# PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE DISPERSE BLUE BY USING ZnO/Mn NANOCATALYST

**Dadheech Anjali[1] and Meena K.S.[2]**

Research scholar[1], Assistant Professor[2]

Department of Chemistry, M.L.V. Government College, Bhilwara 311001, Rajasthan, India.

***Abstract :*** Photocatalytic degration of disperse blue 79:1 with UV light by using synthesis of ZnO/Mn catalyst. Mn doped ZnO nanoparticles. ZnO/Mn doped nanoparticles synthesized using coprecipitation method. The characterisation of synthesized ZnO/Mn by XRD, SEM, EDX, and UV–Visible absorption. The operating parameters study are attention of catalyst dose, attention range of pH. After 60 minutes of irradiation, 98% dye elimination was reported under the acceptable operating conditions.

***Keywords*** **- Disperse blue dye, Photocatalytic degradation, ZnO/Mn catalyst.**

## 1. INTRODUCTION

Wastewater from the textile dye industries possesses a serious big environmental problem. These industries dispose untreated colored and toxic effluents into the nearby water bodies, there by causing serious environmental pollution[1]. Development of technological systems for the removal of organic dyes presently was used[2]. These include physical methods and chemical methods[3-4]. Physical and biological methods do not destroy the pollutant to another stage which again creates disposal problem. The uses of nano materials because of their excellent physical and chemical properties as compared to bulk materials[5]. Nano particle synthesis of silver[6] particles by green method, manganese ferrite nano particles using chemical method[7].

The fundamental properties of nano material depend on size of nano particles, doping concentrations, synthesis temperature. The properties of ZnO nano particles can be controlled by introducing the doping element. Doping of transition metal ion in the ZnO has lead to the new energy level where electrons are trapped in this level inhibiting electron hole recombination during irradiation[8]. Mn doped ZnO has more efficient than ZnO in magnetic, semiconducting, optical properties and promising catalyst for degradation of dyes[9]. Doping of Mn greatly improved the photocatalytic efficiency of ZnO moreover various operational parameters such as pH of the waste water, initial dye concentration, catalyst loading affect the activity of the photocatalyst[10-12].

## 2. MATERIALS AND METHODS

### 2.1 Materials

All the chemical reagents used are of analytical grade procured from Merck, India and are used without no additional purification.

Used Chemicals used are

- Zinc Acetate dihydrate ($Zn(CH_3CO_2)_2.2H_2O$.
- Manganese Acetate tetrahydrate ($Mn(CH_3CO_2)_2.4H_2O$
- Sodium hydroxide (NaOH) is used as precipitating agent.
- A solution of Disperse Blue79:1 dye in distilled water is used.

### 2.2 Preparation of ZnO/Mn photocatalyst

The synthesis of Mn doped ZnO nano particles appropriate amount of the Zinc acetate and Manganese acetate taken and dissolved in 500 ml of distilled water under constant stirring about 15 min. An equal solution of NaOH is prepared and added drop by drop to the solution of Zinc acetate and Manganese acetate and pH of the solution maintained at 11 for the reaction to take place. After some time of the reaction solution again stirred for completion of reaction. After completion of the reaction a precipitate is formed. To get away of any insoluble contaminants that might have been in the produced precipitate, The precipitate was taken out of the solution and rinsed with distilled water several times17-18. It was centrifuged, filtered, and then dried for one night in the oven. (The dried precipitates were ground to obtain the catalyst in the powder form.

### 2.3 Characterisation of photocatalyst

The structural properties of the synthesized manganese doped ZnO nanoparticles were characterised by XRD19-20. The chemical composition and the morphological analysis were carried out using Scanning electron microscope equipped with energy dispersive spectrometer. Optical absorbtion spectra were taken using UV- Visible spectrometer21-23.

### 2.4 Photocatalytic activity

The photocatalytic degradation of Disperse blue79:1 dye using Mn Doped ZnO as photocatalyst under the illumination of UV light of 254 nm in photochemical reactor. The photo reactor consist of magnetic stirrer and source of UV light which is enclosed in a closed tight chamber. The degradation of Disperse Blue 79:1 was studied at concentration of dye at 1x10-3M dye solution was prepared by dissolving the 0.625 g of dye in 1000ml of distilled water. Reaction solution was prepared by mixing 3ml of dye solution (1x103M) and 0.05gm of ZnO/Mn catalyst . In the photochemical degradation process 0.3 gm of the catalyst was taken into the Disperse Blue 79:1 dye solution. The suspension was kept magnetically stirred and illuminated with UV light and the time of degradation of the dye calculated at the regular interval of time. Absorption maxima observed and at the maximum absorption the dye degradation observed at different parameters of observation. The degradation of the dye was monitored by measuring the absorbance spectrum of the solution in an Systronics spectrophotometer 106.

## 3. Results and discussions

### 3.1 Characterisation

The crystalline phase composition and the size of the synthesized Mn doped ZnO nano catalyst was determined by the X-ray diffraction pattern by X-ray differactometer model number Panalitycal X Pert Pro of Netherland. Fig. 1 shows X-Ray diffraction pattern of Zn1-xMnxO clearly shows distinct peaks at 2θ = 31.72, 34.38, 36.19, 47.48, 56.67, 62.84, 67.87, and 69.07. The peaks have been identified as peaks of hexagonal ZnO (wurtizite structure) crystalline with various diffracting planes (100), (002), (101), (102), (110), (103), (112) and (201) respectively. Using Debye-Sherrer equation- d= k□/ □ cos □ . All the observed peaks are very sharp it shows the high crystallinity of ZnO/Mn nano particles24.

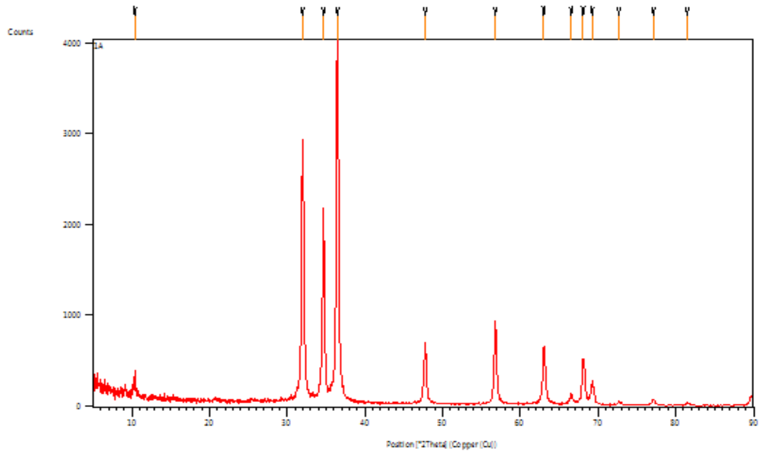



fig-1 the xrd pattern of mn- doped zno nano particles

Scanning electron microscopy is the technique of resolving the particles sizes, morphology and size distribution. SEM was detected by model Nova nano FE-SEM 450 FEI of Netherland Fig. 2 (a), 2(b) shows the scanning electron micrograph of the doped ZnO samples which indicates the particles are formed at nano scale and are of spherical in shape. These images of the SEM analysis of ZnO/Mn particles shown below confirmed the formation of particles at nano scale 20-30 nm using IMAGEJ software. The quantitative analysis of the presence of Zinc, Oxygen, and Manganese in the synthesized sample is studied by EDX analysis by EDX instrument Bruker, USA as Fig 3. Shows the EDX pattern of ZnO/Mn samples. From the EDX pattern the presence of Manganese atoms detected confirming the successful doping of the Mn atoms to the lattice of ZnO.

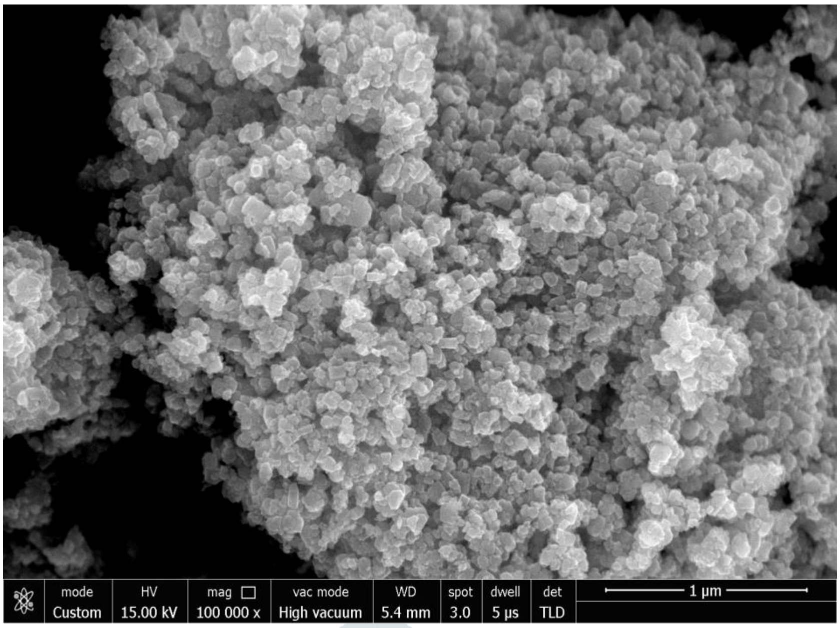



fig-2(a) the sem micrograph of zno/mn nanoparticles

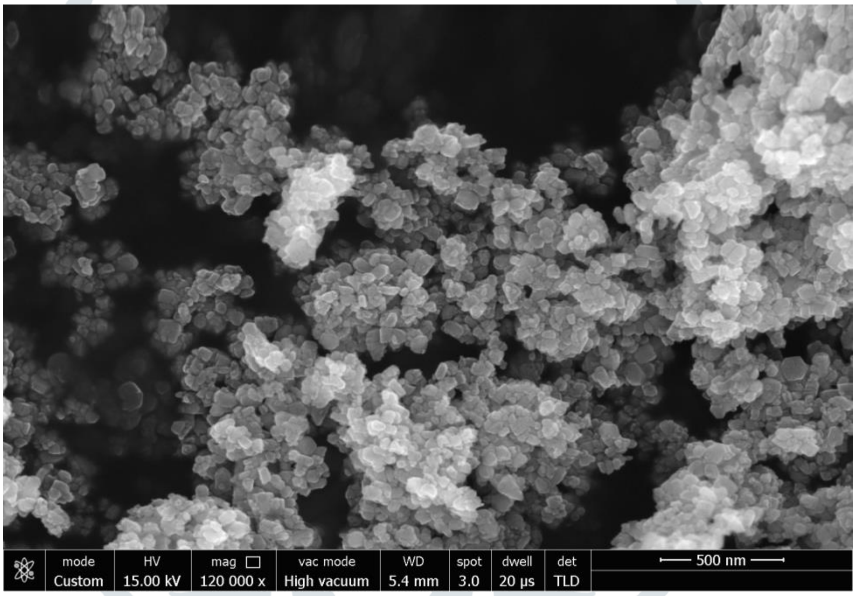



fig-2(b) the sem micrograph of zno/mn nanocatalyst

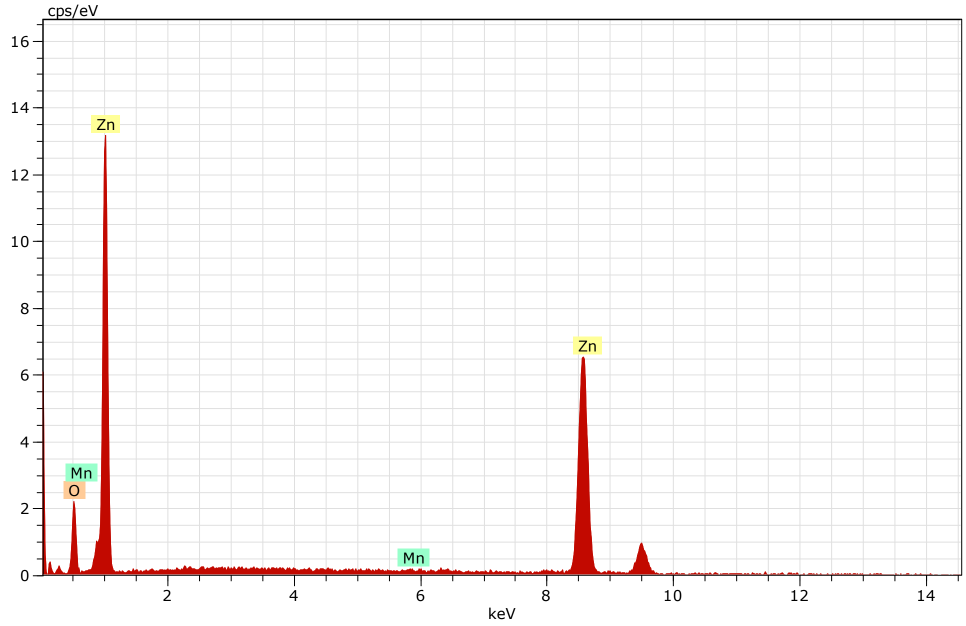



fig. 3 sem-edx spectrum of zno/mn nanoparticles

UV- Visible absorption spectrum of the ZnO / Mn sample shown in the Fig. 4. Sample of ZnO / Mn shows the good absorption of the light in the UV region. Absorption of UV light on the region of 300 nm shows the formation of nano particles blue line showing in the graph and in the graph black line shows the Absorption of U.V. light by ZnO and in the middle of graph pink line shows the Ag doped ZnO.

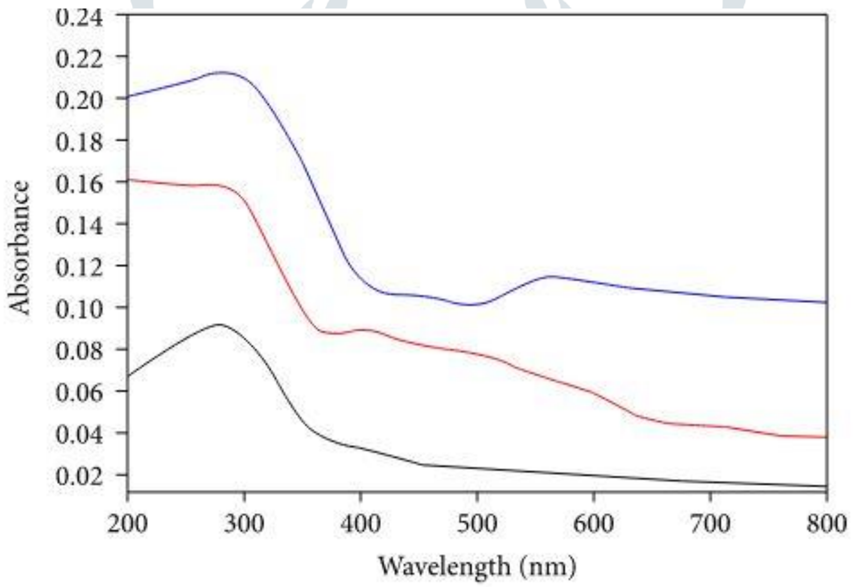



fig. 4 uv absorption maxima of ZnO/ Mn nano particles photocatalytic study

### 3.2 Photocatalytic Degradation

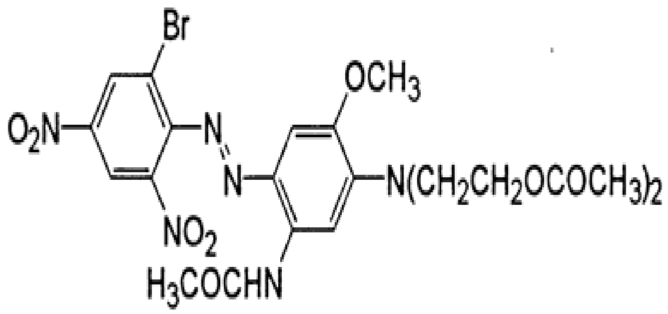
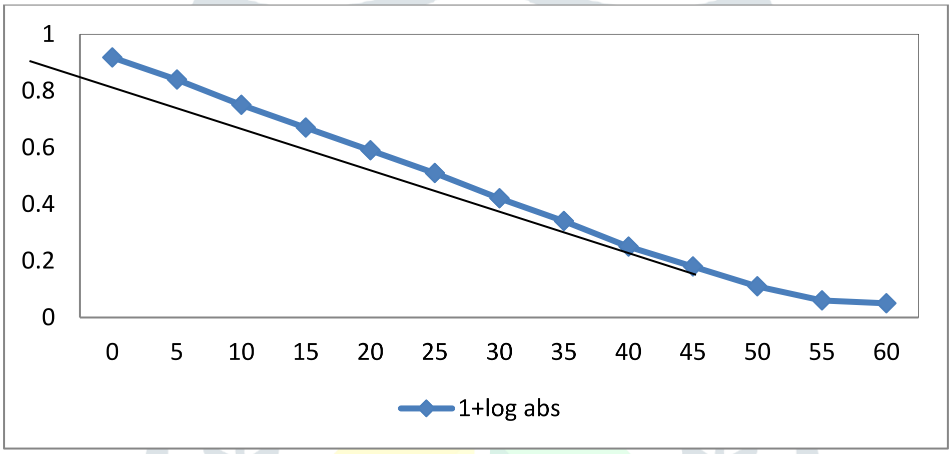



fig.5 chemical structure of disperse blue 79:1

**Molecular formula $C_{23}H_{25}BrN_6O_{10}$ Molecular weight 625.38**

The photocatalytic decomposition experiments performed of this dye at 565 nm. The optimum requirements for the photo degradation of the dye were 3.0x10-5 M, amount of catalyst 0.05gm/100 ml of dye solution and pH 8.5 observed.




Time in min

fig.6- a graphical plot of 1+log abs versus time for a typical run

In Fig. 6 a graph plotted between the Absorbance and the time and it was observed that with the increase in the time of irradiation absorbance decreases which show that in the presence of the catalyst degradation of textile dye occur. We can infer from the plot's linearity that the dispersion blue's photocatalytic decomposition follows first order kinetics. Rate constant K obtained for photodegradation is-

Rate constant (k) = 2.303 x slope = 2.06 x 10-4 sec-1

Studies on the impact of several parameters, particularly pH, dye concentration, and photocatalyst dose, have been conducted.

#### 3.2.1 Effect of catalyst supply on the rate of color removal

Catalyst supply has a role on how rapidly colour is removed. All other factors kept static while the catalyst's quantity was altered, and its effects on the pace of photochemical disintegration were observed. The effects at the different parameters have been studied like pH, concentration of dye, dose of photocatalyst.

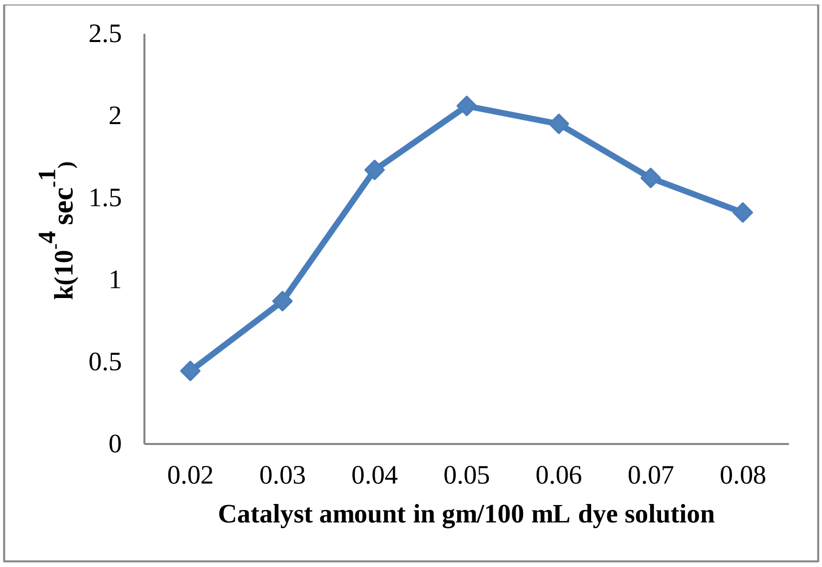



fig. 7 effect of amount of catalyst on the rate of decolourisation of disperse blue 79:1 dye

The outcome illustrates that, up to 0.05 gm/100 ml of dye solution, increased catalyst causes the rate of degradation to accelerate, after which the rate of degradation becomes fairly constant. The surface area of the catalyst grows as the amount of catalyst increases in the aqueous dye solution. Strong oxidising agents just like OH· radical cause the molecule to deteriorate. The amount of catalyst increases with same concentration of dye. Then further dye molecules are not therefore the adsorption for photo degradation of dye molecule. Additional catalyst not affects the rate of photo degradation of the dye molecule and rate remains constant.

### 3.2.2 Effect of pH on the rate of photo decolourisation of the dye molecule

The outcome demonstrates that, up to 0.05 gm/100 ml of dye solution, more catalyst causes the rate of degradation to rise, after which the rate of degradation becomes nearly constant. The surface area of the catalyst grows as the amount of catalyst increases in the aqueous dye solution. Strong oxidising agents like the OH radical cause the molecule to deteriorate. When the dye concentration is the same, the amount of catalyst increases. The adsorption for dye molecule photodegradation is thus prevented by additional dye molecules. The rate of the dye molecule's photodegradation is unaffected and remains constant in the presence of additional catalyst.

### 3.2.3 Effect of pH on the dye molecule's rate of photodecolorization

In this work photo degradation was performed at various range of pH 5.0 to 9.5. 8.5 pH observed to optimum pH for the degradation of the dye molecule. Here all subsequent experiments were carried out at pH 8.5. Above pH 8.5 no satisfactory results observed as the pH of the solution rises up to 8.5 number of OH· Ions increased. These OH· will further generate OH· radicals by joining with the catalyst. The degree to which the textile dye is degraded by photocatalysis is significantly influenced by the pH of the reaction mixture.

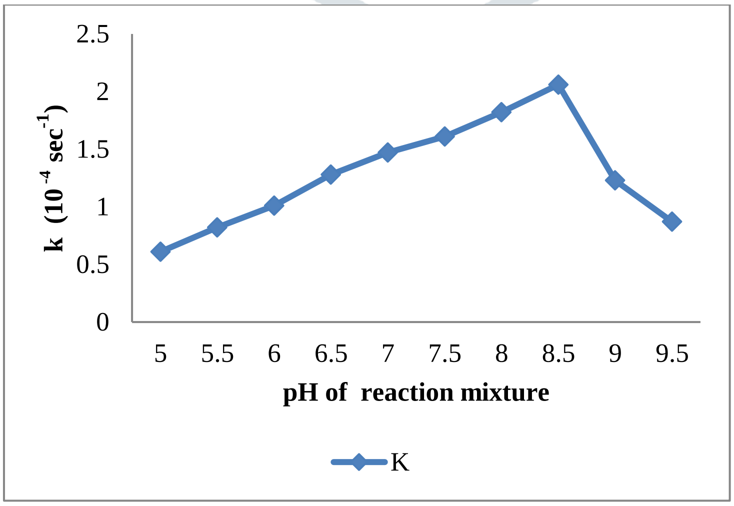



fig. 8 effect of ph on the rate of decolourisation and degradation of the textile dye disperse blue 79:1

### 3.2.4 Effect of dye concentration variation on the rate of dye deterioration

With all other variables held constant, the impact of colour attention on the breakdown of disperse blue 79:1 was detected at varied attention levels ranging from 1.0 x 10-5M to 6.0 x 10-5M. The least amount of response was observed at3.0 X 10-5M color result. Further the rate of print declination of color starts to drop with the rate of declination increased as the thickness of the hydroxyl molecules' concentration for the entire colour patch increases. Motes of color adsorb on the face of color and declination occurs. When we increase the attention of the color catalyst face get impregnated and at that time the violent colour of the color doesn't permit light to reach the catalyst face and the declination of the color starts to drop.

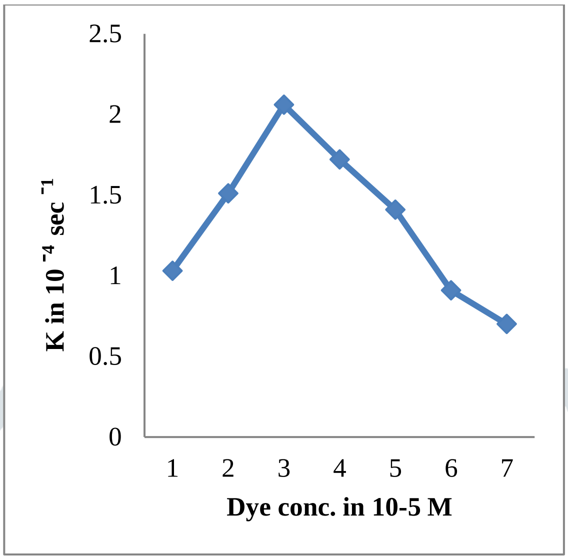



fig. 9 effect of dye disperse blue 79:1on the rate of degradation

## 4. CONCLUSION

Synthesis of ZnO/Mn catalyst done at nano scale and it was confirmed by the UV absorption, SEM, SEM-EDX, XRD. Synthesized catalyst was found to be effective in the photo degradation of the textile dye Disperse Blue 79:1. It is observed that the degradation of the dye disperse blue 79:1 depends on the various reaction parameters such as pH, concentration of the catalyst, concentration of the dye. The optimum conditions found for the dye degradation are pH= 8.5, 0.05gm of ZnO/Mn catalyst/ 100 ml of dye solution 3X10-5 M dye concentration in the dye solution. Use of ZnO/Mn nano photocatalyst to remediate textile wastewater is suggested.

## 5. ACKNOWLEDGEMENT

Authors are acknowledged and appreciative to the Principal and Head of Department of Chemistry, M.L.V Government College, Bhilwara for providing necessary facilities. Sincere thanks to the staff, laboratory of Material Research Centre, Malviya National Institute of Technology, Jaipur, Rajasthan for providing XRD, SEM, and SEM EDX images and analysis.

## 6. REFERENCES

1. Y Hu, H Cheng, Environmental Science and Technology, Application of stochastic models in identification and apportionment of heavy metal pollution sources in the surface soils of a large scale region, *ACS*, **47**, 3752 **(2013)**

2. B. S. Padhi, Pollution due to synthetic dyes toxicity and carcinogenicity studies and remediation *International Journal of Environmental Sciences*, **3**, 940-955 **(2012)**

3. E. Forgacs, T. Cserhati, G. Oras, Removal of synthetic dyes from waste water, *A review Environment International*, **30**, 953-971 **(2004)**

4. Q. Wan, T.H. Wang, J. C, Zhao, Enhanced photocatalytic activity of ZnO nanotetrapods, *Applied Physics Letters*, **87**, 083105 **(2005)**

5. S. Bhattacharya, I. Saha, D. Mukhopadhyay, D. Chattopadhyay, U. C. Ghosh, D. Chatterjee, The role of nanotechnology in water treatment and purification potential applications and implementations, *International Journal of Chemical Sciences and Technology*, **l3**, 59-64 **(2013)**

6. A. Dadheech. K.S. Meena, Green synthesis and characterisation of silver nanocatalyst by using Coriandrum Sativum L., *Poll Res*. **39**, 237-241 **(2020)**

7. S. Pande, M.M. Islam, S.C. Mohantal, Nasiruddin, Single step synthesis of Manganese ferrite nano particles with enhanced Maganetization via chemical coprecipitation rule, *J. Sci. Res*. **11**, 225-234 **(2019)**

8. K. Vignesh, A. Suganthi, M. Rajarajan, S. A. Sara, Photocatlytic activity of AgI sensitized ZnO nano particles under visible light irradiation Powder Technology, **224**, 331-337 **(2012)**

9. M. Uddin, M. A. Hasnat, A. J. Samed, R. K. Majumdar Influence of TiO2 and ZnO photocatalysts on adsorbtion and degradation behaviour of erythrosine., Dyes and Pigments **75,** 207-212 **(2007)**

10. M.S. Akhtar, M.A. Alam, K. Tauer, M.S. Hossan, M. K. Sharafat, M. M. Rahman, H. Minami, H. Ahmad, Core shell structured epoxide functional NiO/SiO2 nano composite particles and photocatalytic decolorisation of congo red aqueous solution.Colloid surfaces, A: Physicochem. Eng. Aspects, **529**, 783-792 **(2017)**

11. M. T. Uddin, Y. Sultana, M. A., Nano sized SnO photocatalysts, Synthesis, characterisation and their application for the degradation of methylene blue dye, Islam, J. Sci. Res. **8**, 399-411 **(2016)**

12. M. Goncalves, A. Campos, M. Pinto, P. Nkeonye, A. Oliveria, P. Plasencia, M. Joao, S. queiroz, Photochemical treatment of solutions of azo dyes containing azo dyes, Chemosphere, **39,** 781-766 **(1999)**

13. N. Daneshvar, D. Salary, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO2. Journal of Photochemistry and Photobiology, A: Chemistry, **162,** 317-322 **(2004)**

14. R. Wang, H. Xin, Y. Yang, H. Liu, L. Xu, J. Hu, The characteristics and photocatalytic activities of silver doped ZnO nanocrystallites. Applied Surface Science, **227**, 312-317 **(2004)**

15. C. Xu, L. Cao, G. Su, W. Liu, H. Liu, Y. Yu, X. Qu, Preparation of ZnO/Cu2O compound photocatalyst and application in treating organic dyes, Journal of Hazardous Materials, **176**, 807-813 **(2010)**

16. N. Elamin, A. Elsanousi, Synthesis of ZnO nanostructures and their photocatalytic activity. Journal of Applied and Industrial Sciences, **1**, 32-35 **(2013)**

17. R. Ullah, J. Dutta, Photocatalytic degradation of organic dyes with manganese doped ZnO nano particles. Journal of Hazardous Materials, **156**, 194-200 **(2008)**

18. D. Jung, Synthesis and characterisation of transition metal doped ZnO, Solid State Sci. **12**, 466-470 **(2010)**

19. R. Chouhan, A. Kumar, R.P. Chaudhary, Photocatalytic studies of silver doped ZnO nano particles synthesized by chemical precipitation method, *Journal of Sol Gel Science and Technology*, **63**, 546-553 **(2012)**

20. K. Dhanshree, T.,Elangovan, Synthesis and characterisation of ZnO and Mn doped ZnO nanoparticles *International Journal of Science And Research*, **4**, 11. 1816-1820, ID NOV151529. **(2015)**

21. Y. Akyol, H. Yatmaz, Bayramoglu, Photocatalytic decolorisation of remazol red in aqueous ZnO suspensions *Applied Catalysis B: Environmental*, **54**, 19-24 **(2004)**

22. S. Hossini, M. Sarsari, P. Kameli, H. Salamati, Structural optical and photocatalytic activity of Ag, doped ZnO nano particles obtained by sol-gel method, *Journal of Alloys and Compounds*, **640**, 408-415 **(2015)**

23. M. Ashebir, G. M. Tesfamariam, G.Y. Nigussie, T. W. Gebreab Structural, Optical and photocatalytic activities of Ag doped and Mn doped ZnO nano particles, *Hindawi Journal of Nano Materials*, **2018** , 9 **(2018)**