Rajasthan) - 342005 INDIA, E-mail-swati.bardawat@gmail.com

Second Author – Dr.R.C.Meena, Associate professor, M.sc.,Ph.D, Department of Chemistry, Jai Narain Vyas University, Jodhpur(Rajasthan) -342005 INDIA, E-mail-rcmeena007@rediffmail.com

Third Author – Swati, Research scholar, M.sc, Ph.D, Department of Chemistry, Jai Narain Vyas University, Jodhpur (Rajasthan) -342005 INDIA, E-mail-swati.bardawat@gmail.com