Journal of Advances in Developmental Research (IJAIDR)

E-ISSN: 0976-4844 ● Website: www.ijaidr.com ● Email: editor@ijaidr.com

Synthesis of Pure ZNO Nano Crystals and its Photocatalytic Activity

Dr. P. Laveena Manjulatha

Asst prof of Physics

Department of Physics, MALD Government Degree College, Jogulamba Gadwal-509125, India.

Abstract:

ZnO nanocrystals have been synthesized by various routes, which are classified by physical, biological & chemical methods. Solution based synthetic methods mainly employ chemicals such as Zinc acetate dehydrate, Zincnitrate, sodium hydroxide, ammonium hydroxide, organic amine set. Although different biological based synthetic methods are known for ZnO nanocrystals are sought by researchers. Biological process has led to the development of an eco-friendly approach for the synthesis of nano particles. The use of non-toxic materials like plant extract & bacteria for synthesis of silver nano particles offers numerous benefits of pharmaceutical application. Synthesis of ZnO nano structures using L-lysine, amino acid and lemon juice have been reported by various researchers. Bio-synthesis of gold nano particles by plant alfalfa have been reported. The development of eco-friendly methods of synthesis of nanoparticles should make an increasing awareness on green chemistry.

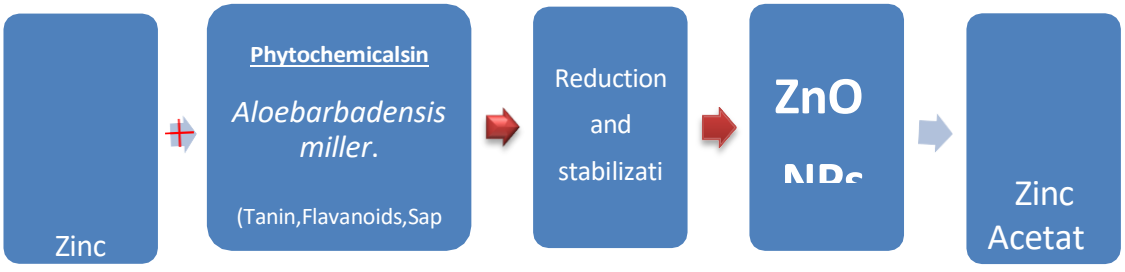
Keywords: ZnO nanocrystals Zinc acetate dehydrate Zincnitrate, sodium hydroxide, ammonium hydroxide

INTRODUCTION

In our laboratory a novel attempt of green synthesis of ZnO nanocrystals are prepared by using *aleovera* leaf extract and Zinc acetate

Dehydrate $Zn(COOCH3)2.2H2O$. The botanical name of Aleo vera plant was referred as *Aloe barbadensis miller*. The study reports the formation of ZnO nanocrystals are achieved through Aleo vera. Aleo vera contains phytochemical active compounds such as tannin, saponon, flavonoids and terpenoids. (S.Arun kumar*et al.* 2009). Presence of these compound in plant is acta sastabilizing agents for conversion of bulk compound to nanoparticles which shown in figure 3.1 (Fatemeh Davar *et al.* 2015).

Figure 1.1Phytochemicals action of *Aloebarbadensis miller* leaf extract



CHARACTERIZATION TECHNIQUES

The structure, crystal phase and crystallite sizes of the synthesized nanocrystals are identified by powder X-ray diffraction (PXRD) studies using Shimadzu**,** XRD-6000 diffractometer at room temperature with CuKα radiation (λ=1.5406Å) and accelerating voltage of 40 kV and the emission current of 30 mA. The formation of ZnO nanocrystals and morphology of samples was analyzed by scanning electron microscope (JOEL JSM-6390LV). The photocatalytic activity of the synthesized samples are characterized by UV-Vis Spectrophotometer (Bigvision 2371). The samples are kept in quartz photochemical reactor, 12W ultra violet lamp (Philips) with wavelength peak at 354nm used as a light source

RESULTS AND DISCUSSIONS

Powder X-ray Diffraction (PXRD)studies

PXRD studies of chemically synthesized pure ZnO nanocrystal

The structure, crystal phase and crystallite sizes of the synthesized nanocrystals are identified by powder X-ray diffraction (PXRD) studies .Figure 3.2 shows that diffraction peaks of ZnO nano crystals by chemical synthesis. The peaks present at 2θ(degree) of 31.95, 34.70, 36.52, 47.78,57.07,63.15,67.72,68.94respectivelyindexedto(100),(002),(101),
(102), (110), (103), 112) and (201) planes of ZnO wurtzite structure which are well matched with the standard JCPDS No: 36-1451. The calculated lattice parameter values are a=3.267 Å and c=5.243 Å, the values are in good agreement with standard values of ZnO wurtzite structure. The lattice parameters have been calculated using the relation (T.S.Senthil *etal.* 2013)in formula (3.1)

$$1/d^2=4/3[(h^2+hk+k^2/a^2)]+l^2/c^2 \quad (3.1)$$

The calculated values are a=3.248 Å and c=5.215 Å, the values are in good agreement with the reported standard values a=3.249 Å and c=5.206 Å(JCPDS no. 36-1451). The average particle size (D) are calculated using the Scherer's semi empirical formula (3.2)

$$D= k\lambda / \beta\cos\theta \quad (3.2)$$

Where λ is the wavelength of the X-ray (1.5406 Å), k is the shape factor (≈ 0.94), β is the full width at half maximum (FWHM) and θ is the Bragg angle (degree). The value of FWHM was obtained by performing profile fitting using an XRD pattern processing soft ware. The average crystallite size of ZnO nanocrystals by chemical method was estimated to be 34 nm.

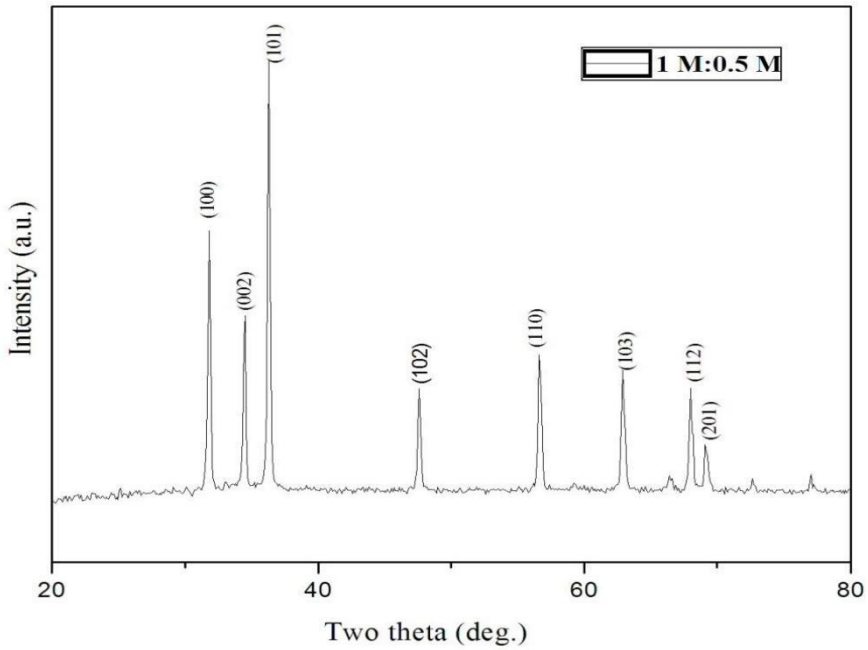


Figure 1.2 XRD-pattern of ZnO nanocrystals prepared by chemical method

PXRD studies of biologically synthesized pure ZnO nanocrystal

The X-raydiffraction pattern of the synthesized ZnO nanocrystals by biological method is shown inthe figure 3.3.The sharp and clear diffraction peaks reveals that the synthesized ZnO crystals have high quality. All the diffraction peaks in the XRD pattern could be indexed to the hexagonal structure of ZnO with fine crystalline. The diffraction peaks at 2θ(degree) of 31.76,34.43,36.267,47.569,56.62,62.88,67.98and69.12arerespectively
indexed to (100), (002), (101), (102), (110), (103), (112) and (201) planes of ZnO.The average crystallite size of ZnO nanocrystals by biological method was estimated to be 31 nm.

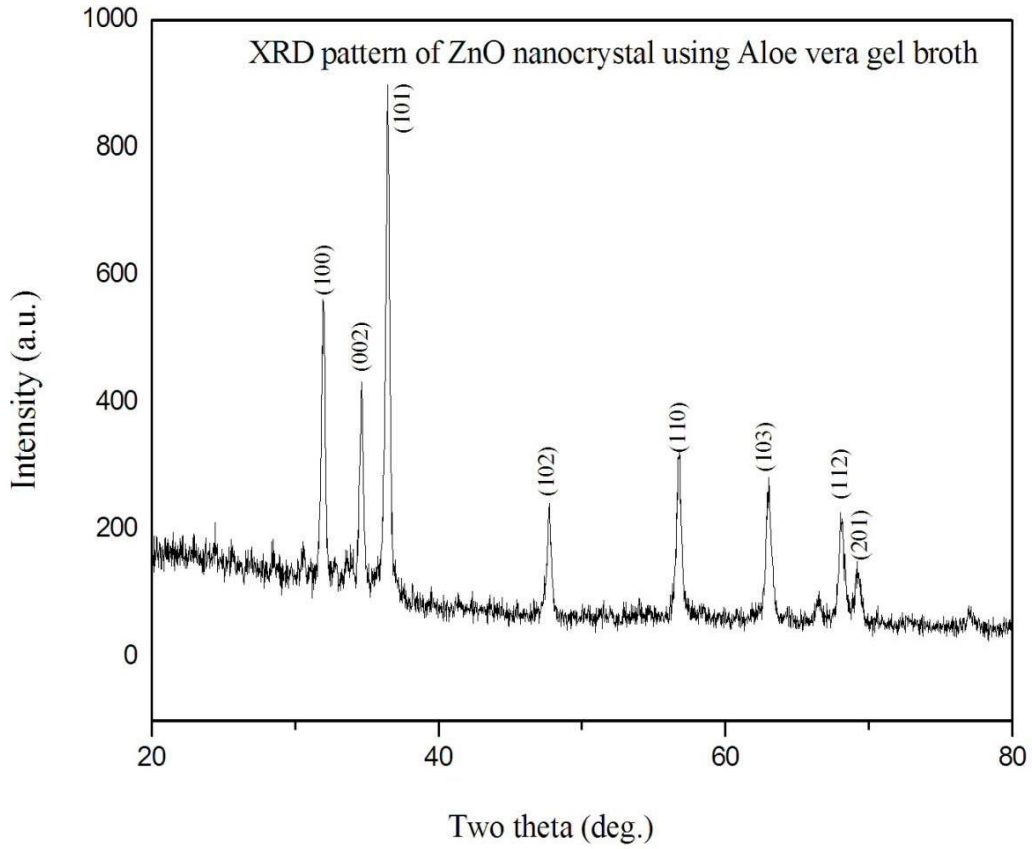


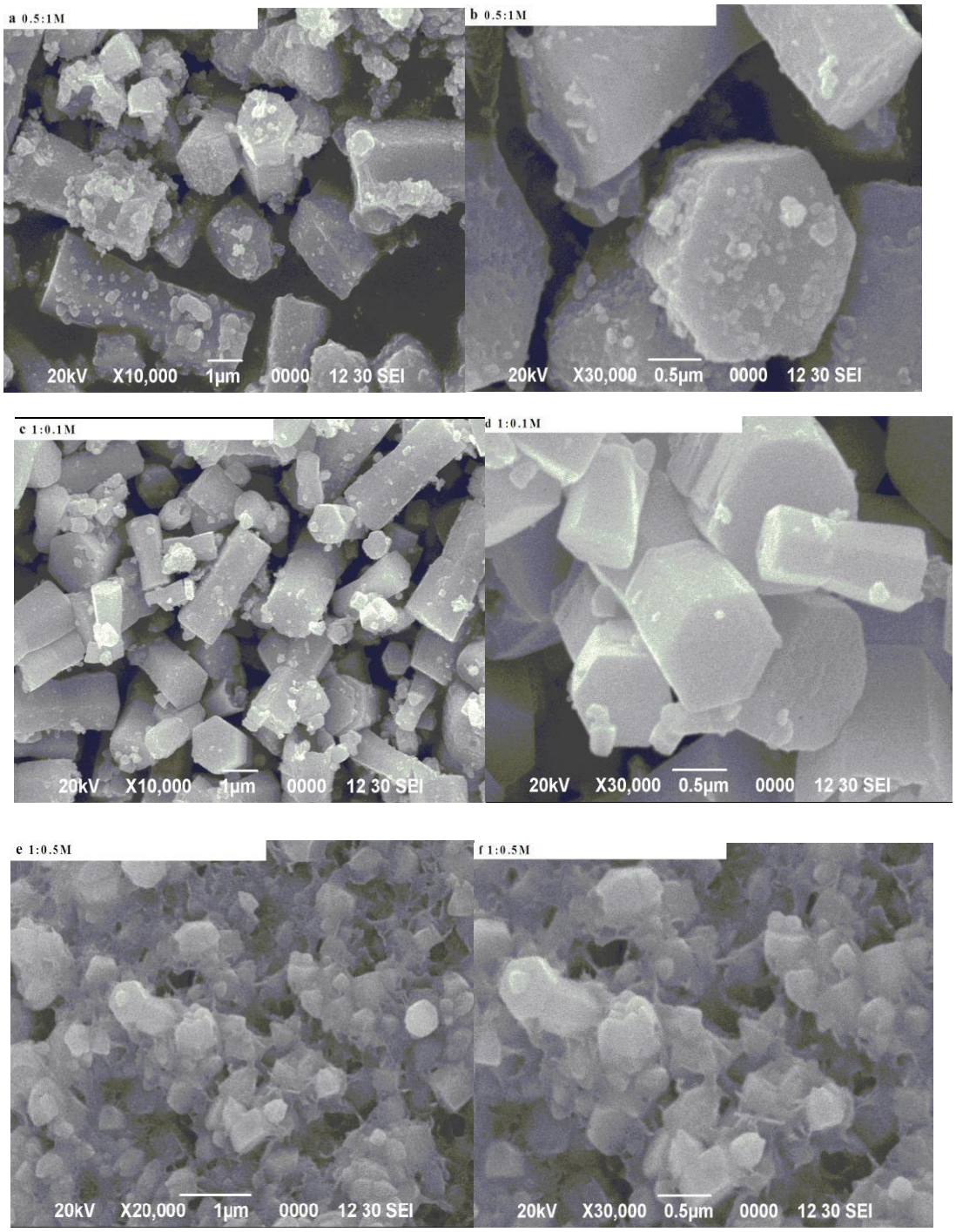
Figure1.3 XRD-patternofgreensynthesisofZnOnanocrystals

The diffraction peaks of pure ZnO nanocrystals synthesized both methods have the hexagonal wurtzite structure. Compare to biological synthesis, chemically synthesized ZnO nanocrystals shows sharp and straight peaks. At the same time, there is no additional peaks in the pattern, which indicates that all the precursors have been completely decomposed. All the synthesized nanocrystals are in mesophorous state.

Scanning Electron Microscopy (SEM)analysis

SEM analys is of chemically synthesized ZnO nanocrystals

The SEM images of the synthesized ZnO nanocrystals using chemical method is shown in Figure3.4 . From the figure it clearly shows that the ZnO nanocrystals synthesized from chemical method possess rod like structures, and agglomerated hexogonal shapes. The ZnO nanocrystals synthesized using 0.5:1 M and 1:0.1 M concentration have clearly agglomerated as hexagonal shape.



SEMimageofZnOnanocrystalsfromchemical method

SEM analysis of biologically synthesized ZnO nanocrystals

The SEM images of the synthesized ZnO nanocrystals using biological method is shown infigure 3.5. ZnO nano particles from biological method seems like a nano flakes. Difference of the surface morphology between chemically synthesized ZnO and biologically synthesized ZnO nanocrystals was obviously observed from the images. The figure also shows that ZnO nanocrystals synthesized from biological method gives irregular bulks than the ZnO nanocrystals synthesized from chemical method

(1:0.5 molar concentrations).

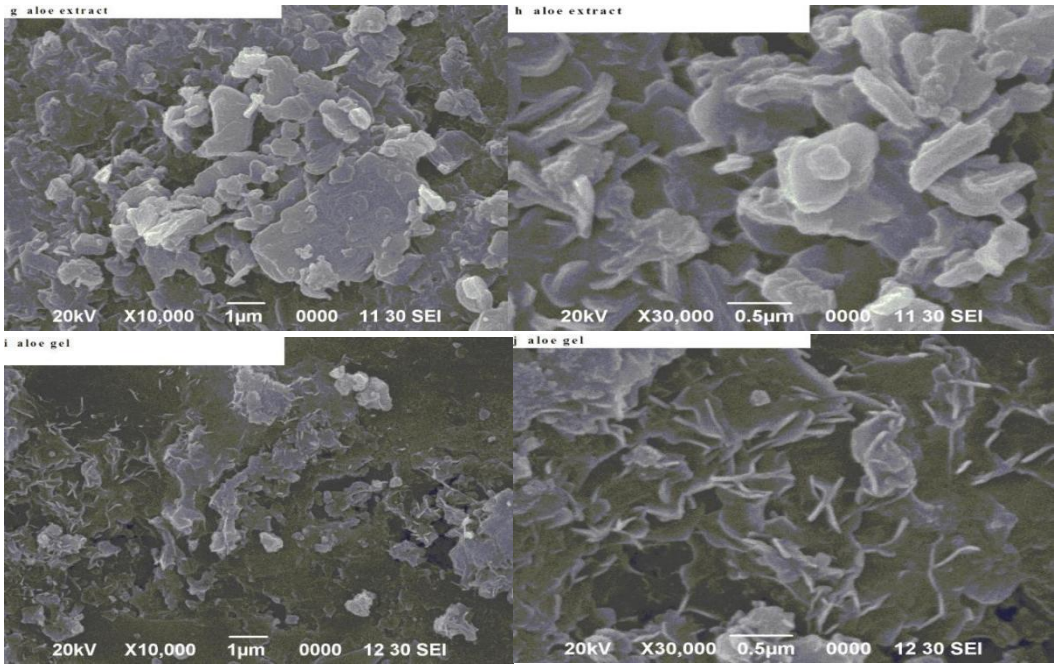


Figure1.5 SEM image of ZnO nanocrystals from biological method

Spectrophotometer analysis

The photocatalytic activity of the synthesized samples are characterized by UV-Vis Spectrophotometer .The experimental suspension was prepared by adding 0.25gm catalyst into 250 ml methylene blue aqueous with concentration of 10 ppm. The optical absorption in the UV region and corresponding photo efficiency influences the use of ZnO nanorods and nano flakes for photo catalytic activities. The dye degradation efficiency was calculated using the following formula (3.3) Photo degradation(%)=[C0-C/C0]X 100 (3.3) Where C0 is initial concentration of MB dye before irradiation (t=0) and C is concentration of MB after certain irradiation time.

PHOTO CATALYTIC ACTIVITY

The samples are kept in quartz photochemical reactor, 12W ultra violet lamp (Philips) with wavelength peak at 354nm used as a light source.The progress of photocatalytic degradation was carried out by different time interval (1h, 2 hrs, 3 hrs, 4hrs).The photocatalytic activity of the ZnO nanorods and nano flakes was evaluated by the degradation of 10ppm of MB at natural pH. Photocatalyst and MB dye taken for continuous stirring for an hour in dark to reach an adsorption – desorption equilibrium between catalyst and dye molecule. The adsorption was measured each 15 mins using spectrophotometer until it will be nearly constant. Because phocatalytic systemal ways includes a photosensitizer. Commonly, a photo sensitizer itself unstable under dark conditions (Kanakkanmavudi. B. Jaimy *et al*, 2011).The comparative analysis of the effect of irradiation time of the catalyst on the absorbance of MB dyefor ZnO nanorods and nano flakes are shown in figure 3.7.

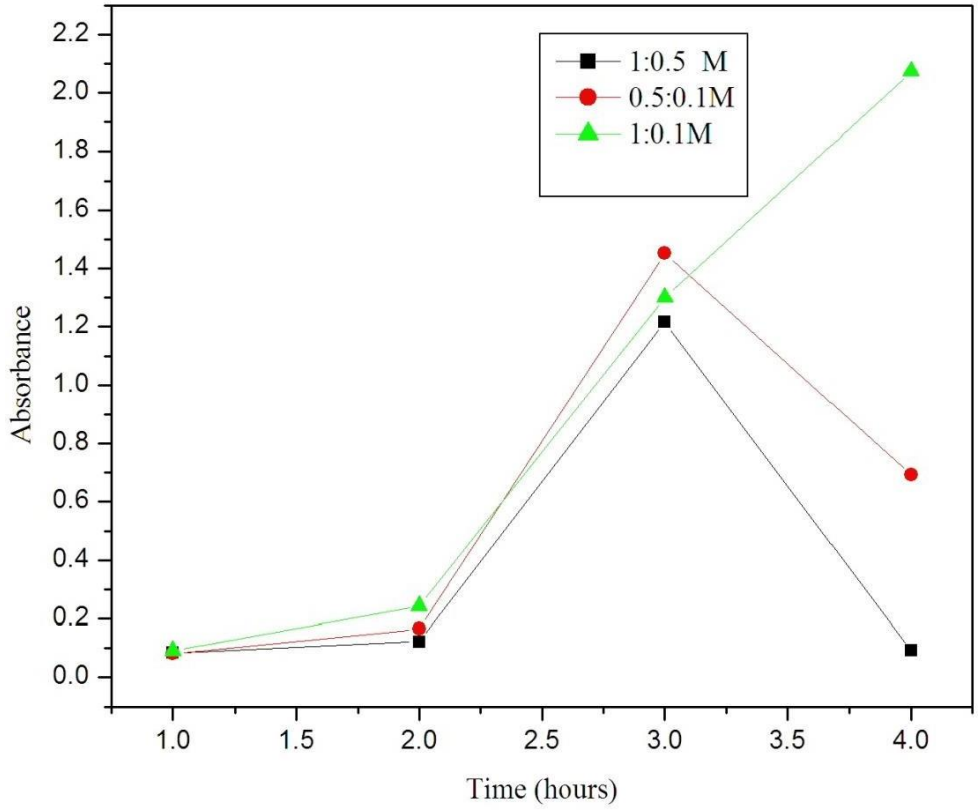
Photocatalytic activity of ZnO Nanorods

The photocatalytic activity of ZnO nanorods can be seen that initial slopes of the curves representing

rate of absorbance, it increase greatly by increasing the irradiation time from1 hour, 2 hrs and3 hrs and 4hrsofthe catalyst(figure 3.6). And indicates the comparison of all the molar concentrations of ZnO nanorods synthesized using chemical method, it clearly infers that the 1:0.1 M concentration achieves higher photocatalytic activity. By increasing time the concentration of MB dye decereased. The photodegradation efficiency of 1:0.1 concentrations at 4 hrs irradiation time achieves76%.Thenanorods show higher surface area than the other structure

it is the reason for better catalytic activity (R.Saravanan *et al.*2011). Due to this more negative surface charges are produced on the ZnO nanorod surface, these charges readily attract the methylene blue molecule and degrade it.

Figure1.6 Photocatalytic activity of ZnO nanorods



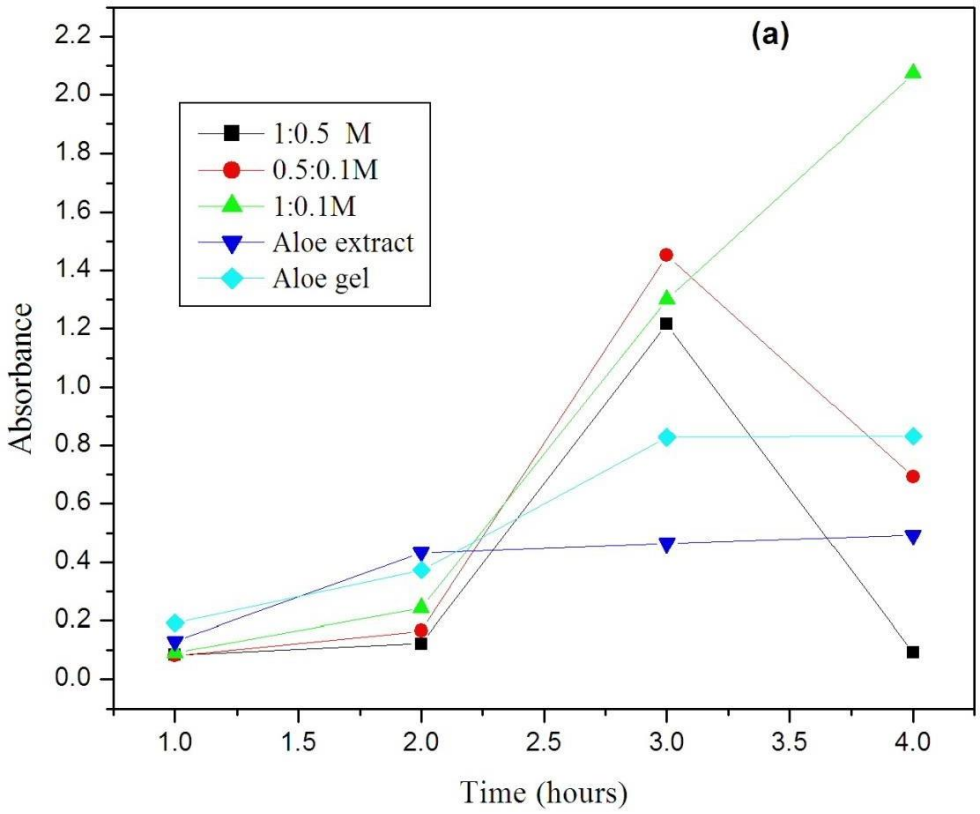
Photocatalytic activity of ZnO nano flakes

In biological method compare to aleo leaf extract gel broth achieves high photocatalytic activity. By using aleo gel broth photo degradation percentage of anan of lakesachieves only 52%.In the figure

3.7 clearly shows that the ZnO nanocrystals synthesized from chemical method shows higher catalytic activity than the ZnOnanocrystals synthesized

from biological method. The poor degradation of methylene blue by the nano flakes is due to positive surface charge on the surface. The positive charge on the ZnO surface does not pay attention to attract the methylene blue molecule since it is a cationic dye.

Figure 1.7-Photocatalytic activity of ZnO nanorods and nanoflakes as a function of irradiation time.



Reusability of pure ZnO Nanorods and Nanoflakes

The reusability of the photocatalyst is also an important factor for practical applications and it was studied by recycling experiments. Photocatalytic experimentswereperformedundertheoptimumreactioncondition[pH=7, MB concentration=10 ppm and ZnO nanocrystal dosage=0.25 g] using the same catalyst for two times .The photo degradation percentage of MB dye with chemically synthesized nano rods for the two successive cycling are 76%, 73%, respectively. The procedure is applied for biologically synthesized ZnO nano flakes for two successive cycling are 52%, 50%. Recycling of the ZnO NPs for 2 successive runs have indicated the feasibility of reusing the NPs for several times. This implies that by using bare ZnO NPs an efficient approach for degradation of toxic waste can be achieved.

CONCLUSION

Pure ZnO nanocrystals have been synthesized by chemically and biologically through precipitation method. X-ray diffraction analysis reveals that the prepared ZnO nanocrystals exhibit hexagonal structure. The formation of ZnO nanorods obtained by chemical method and nano flakes are formed by biological method which have been confirmed by SEM analysis. The Zinc Oxide nano particles show distinct poly disparity and the average particle size of nanorods was 31 nm and nano flakes 34 nm.ZnO nanorods synthesized using 1:0.1 molar concentration achieves higher photocatalytic activity of degradation of MB dye than the other concentrations and biological synthesized ZnO nano flakes. The dye degradation efficiency of nanorods achieves 76% of 4 hrs irradiation time.The formation of

nanorods during chemical synthesis is the reason for higher photocatalytic activity compare to nanoflakes.Because nano rod shows higher surface area than the other structure it may the reason for better catalytic activity.

Acknowledgement: Author is thankful to the Nanoscience lab HOU Hyderabad.
Conflict of Interest: Author has no conflict of interest

REFERENCES:

1. Zafar, N.; Madni, A.; Khalid, A.; Khan, T.; Kousar, R.; Naz, S.S.; Wahid, F. Pharmaceutical and Biomedical Applications of Green Synthesized Metal and Metal Oxide Nanoparticles. Curr. Pharm. Des. 2020, 26, 5844–5865.
2. Annu, A.A.; Ahmed, S. Green synthesis of metal, metal oxide nanoparticles, and their various applications. Handb. Ecomater. 2018, 1–45.
3. Musa, I.; Qamhieh, N. Study of optical energy gap and quantum confinement effects in zinc oxide nanoparticles and nanorods. Dig. J. Nanomater. Biostruct. 2019, 14, 119–125.
4. Kim, K.J.; Kreider, P.B.; Choi, C.; Chang, C.H.; Ahn, H.G. Visible-light-sensitive Na-doped p-type flower-like ZnO photocatalysts synthesized via a continuous flow microreactor. RSC Adv. 2013, 3, 12702–12710.
5. Fortunato, E.; Gonçalves, A.; Pimentel, A.; Barquinha, P.; Gonçalves, G.; Pereira, L.; Ferreira, I.; Martins, R. Zinc oxide, a multifunctional material: From material to device applications. Appl. Phys. A 2009, 96, 197–205.
6. Ates, T.; Tatar, C.; Yakuphanoglu, F. Preparation of semiconductor ZnO powders by sol–gel method: Humidity sensors. Sens. Actuators A Phys. 2013, 190, 153–160.
7. Balcha, A.; Yadav, O.P.; Dey, T. Photocatalytic degradation of methylene blue dye by zinc oxide nanoparticles obtained from precipitation and sol-gel methods. Environ. Sci. Pollut. Res. 2016, 23, 25485–25493.
8. Irani, M.; Mohammadi, T.; Mohebbi, S. Photocatalytic degradation of methylene blue with ZnO nanoparticles; a joint experimental and theoretical study. J. Mex. Chem. Soc. 2016, 60, 218–225.
9. Shinde, D.R.; Tambade, P.S.; Chaskar, M.G.; Gadave, K.M. Photocatalytic degradation of dyes in water by analytical reagent grades ZnO, TiO2 and SnO2: A comparative study. Drink. Water Eng. Sci. 2017, 10, 109–117.