ISSN: 2321-3132

Research Article

International Journal of Chemistry and Pharmaceutical Sciences

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Photocatalytic Transformation of Acid Red-8 by Heterogeneous Photocatalysis using MBIR Dowex-11 as photocatalyst in Aqueous Solution

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Received: 2 February 2014, Accepted: 8 April2014, Published Online: 27 April 2014

Abstract

Heterogeneous photocatalysis is emerging as a sustainable technology for solving environmental problems that overcomes many of the drawbacks of the traditional water treatment methods. Transformation of Azo dyes is challenging for researchers and environmentalists. Transformation of these azo dyes by recently developed photo catalyst Methylene Blue immobilized Resin Dowex-11 is better alternate to replace costly traditional treatment technologies for industrial application. A result of experiment is exiting and we recover 100% transparent water from dye polluted wastewater. We use Acid red-8 as model azo dye for experimental purpose. The rate of transformation is determined spectrophotometrically by varying pH, light intensity, dye concentration and amount of catalyst.

Keywords: Azo Dye, Photocatalysis, Transformation, Acid Red-8, Dowex-11

Contents

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Manuscript ID: IJCPS2011

PAPER-QR CODE

1. Introduction

Today photocatalytic technology becomes more and more attractive to industry because global environmental pollution has come to be recognized as a serious problem. Photocatalytic processes to degrade organic pollutants in water have been the subject of recent research. The removal of the non-biodegradable organic chemicals is a crucial ecological problem. Notwithstanding the substantial advantages of PCD (photo catalytic degradation), this technique is yet to be implemented on large scale for treatment of industrial wastes.Heterogeneous photo catalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants organic reactive dye [1-4].

Ever since 1977, when Frank and Bard [5-6] first examined the possibilities of using TiO_2 to decompose cyanide in water. But this technology has not yet been successfully commercialized in past because of problems connected to separation of TiO_2 particles from suspension. To solve this problem, supported catalyst has been developed [7-10]. Photo degradation of azo dyes by chitosan capped CdS composite nano particles and in aqueous phase nano photo

catalyst is also investigated [11-12]. Poulios et al. [13] studied photo catalytic degradation of Auramine O in aqueous suspension using ZnO and TiO_2 separately in a batch reactor. They found that the rate of degradation of pollutants is faster with ZnO than with TiO_2 (Deussa P25). The biggest advantage of ZnO is that it absorbs a larger function of solar spectrum than TiO_2. Therefore it is a great interest to use the freely available and inexhaustible solar light for photocatalysis [14].

Earlier, Grzechulska and Morawski [15] reported the photo catalytic decomposition of azo dye using TiO_2 with UV light. Shu et al. [16] reported the degradation of azo dye by the UV/H_2O_2 process. Degradation of textile industry wastewater and transformation of C.I. Reactive Orange4 and its simulated dye bath wastewater by heterogeneous photocatalysis [17, 18]. The photocatalytic degradation of reactive black-5 using different semiconducting oxides TiO_2, UV-100 TiO_2, ZnO, andTiO2/WO3 four parallel black light blue fluorescent tubes were used as the UV-light source [19]. Degradation of Acid Green 16 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 [20]. Use of semiconducting iron (II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta et al. [21].The degradation is more with solar/ZnO process than with solar/TiO2 –P25 process at pH 9 reported by Krishna Kumar and Swaminathan [22]. Degradation of Ponceau-S and Sudan IV with methylene blue immobilized resin Dowex 11 photocatalyst [23].

Visible light sensitive photo catalyst has been developed by Meena et al. [24-26]. The development of visible light photo catalyst is an impressive task in order to utilize the solar energy effectively. The main objective of the present work is to seek attention of researchers towards utilization of visible light for degradation of azo dye Acid Red-8 by recently developed photo catalyst (MBIR) Dowex11.

2. Materials and Methods

2.1 Reagent and chemicals

Acid red 8 ($C_{18}H_{14}N_2Na_2O_7S_2$; mol. wt. - 480.42; λ_{max} – 508nm; C. I. - 14900) was obtained from LOBA Chemicals India (Fig-1). Photo catalyst was prepared by using Dowex-11 resin (20-50 mesh) (Sisco Chemicals India, Mumbai) and Methylene Blue hydrate (LOBA Chemicals India). For immobilization DOWEX-11, resin added to the solution of Methylene Blue (10^{-3} M). Put the solution in dark for 3 days for complete immobilization of methylene blue 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.

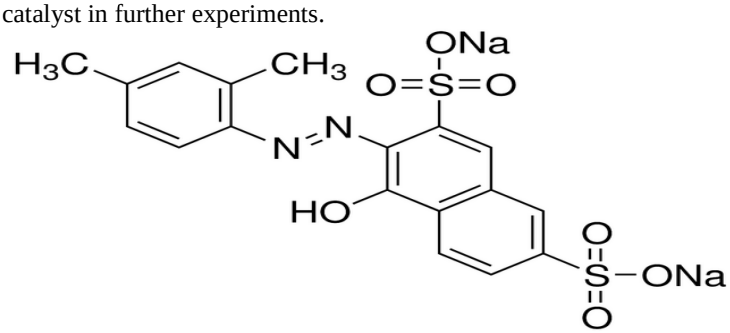

Figure 1. Acid Red 8 dye structure

2.2 Analytical Methods

Photoreaction carried out in a glass reactor, which contains a mixture of dye (Acid red 8) and photo catalyst. Solution continuously stirred by magnetic stirrer during the experiment. Solution illuminated by 200W halogen lamp placed above reactor. At 10 min time interval, 10ml solution taken out from reaction mixture and filtered the catalyst particles. In all cases, 50ml. of the Acid red 8 dye solution containing appropriate quantity of the Methylene blue immobilized resin Dowex-11 catalyst used. After stirring continuously in the dark for 2 min the suspension irradiated by UV irradiation and it treated as the starting point (t=0) of the reaction, where the optical density of dye solution designated as Co 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 efficiency calculated by using the equation given below:

$$CR\% = \frac{(Co - C)}{Co} * 100$$

Where Co and C are optical density of dye solutions at initial time and at time t respectively.

2.3 Chemical Reaction of Dye Transformation

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 Methylene Blue. Intermolecular

electronic transition starts between photo catalyst, Methylene Blue dye molecules, water molecules and Acid Red 8 dye molecules resulting into highly oxidizing agents, holes, hydroxyl radicals and super oxide ions (Fig-2), which transfer azo dye in simple organic compounds. Main factors influencing photo catalytic transformation 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 Methylene Blue. Further intermolecular electronic transition occurs between photo catalyst, Methylene Blue 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.

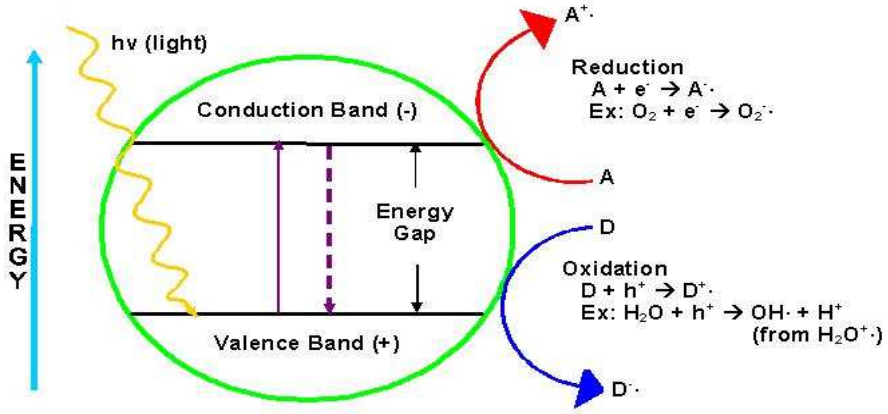

Figure 2. Photo catalytic action: Generation of holes, hydroxyl radicals and super oxide ions

3. Results and Discussion

3.1 Effect of pH:

The effect of pH on the transformation of acid red 8 investigated by keeping all other experimental conditions constant and varying the initial pH of acid red 8 from 3.5 to 11. It can be observed that the bleaching of acid red 8 increased with increasing pH value from 3.5 to 9.0 (Fig. 2). On further increasing pH, rate of transformation starts to decrease. Maximum bleaching obtained at pH 7.5. At this pH acid red 8 was reduced by 89.95% after 160 minutes. Increase in the rate of photo catalytic transformation may be due to more availability of hydroxyl ions by combining with holes, which formed due to electronic excitation in catalyst in pH range 7.5-9.0. Formations of hydroxyl radicals are responsible more for photo catalytic transformation than super oxide ions (O^-) (Fig-3).

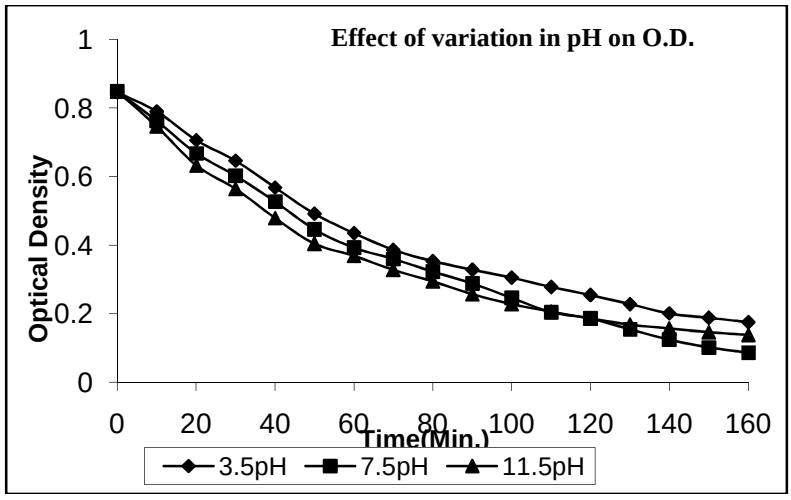

Figure 3. Effect of variation in pH on O.D.

3.2 Effect of catalyst loading:

Experiments performed to study the variations in the transformation of acid red 8 at different catalyst loading. It can be observed that the bleaching of acid red 8 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 transformation (Fig-4).

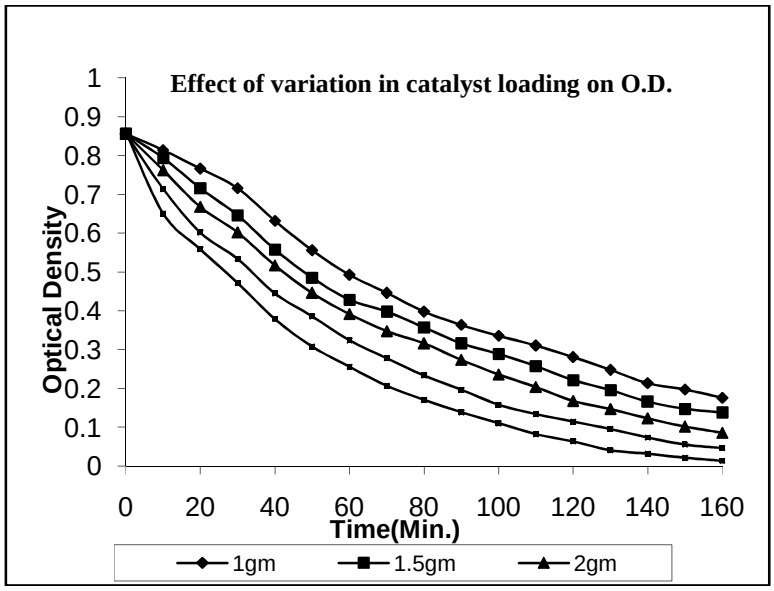

Figure 4. Effect of variation in catalyst loading on O.D

3.3 Effect of initial dye concentration:

The effect of initial concentration of acid red 8 on the transformation process investigated over the concentration range from 10mg/l to 70mg/l with constant catalyst loading 2.0gm. As the dye concentration increased, rate of the transformation decreased 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 transformation; ii)Since catalyst surface area is fixed, so as concentration of dye increases rate of transformation 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 transformation (Fig-5).

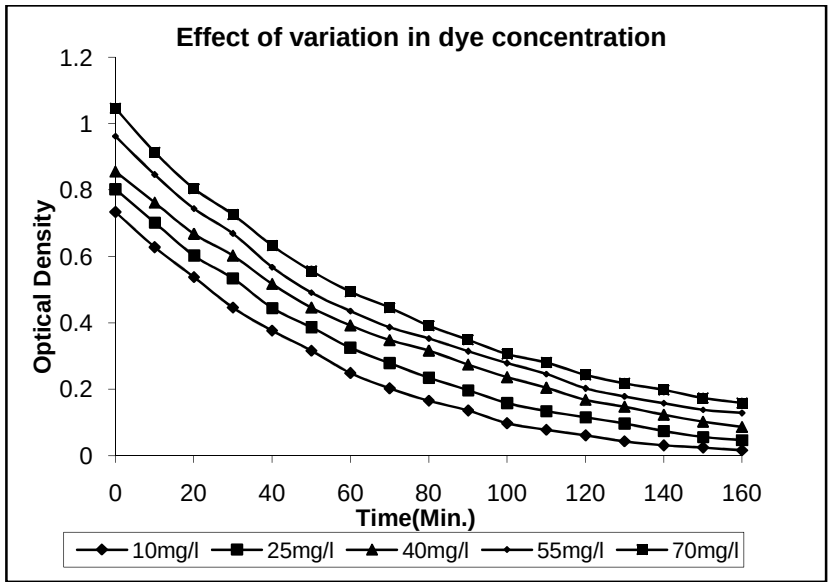

Figure 5. Effect of variation in dye concentration

3.4 Effect of light intensity:

As light intensity increased, rate of transformation of dye molecules increased up to a certain limit, and after that, no changes were observed (Fig-6). 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 transformation of dye molecules also increases.

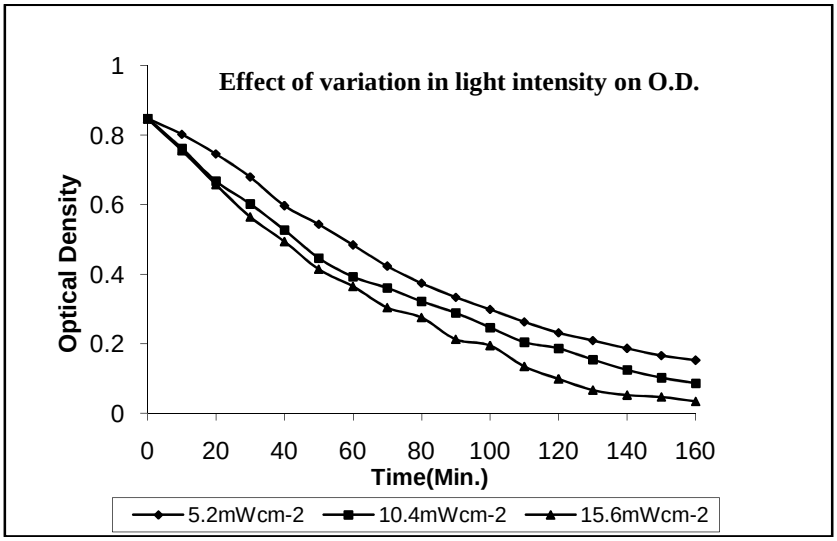

Figure 6. Effect of variation in light intensity on O.D

3.5 Kinetic Study

Photocatalytic transformation of Acid red 8 was observed at λ_{max} = 508 nm. The optimum conditions were obtained at initial dye concentration: 40 mg/L, catalyst loading: 2.0gm/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 (Fig-7). This indicates that the photocatalytic transformation of Acid red 8 follows pseudo first-order kinetics. The rate constant (K) for the reaction was determined using the expression. Rate = K [Acid red 8], K = 2.303 × Slope. The rate constant for this reaction is K = 1.28 * 10^{-2} min^{-1}.

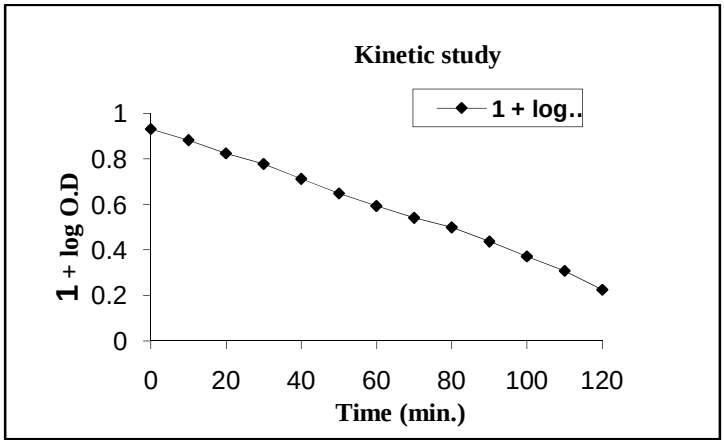

Figure 7. Kinetic study

4. Conclusion

In conclusion, this study has proved that Methylene Blue immobilized resin Dowex -11 is an efficient catalyst for transformation of azo dyes in to simple molecules in presence of ultraviolet radiations. The photo catalytic transformation efficiency has been generally found to increase in catalyst loading and decrease with increase in initial dye concentration because the increase in the concentration of a dye solution, the photons get intercepted before they can reach the catalytic surface decreasing of the catalyst and all the transformation occur at an optimal pH 7.5 value. On increasing light intensity, transformation rate increased up to a certain extent, after that, no further

changes are observed. The transformation of Acid red 8 by Methylene Blue immobilized resin Dowex-11 followed pseudo first order kinetics with respect to the concentration of Acid red 8. No obvious decline in efficiency of the catalyst was observed after 5 repeated cycles and this demonstrated the stability and reusability of the catalyst. Methylene blue Immobilized Resin Dowex 11 used as solar photo catalyst gives very good results and successfully improved the transformation rate of organic dyes. Therefore this technology has the potential to improve the quality of the waste water from textile industries and many others.

5. Acknowledgement

The Head of the department is gratefully acknowledged for providing necessary facilities.

6. Refrences

1. Galindo C., Jacques P., Kalt A., Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74 (AB74), *J. Photochem. Photobiol.A: chem.* 141, 47, **2001.**
2. Serpone N., Pelizzetti E., Photocatalysis: fundamentals and applications. Wiley Interscience, Amsterdam, New York **(1989)**.
3. Fox M. A., Dulay M. T., Heterogeneous Photocatalysis, *Chem. Rev.* 93, 341**, 1993**.
4. Khodja A. A., Sehili T., Pilichowski J.F., Boule P., Photocatalytic degradation of 2-phenylphenol on TiO_2 and ZnO in aqueous suspensions, *J. Photochem. Photobio. A: Chem* 141, 231**, 2001**.
5. Frank S. N., Bard A.J., Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solution at TiOZ powder.*J. Am.Chem. Soc.* 99, 303**, 1977**.
6. Frank S. N., Bard A.J., Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solution at semiconductor powders, *J. Phys. Chem.* 81, 1484**, 1977**.
7. Khataee A. R., Kasiri M. B., Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: Influence of the chemical structure of dyes, *J. Mole. Catal. A: Chem.* 328, 8**, 2010.**
8. Tanaka K., Padermpole K., Hisanaga T., Photocatalytic degradation of commercial azo dyes, *Water Res.* 34, 327**, 2000**.
9. Dasilva C. G., Faria J. L., Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation, *J. Photochem. Photobio. A: Chem.* 155, 133**, 2003**.
10. Abo-Farha S. A., Comparative Study of Oxidation of Some Azo Dyes by Different Advanced Oxidation Processes: Fenton, Fenton-Like, Photo-Fenton and Photo-Fenton-Like, *J. Am., Sci.* 6, 130, **2010**.
11. Ru J., Zhu H., Li X., Xiao L., Visible light photocatalytic decolourization of C. I. Acid Red 66 by chitosan capped CdS composite nanoparticles, *J. Chem. Engg.* 152, 537**, 2009**.
12. Kansal S. K., Ali A. H., Kapoor S., Photocatalytic Decolorization of Biebrich Scarlet Dye in Aqueous Phase using Different Nanophotocatalysts, *Desalination* 259, 147**, 2010**.
13. Poulios I., Avranas A., Rekliti E., Zouboulis A., Photocatalytic oxidation of Auramine O in the presence of Semiconducting Oxides, *J. Chem. Techno. Biotechno.* 75, 205**, 2000**.
14. Sakthival S., Kish H., Photocatalytic and Photo electrochemical Properties of Nitrogen-Doped Titanium Dioxide, *Chem. Phys. Chem.* 4, 487**, 2003**.
15. Grzechulska J., Morawski A.W., Photocatalytic decomposition of azo-dye acid black 1 in water over modified titanium dioxide, *Appl. Catal B.* 36, 45**, 2002**.
16. Shu H. Y., Chang, M. C. Fan H. J., Decolorization of azo dye acid black 1 by the UV/H_2O_2 process and optimization of operating parameters, *J. Hazard. Mater.* 113, 201**, 2004**.
17. Hachem C., Bocquillon F., Zahraa O., Bouchy M., Decolorization of Textile Industry Wastewater by the Photocatalytic Degradation Process, *Dye Pig.* 49, 117**, 2001**.
18. Sameiro M., Goncalves T., Pinto Elisa M. S., Peter N., Oliveria, Campos, Ana M.F., Degradation of C.I. Reactive Orange 4 and its Simulated Dye Bath Wastewater by Heterogeneous Photocatalysis, *Dyes and Pig.* 64, 135**, 2005**.
19. Poulios I., Tsachpinis I., Photocatalytic Degradation of Reactive Black 5, using Different Semi Conducting Oxides, TiO2, UV-100 TiO2, ZnO, and TiO2/WO3, *J. Chem. Tech. Bio. Technol.* 74, 349**, 1999**.
20. Sakthivel S., Neppolian B., Shankar M. V., Arabindoo B., Palanichamy M., Murugesan V., Degradation of Acid Green 16, *Sol. C* 77, 65**, 2003**.
21. Ameta R., Vardia J., Punjabi P. B., Ameta S. C. Use of semiconducting iron(III) oxide in photocatalytic bleaching of some dyes,, *Indian J. Chem. Tech.* 13, 114**, 2006**.
22. Krishnakumar B., Swaminathan M., Solar Photocatalytic Degradation of Acid Black 1 with ZnO, *Ind.J. Chem.* 49, 1035, **2010**.
23. Meena R. C., Pachwarya R. B., Kumar V., Arya S., Degradation of Textile dyes Ponceau S, Sudan IV Using Recently Developed Photo catalyst, Methylene Immobilized Resin Dowex-11, *American J. Environ. Sci.* 5, 444, **2009**.

24. Meena R. C., Pachwarya R. B., Photo catalytic degradation of Model textile dye present in wastewater of Textile Industries using newly developed photo catalyst, *J. Scient. Ind. Res.* 68, 730 **2009**.
25. Pachwarya R. B., Meena R. C., Degradation of Azo Dye Ponceau-S,S-IV from the waste water of Textile industries in a new photo catalyst reactor with high efficiency using recently developed photocatlyst MBIRD-11, *Energy Source, Part A* 33, 1651, **2010**.
26. Meena R. C., Sindal R. S., Munesh, Visible light irradiate photocatalytic degradation of textile dye with a newly developed photocatalyst MBIR Dowex-11, *J. Indian Chem. Soc.* 90, 373, **2013.**