



# Facial Fabrication of ZnO Nanomaterials for Effective Degradation of Direct Yellow 9 Dye Under Sunlight Radiation

Hansraj Poswal and A.S. Meena\*

Research Scholar and Assistant Professor

Department of Chemistry, University of Rajasthan, Jaipur-302004, Rajasthan, INDIA.

**Abstract :** Water pollution by organic pollutants (Dyes) becomes a major environmental problem. Here we report the synthesis ZnO nanomaterials via coprecipitation method using zinc acetate dihydrate as precursor. The fabricated sample was characterized by FESEM-EDS, FTIR, UV-VIS techniques. FESEM images expressed that nanomaterial images are needle and polygon shaped with little agglomeration. Optical properties are determined by UV-VIS spectroscopy. Photocatalytical activity was tested against with Direct Yellow 9 dye by variation in dose of dye and nanomaterial and also variation in pH.

**IndexTerms:** Photocatalyst, Direct Yellow 9, Photodegradation, Semiconductor.

## I. INTRODUCTION

Water is most important natural resource on earth, but pollution of water is becoming a tremendous problem. Organic dyes, released from industrial wastewater such as cosmetic, textile, leather, printing, drug, and rubber industries, are major group of pollutants.<sup>[1]</sup> The improper disposal of these residual dyes and dye wastewater into water sources by some industries and textile manufacturers has recently become a major source in the pollution of waterways.<sup>[2]</sup> These are extremely dangerous for people, animals, and the aquatic ecology due to their poor biodegradability and carcinogenic tendencies.<sup>[3]</sup> Due to their non-biodegradability and adverse effects on humans due to their high potential to be carcinogenic, organic dyes have received special attention as important environmental pollutants.<sup>[4,5]</sup> Due to the complex structure of organic dyes and their great stability in wastewater, it is a challenging, expensive, and time-consuming operation to degrade these dyes. For the treatment of wastewater containing organic dyes, a variety of techniques have been used, including biological, chemical, physico-chemical methods, and combinations of these protocols such as dissolved microorganisms, air floatation, active carbon adsorption, chemical and biochemical mediated reductions, and more.<sup>[6-10]</sup> However, the majority of these approaches have some drawbacks. Because of its eco-friendliness, cost-effectiveness, long lifespan, and ability to completely conversion f o pollutants into non-hazardous products, using semiconductor materials as photocatalysts (primarily metal oxides such as TiO<sub>2</sub>, SnO<sub>2</sub>, CuO, and ZnO) is found ht to be the most appealing and feasible way to address the crucial problem of water pollution.<sup>[11-14]</sup> Popular metal oxide semiconductor materials ZnO and TiO<sub>2</sub> have received a lot of attention because of their improved thermal stability, photosensitivity, and non-toxicity.<sup>[15]</sup> Because of cheaper, easy to synthesis, and eco-friendly nature ZnO nanomaterials are videly used as photocatalyst. it is an n-type direct wide bandgap ( $E_g = 3.2-3.4$  eV) semiconductor nanomaterial.<sup>[16,17]</sup> It may generate photo-excited holes and electrons with a strong oxidising capacity. Numerous methods, including hydrothermal<sup>[18]</sup>, precipitation<sup>[19]</sup>, microwave<sup>[20]</sup>, micro emulsion<sup>[21]</sup>, solvothermal<sup>[22]</sup>, supercritical water<sup>[23]</sup>, and mechanical procedures<sup>[24-25]</sup>, have been reported for the synthesis of ZnO nanomaterials (NPs). Co-precipitation is the best approach out of all of them due to its low cost, high uniformity, and simplicity of synthesis. The catalytic performance of synthesized ZnO NMs was investigated for the degradation of direct yellow 9 dye.

## II. Experimental

### A. Materials

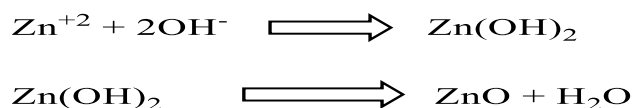
Zinc acetate dihydrate [ $Zn(CH_3COO)_2 \cdot 2H_2O$ ], potassium hydroxide (KOH), N, N, N, N-Cetyl trimethylammonium bromide (CTAB), ethyl alcohol, and Direct Yellow 9 were used. All chemicals were of analytical grade and used without any further purification.

### B. Preparation of ZnO Nanomaterials

For the synthesis of ZnO nanomaterials, in a typical method, 0.05 mole of  $Zn(CH_3COO)_2 \cdot 2H_2O$  and 3 mL of  $CH_3COOH$  dissolved in 100 mL of double distilled water with constant magnetic stirring for 25 min., then 1 gm of CTAB was added and stirred again for almost 60 min. Further, the pH of the solution was set up at 11 by adding 2M of KOH solution dropwise under constant stirring and the temperature of the mixture was increased to 80°C, a viscous white precipitate appeared which was continuously stirred for 2 hours at 80°C. Afterward, the obtained white precipitated was refluxed for 1 hour at 140°C. The suspension was kept uninterrupted overnight and allowed to cool down naturally to room

temperature. The white precipitate was recovered by centrifugation and repeatedly washed with double distilled water and ethyl alcohol, and dried for 4 h in a hot air oven at 85 °C temperature. The obtained white powder was used for characterization and photocatalytic studies of organic dye.

**Reactions:**



**C. Characterization**

Bond nature of ZnO NMs was investigated by Fourier-transform infrared (FTIR) spectrum. FESEM and EDX were used to study the morphology and the composition of fabricated NMs. The concentration of dyes in the treated solution and band gap in between VB and CB were investigated by UV – visible absorption spectrophotometer in the range of 200-800 nm.

**D. Studies of Photocatalytic Activities**

Direct Yellow 9(DY9) dye was used as modal water pollutant in aqueous medium, purchased from loba chemicals. Reaction condition was optimised by variation in pH, dose of nanomaterials, dose of dye with respect to time. 250W sodium lamp photoreactor was used to for experimental setup, sample was sited at 10cm away from lamp. For the establishment of adsorption-desorption equilibrium the dye solution was allow to kept in dark chamber for 40 minutes after the introduction of nanomaterial with dye solution. After that, the mixture was exposed to visible light in photoreactor under constant stirrer and 5 mL of dye solution was removed in predetermined time intervals, centrifuged for removal of photonanocatalyst and to determine to the residual concentration of dye in solution the absorbance was measured using a UV-visible spectrophotometer with a quartz cuvette with an optical length of 10 mm. The degradation percentage of dye was calculated using the equation as given follow equation:

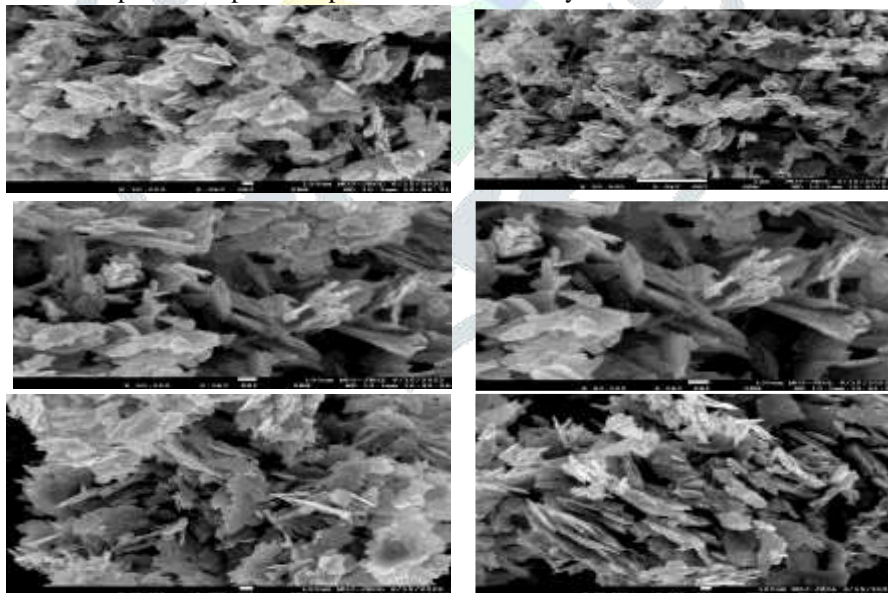
$$\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \text{ or } \frac{A_0 - A_t}{A_0} \times 100$$

Where  $C_0$  and  $C_t$  are the initial concentration at adsorption-desorption equilibrium and after a period of irradiation, while  $A_0$  and  $A_t$  are the absorbance of dye solutions after adsorption-desorption equilibrium and after irradiation of different time intervals.

**III. Result and Discussion**

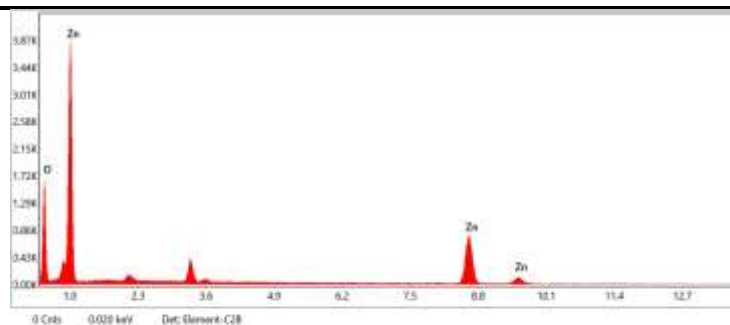
**1. Morphological and Elemental Analysis**

FESEM-EDS spectroscopy was used for the study of morphology and elemental composition of prepared ZnO NMs. The FESEM images of ZnO NMs are illustrated in Fig. 1. As shown in FESEM images, ZnO NMs have needle-polygonal shapes with little agglomerations. These agglomerations could be attributed to the high tendency of NMs to form large clusters. On the other hand, EDS analysis confirmed the successful synthesis of ZnO. The EDS spectra representing in (Fig.2), showing the chemical composition of sample. EDS spectra explains the successful synthesis of ZnO NMs.



FESEM IMAGES OF ZnO

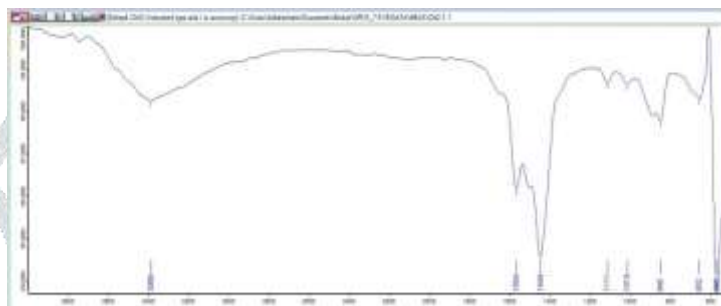
Figure-1: FESEM of ZnO Nanomaterials



**Figure-2:** EDS of ZnO Nanomaterials

### 2. Fourier-Transform Infrared (FTIR) Spectra

FTIR spectra for the synthesized sample is shown in Fig. 3, the strong absorption peaks in FTIR spectra observed at  $3386\text{ cm}^{-1}$  indicate the existence of O-H stretching vibration of  $\text{H}_2\text{O}$  water molecules. The peaks reported between  $1140\text{--}1570\text{ cm}^{-1}$  show the presence of  $\text{CO}_2$  molecules absorbed by samples. The absorption peaks that appeared within  $400\text{--}650\text{ cm}^{-1}$  represent the metal-oxygen bonds [26]. The peak around  $565\text{ cm}^{-1}$  (Fig.3) indicates the Zn-O stretching vibration [27].



**Figure-3:** FTIR of ZnO Nanomaterials

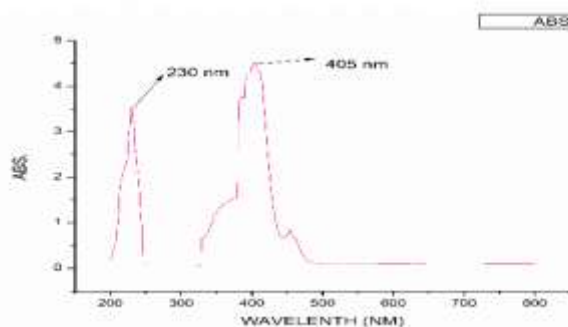
### 3. Optical Properties

#### A. ZnO Nanomaterials

To analyze the optical properties of prepared ZnO-NMs UV-vis absorption spectra was recorded as shown in Figure-4. ZnO exhibits strong absorption spectra at  $326\text{ nm}$ .

#### B. Direct Yellow 9 Dye (DY9)

UV-VIS spectra was plotted against absorbance at Y axis with respect to wavelength at X axis, which is represented in figure 5. Spectra shows two maxima at  $230\text{ nm}$  and  $405\text{ nm}$ . Spectra shows two types of transitions in UV-VIS. Transitions related to  $405\text{ nm}$  are responsible for colour. All further UV-VIS data for DY9 are recorded at  $405\text{ nm}$ .



**Figure-5:** UV-VIS Spectra of Direct Yellow Dye

#### C. Photocatalytic activity

To investigate the photocatalytic activity of prepared ZnO photocatalyst  $100\text{ mL}$  of dye solutions have  $15\text{ mg}/100\text{ mL}$  dye concentration and  $15\text{ mg}$  of catalyst doses were irradiated under visible light at optimized pH in a photoreactor. The degraded amount of DY9 dye was measured by recording UV visible absorption spectra at  $405\text{ nm}$ . As shown in Fig. 5 the attributed absorption peak of DY9 dye at  $405\text{ nm}$  is continuously declining with time due to the photodegradation of DY9 dye into non-hazardous products. In  $100\text{ min}$  of visible light irradiation, the dye is about to completely degraded and there was no absorption peak recorded after  $100\text{ minutes}$  in results.

#### D. Effect of Reaction Parameters on Photocatalysis

##### i. Effect of Dose of Nanomaterials

As we know nanomaterials are the photocatalysts for the degradation of dyes. Amount of these photocatalysts affects the rate of degradation. As we know these photocatalysts provides the surface area for the photodegradation of dye so, by increasing amount of nanomaterials no. of active sites increase so rate of photodegradation also increase. The effect of nanomaterial amount on photodegradation of DY9 was studied by varying nanomaterial dose amount from  $15\text{ mg}$  to  $25\text{ mg}$  under optimized reaction with  $15\text{ mg}/100\text{ mL}$  dye solution. The results shown in figure-6.

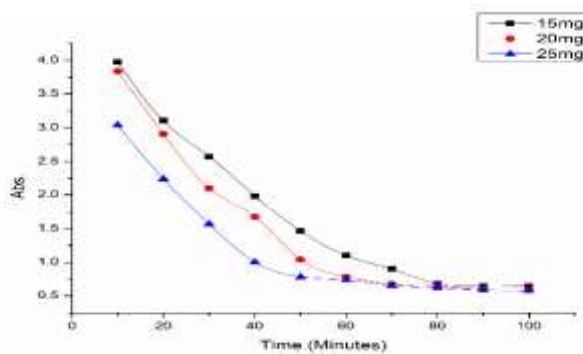


Figure-6: Effect of Dose of Nanomaterials

### ii. Effect of dye solution pH

Photodegradation of DY9 dye in aqueous medium is largely affected by pH of medium, by changing the pH of media rate of degradation affected significantly. It happens, because of the different of interaction of DY9 with photocatalyst at different pH value. For the photodegradation process of DY9 dye, the effect of solution pH was investigated at different pH i.e. 7, 9, 11 and 13 using 100mL of 15mg/100ml dye solution with 15mg of catalyst dose amount under visible light illumination. The results as shown in Figure-7 reveal that degradation rate is increase on increasing solution pH and determined highest for pH = 11. Since the main degrading agent in the media are hydroxyl radicals. At lower pH solution the generation of degrading agents (oxidizing radicals) becomes difficult. By increasing pH the quantity of degrading agents increase and becomes maximum at 11pH. Further increment in pH is responsible for the ionisation of dye which make it anionic so, degrading agents cannot approach effectively to photodegradation.<sup>[28]</sup>

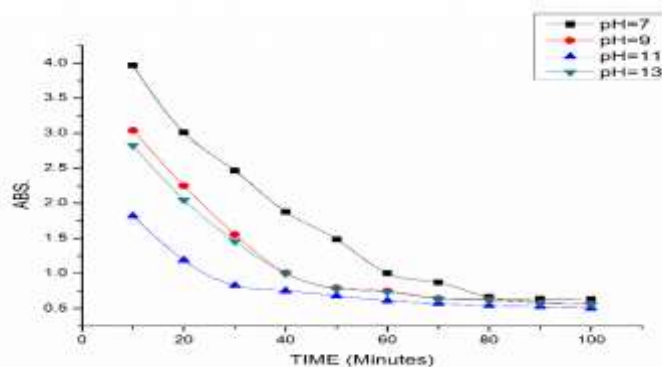


Figure-7: Effect of dye solution pH

### iii. Effect of Initial Dye Concentration

Degradation of dyes at the surface of any photocatalyst follow 1<sup>st</sup> order kinetics. Initial dye concentration also affects the degradation rate of itself by photocatalyst. As the initial dye concentration increase and dose amount of photocatalyst remains unchanged the rate of photodegradation decrease. It is because of by increasing initial dye concentration occupancy of active sites by molecules increase and efficiency of photocatalysts decrease. When we increase dye concentration from 15mg/100ml concentration to 20mg/100ml and 25mg/100ml, degradation rate progressively decreases which is represented in figure-8.

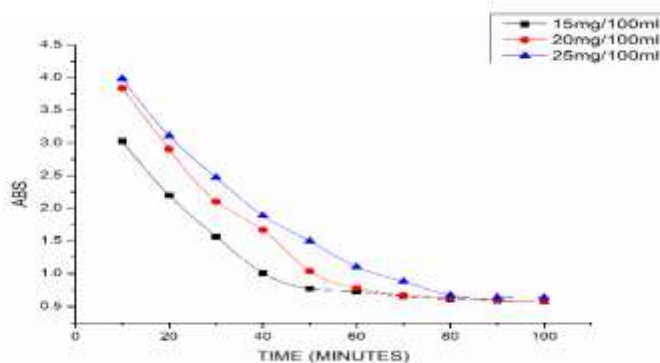


Figure-8: Effect of Initial Dye Concentration

## IV. ACKNOWLEDGEMENT:

The authors are grateful to the Head of the Chemistry Department at the University of Rajasthan in Jaipur for providing the facilities needed to carry out this research, and one of the author (A.S. Meena) is appreciative of the DST at the Government of Rajasthan in Jaipur for providing financial support for this research work..

## REFERENCES

1. Crini, G. 2006. *Bioresour.Technol.* 97: 1061-1085.
2. El-Sharkawy, E.A., Soliman, A.Y., Al-Amer, K.M. 2007. *J. Colloid Interface Sci.*, 310 (2): 498-508.
3. Jadhav, V., Chikode, P., Nikam, G., Sabale, S. 2016. *Mater. Today Proc.*, 3(10): 4121-4127.
4. Saleh R., Djaja, N.F. 2014. *Superlattices Microstruct.*, 74: 217-233.

5. Balcha, V., Yadav, O.P., Dey, T. 2016. *Environ. Sci. Pollut. Res.*, 23: 25485-25493.
6. Holkar, C.R., Jadhav, A.J., Pinjari, D.V., Mahamuni, N.M., Pandit, A.B. 2016. *J. Environ. Manage.*, 182: 351-366.
7. Robinson, T., McMullan, G., Marchant, R., Nigam, P. 2001. *Bioresour. Technol.* 77: 247-255.
8. Rubio, J., Souza, M.L., Smith, R.W. 2002. *Miner. Eng.*, 15: 139-155.
9. Papic, S., Koprivanac, N., Loncaric, Bozic, A., Metes A. 2004. *Dye. Pigment.*, 62: 291-298.
10. Turgay, O., Ersoz, G., Atalay, S., Forss J., Welandar, U. 2011. *Sep. & Purif. Technol.* 79: 26-33.
11. Fujishima, A., Honda, K. 1972. *Nature*, 238(5358):37-38.
12. McLaren, A., Valdes-Solis, T., Li G., Tsang, SC. 2009. *J. Ame. Chem. Soc.*, 13(35): 12540-12541.
13. Sakwises, L., Pisitsak, P., Manuspiya, H., Ummartyotin, S. 2017. *Results in Physics*, 7: 1751-1759.
14. Sonia, S., Poongodi, S., Kumar, P.S., Mangalaraj, D., Ponpandian, N., Viswanathan, C. 2015. *Mate. Sci. in Semic. Proc.*, 30: 585-591.
15. Zheng, Y., Chen, C., Zhan, Y., Lin, X., Zheng, Q., Wei, K. 2007. *Inorganic Chemistry*, 46(16): 6675-6682.
16. Sun, T., Qiu, J., Liang, C. 2008. *The Journal of Physical Chemistry C*, 112(3): 715-721.
17. Baig, A.U., adamalar, R., Vinodhini, A., Fairrose, S., Gomathiyalini, A., Begum, N.J., Jabeen, S. 2020. *J. Water Environ. Nanotechnol.*, 5(4): 307- 320.
18. Kumaresan, N., Ramamurthi, K., Ramesh, R., Babu, K., Sethuraman, S., Moorthy, B. 2017. *Appl. Surf. Sci.*, 418: 138-146.
19. Raoufi, D. 2013. *Renew. Energy*, 50: 932-937.
20. Nandi, A., Nag, P., Saha, H., Majumdar, S. 2018. *Mater. Today Proc.*, 5: 9831-9838.
21. Pineda-Reyes, A.M., Olvera, M., de la, L. 2018. *Mater. Chem. Phys.*, 203: 141-147.
22. Bai, X., Li, L., Liu, H., Tan, L., Liu, T., Meng, X. 2015. *ACS Appl. Mater. Interfaces*, 7: 1308-1317.
23. Golmohammadi, M., Towfighi, J., Hosseinpour, M., Ahmadi, S.J. 2016. *J. Supercrit. Fluids*, 107: 699-706.
24. Akhoun, S.A., Rubab, S., Shah, M.A. 2015. *Int. Nano Lett.*, 5: 9-13.
25. Meena, P.L., Poswal, K., Surela, A.K. 2021. *J. Water Environ. Nanotechnol.*, 6(3): 196-211.
26. Saravanan, R., Karthikeyan, S., Gupta, V.K., Sekaran, G., Narayanan, V., Stephen, A. 2013. *Materials Sci. & Eng.: C*, 33(1): 91-98.
27. Oda,, A.M., Ali H.H., Lafta, A.J., Esmael, H.A., Jameel, A.A., Mohammed, A.M. 2015. *Int. J. Chem.*,7(2): 39-45.
28. Kumari, V., Yadav, S., Jindal, J., Sharma, S., Kumari, K., Kumar, N. 2020. *Advanced Powder Technology*, 31(7): 2658-2668.

