

Biosynthesis, Characterization of ZnO Nanoparticles by Using *Pyrus Pyrifolia* Leaf Extract and Their Photocatalytic Activity

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ABSTRACT: The synthesis of semiconductor nanoparticles is an expanding research area due to the potential applications in the development of nanotechnologies. Especially, biosynthesized nanoparticles have become an important branch of nanotechnology. In the present work, we describe a low-cost and simple procedure for biosynthesis of Zinc oxide nanoparticles (ZnO NPs) using *Pyrus Pyrifolia* leaf extract. The structural, morphological and optical properties of the synthesized nanoparticles have been characterized by using UV-Vis spectrophotometer, XRD, FTIR, AFM, and FE – SEM with EDX analysis. The synthesized ZnO NPs were characterized by a peak at 376 nm in the UV-Vis spectrum. FT-IR confirmed the presence of functional groups of both leaf extract and ZnO NPs. The morphological characterization of synthesized nanoparticles was analysed by FE – SEM. The intense, narrow width of Zinc and Oxygen have high purity and crystalline size were identified using EDX. The size and topological structure of the ZnO NPs was measured by AFM with crystalline size of around ~45 nm. In addition, the synthesized NPs are wurtzite hexagonal structure with an average grain size 22 nm was found from XRD pattern. The applications of CuO NPs exhibit potential photocatalytic activity towards the degradation of methylene blue (MB) dye depend upon time exposure to under solar irradiation.

KEYWORDS: Green synthesis, ZnO nanoparticles, *Pyrus Pyrifolia*, Methylene blue, XRD, FTIR, UV-Vis, FE – SEM, EDX, AFM, Photocatalytic activity.

1. INTRODUCTION

In recent years, metal and metal oxide nanoparticles have been intensively studied in the past decade. The nanosized materials have been an important subject in the field of basic and applied sciences. Nanomaterials have different size and shapes so, its appealed considerable attention because of their peculiar physicochemical properties compared to the bulk materials. Nowadays, there are plenty of opportunities to fully employ in modern clinical technology the novel concepts and phenomena that have appeared in Nanoparticles research field [1].

The nanotechnology is an emerging technology, which can extend to a novel revolution in all field of science. This technology is used with affiliation to optics, electronics, bio medical and materials sciences. Nanotechnology deals with nanoparticles that are atomic, molecular combining are characterized by size 1 nm to 100 nm [2].

Dye contaminants from many other industries like fabric, printing, manufacturing, etc., show a vital role in damaging the environment. These wastages enter into water ecosystem and affect the survival of aquatic organism. The dye contaminants get into the water table and create lot of environmental and health hazard problems. Different methods such as osmosis, adsorption, flocculation and others have been used for dye voiding from river. The photocatalytic treatment offers a capable, relatively low cost and environment friendly method. From the past years, photocatalytic processes along with semiconductor Nanomaterials have been inviting a great deal of attention, as an efficient bio synthesized technology for the decontamination of water. The process of waste water treatment is carried out by using most commonly used semiconductors such as TiO₂, CuO, ZnO, CdS, and WO₃ etc [3, 4].

The bio synthesized ZnO nanoparticles are trusted to be friendly with environment, non toxic, bio safe and bio-compatible. It is desirable for bio medical application such as drug carriers, cosmetics and filling the medical materials [5].

Based on the review of literature, the bio synthesis of ZnO NPs using various plants has been carried out, *Cassia fistula* plant extract [3], *Trifolium pratense* flower extract [6], *Aloe barbadensis miller* leaf extract [7], *Candida*

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albicans [8], *Vitex negundo* extract [9], leaf extract of *Tamarindus indica* (L.) [10], *Nephelium lappaceum* L. peel extract [11], *Solanum nigrum* leaf extract [12], *Azadirachta indica* [13], curry leaf *Murraya koenigii* [14], *Borassus flabellifer* fruit extract [15], *Artocarpus gomezianus* fruits extract [16], *Ocimum basilicum* L. var. *purpurascens* Benth.-*Lamiaceae* leaf extract [17], *Moringa oleifera* leaf extract [18].

In this present study, bio synthesized ZnO nanoparticles using *P. Pyrifolia* leaf aqueous extract. *P. Pyrifolia*. (Family: *Rosaceae*, Genus: *Pyrus*, Section: *Pyrifolia*). The size, structure and morphology of the synthesized nanoparticles have been established on the basis of following elemental analysis and spectral data. UV – Vis spectroscopy, XRD, FTIR, FE – SEM, EDX and AFM have been used to characterize the shape and morphology of catalyst. The ZnO Nps have showed the efficiency in dye degrading MB under sun shine irradiation.

II. MATERIALS AND METHODS

2.1 Materials

Chemicals and glassware were procured from Sigma Aldrich, Pondicherry, India. *Pyrus Pyrifolia* leaves were collected during the month of May 2015 from hilly area, Ooty, Nilgiris district at Tamilnadu in India. The leaves were identified and authenticated by Department of agriculture, Annamalai University, Chidambaram, India.

2.2 Preparation of the leaf extract

The collected *P. Pyrifolia* leaves washed several times with distilled water, to remove the impurities. Leaves had been dried in the sun shade for 15 days. After the leaves were dried it is powdered using mortar. The *Pyrus* leaf powder of 1g was taken for synthesis purpose. The weighed of 1g leaf powder was mixed gently with 150 ml of distilled water, boiled in 80 °C using magnetic stirrer for 20 min; until the colour of the aqueous solution changes from watery to brown. Then the extract was filtered through Whatman No.1 filter paper, stored at room temperature in order to use for further studies.

2.3 Preparation of Zinc oxide NPs

The synthesis of ZnO NPs, 30 ml of *P. Pyrifolia* leaves extract was taken and boiled at (80 °C) by using a magnetic stirrer. When the temperature of the solution was reached at 80 °C, 1g of Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was added. The mixture was boiled until it changed to a light yellow colour paste. Then the paste was collected in a ceramic crucible and heated in an air atmosphere muffle furnace at 400 °C for 3 hrs. We got milk yellow colour powder then it was grained using pestle and mortar. Finally, sample was stored in properly labelled containers and used for further Characterization.

2.4 Characterization

UV–Vis Spectrophotometer (Shimadzu -1800) was used to obtain the absorption spectrum of the ZnO Nps wavelength is 200–800 nm. The purity and crystalline size were characterized by X-ray diffractometer (XPRT-PRO) using Cu-K α radiation of wavelength $\lambda = 1.541 \text{ \AA}$ of synthesized copper oxide nanoparticles. The FTIR spectra of plant leaf extract and synthesized zinc oxide nanoparticles were recorded by FTIR spectrometer KBr pellet method (in the range of 4000–400 cm^{-1})(Shimadzu). The morphology the synthesized ZnO NPs were observed by Field emission scanning electron microscopy (FESEM, Supra- 55, India) and the elemental composition by recorded using (EDX, BRUKER, India). The surface morphology studies were carried out using Atomic force Microscope (AGILENT N 9410 A– 5500).

2.5 Photocatalytic degradation of dye

The photocatalytic activity of biosynthesized ZnO nano particles was studied by degradation of methylene blue (MB) under solar irradiation. The dye solution was prepared by dissolving 1 mg powder of MB in 100 ml distilled water. 10 mg ZnO nanoparticles was added to 50 ml of prepared MB dye solution and the mixer was stirred magnetically for 30 min in shadow before exposing to sunlight. The colloidal suspension was then put under solar irradiation with constant stirring. The average temperature of the atmosphere during the experiment found to be 30 °C with 3.30 hrs mean shine duration. At every 30 min, 5 ml of suspension was collected from the colloidal mixer. The collected suspension was then scanned at different wavelength from 200 to 800 nm using the Shimadzu -1800, UV – Vis Spectroscope to study the dye degradation in presence of ZnO NPs.

III. RESULTS AND DISCUSSION

3.1 UV-Vis absorption spectroscopy analysis

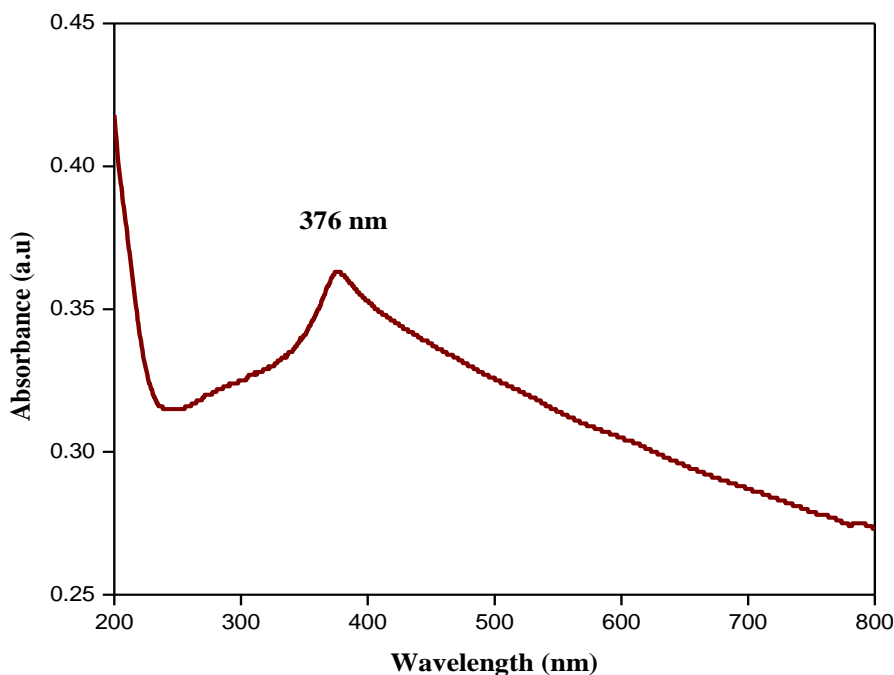


Fig. 1. UV – Vis spectrum of ZnO Nps.

Fig.1 depicts the absorption spectrum of the bio-synthesized ZnO NPs with the absorption peak around 376 nm. It indicates that ZnO NPs displays exciton absorption (at 376 nm) due to their large exciton binding energy at room temperature. The wavelength of 376 nm absorption peak confirms the occurrence of blue-shifted absorption spectrum with respect to the bulk value (377 nm) of the ZnO NPs, due to the quantum confinement effect, which is good agreement of the previous report [18].

3.2 X-ray diffraction analysis

XRD pattern of synthesized ZnO nanoparticles from leaf extract of *Pyrus Pyrifolia* is shown in Fig. 2. The ZnO NPs diffraction peaks clearly indicate highly crystalline structure. The sharp and narrow diffraction peaks appearing at about 2θ of 31.46, 34.29, 36.33, 47.51, 56.50, 62.84, 67.79 and 76.83 (deg) were assigned to (100), (002), (101), (102), (110), (103), (112) and (202) hkl plane values of ZnO nanoparticles. The peak intensity profiles were confirmed the hexagonal wurtzite structure by comparison with the data from JCPDS card No. 89-7102. The calculation of average grain size was attained by using Scherer’s Eq. (1).

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ \AA} \quad \text{----- (1)}$$

Where D is the average crystallite size in Å, K is the shape factor, λ is the wavelength of X-ray (1.5406 Å) Cu -Kα radiation, θ is the Bragg angle, and β is the corrected line broadening of the NPs. The average powder particle size calculated by Scherer’s equation was found to be 19.22 nm. The calculated values are listed in table 1.

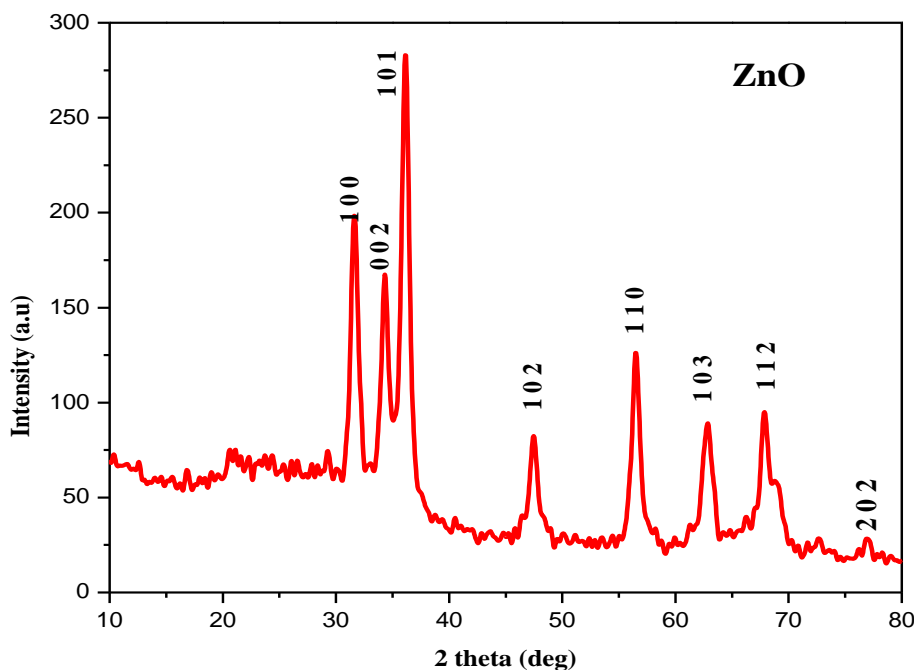


Fig. 2. XRD pattern of ZnO Nps.

Table 1. The structure and geometric parameters of ZnO Nps.

2θ (°)	FWHM (β)	d-spacing (Å)	Cos θ	Crystalline size
31.46	0.29	2.84	0.9625	29.21
34.29	0.39	2.61	0.9555	22.07
36.33	0.29	2.47	0.9501	29.59
47.51	0.59	1.91	0.9152	15.36
56.50	0.59	1.62	0.8808	15.96
62.84	0.78	1.47	0.8533	12.35
67.79	0.49	1.38	0.8300	20.32
76.83	1.18	1.24	0.7834	8.97
			average	19.22

3.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of ZnO nanoparticles synthesized by biological method, the FTIR measurement was carried through the wavenumber range from 400 to 4000 cm^{-1} using KBr pellet method at room temperature. Fig. 3(a) and (b) shows for bio-synthesis ZnO NPs and *P. Pyrifolia* leaf extract respectively. The absorption bands at 3747, 3340, 2927, 2362, 1645, 1431, 1066, and 522 cm^{-1} in *P. Pyrifolia* leaf extract would be shifted into 3751, 3435, 2924, 2362, 1635, 1473,

1022, and 447 cm^{-1} of synthesized ZnO NPs sample. The lower energy region peak appeared at 447 cm^{-1} showing the ZnO bond bending vibration.

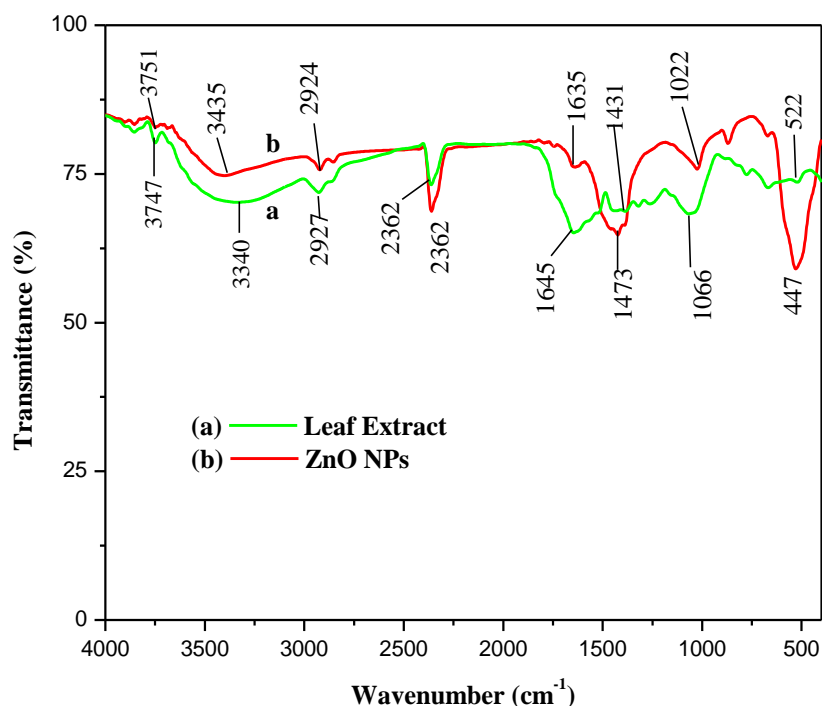


Fig. 3 FT-IR spectra of (a) leaf extract of *P. Pyrifolia* (b) Green synthesized ZnO Nps

The region between 400 and 600 cm^{-1} assigned to metal-oxygen. The FT-IR spectra exhibited the broad peak in higher energy region due to O–H stretching, H-bonded presence of alcohols and phenols around (3340, 3435 cm^{-1}). The vibration band arises at around (2927, 2924 cm^{-1}) C–H stretching and depicts the presence of an alkanes group [13, 18]. The medium and sharp peak region at around 2362 cm^{-1} presence of enol of 1, 3 diketone, -hydroxy aryl ketones. The absorption peaks at around (1645, 1635 cm^{-1}) vinyl, cis-tri substituted, mononuclear aromatics [19]. O – H Stretching vibrations polyols group present at (1431, 1473 cm^{-1}) [20]. Stretching vibrations are located at around 1066, 1022 cm^{-1} represent C – N stretching aliphatic amines.

FTIR spectrum wavenumber indicate the participation of polyols and having functional group alcohols, phenols, alkanes, diketone, -hydroxy aryl ketones, aromatics and aliphatic amines in bioreduction reactions.

3.3 FE – SEM with EDX analysis

After the substantiation of XRD result the sample was proceeded for the further FE – SEM with EDX studies. The size, shape and surface morphology of the ZnO nanoparticles are clearly indicated FE– SEM image as shown in Fig. 4 (a), the micrograph images of ZnO nanoparticles prove that they have granular nano sized range and have a uniform distribution with agglomerated particles of spherical shape [18]. The particle size ranges from 20 to 43 nm as shown in Fig. 4 (a). Energy Dispersive X-ray (EDX) spectrometer analysis is confirmatory presence of elemental Zinc and Oxygen signals of the ZnO NPs. The vertical axis displays the number of x-ray counts although the horizontal axis displays energy in KeV (Fig. 4b). The weight and atomic percentage of Zinc, Oxygen was found to be 67.65, 32.35 and 33.85, 66.15 these corresponds, the spectrum without impurities peaks.

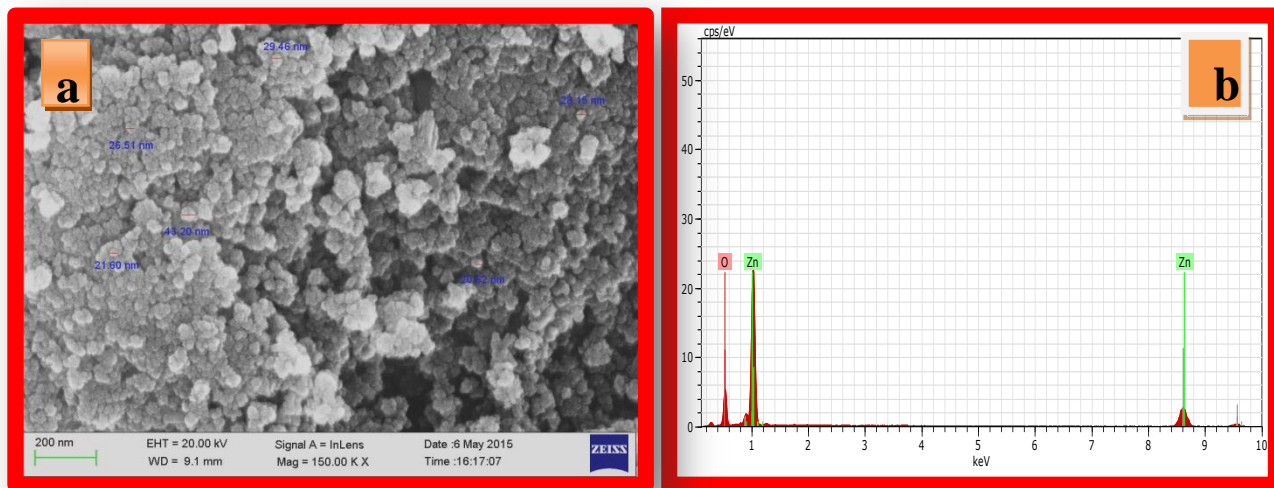


Fig. 4. (a). FE – SEM image of synthesized ZnO Nps, (b) EDX spectrum.

3.4 AFM analysis

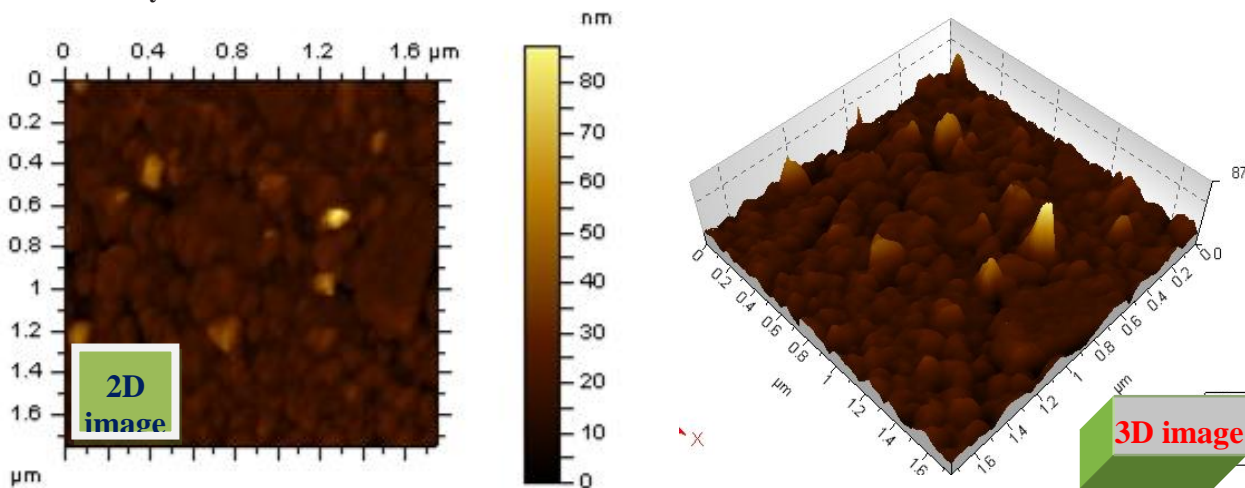


Fig. 5. AFM images show the particle size distribution of ZnO-NPs.

Fig.5. depicts the synthesized ZnO nanoparticles of 2D and 3D images. The Atomic force microscopy was executed to identify the topological appearance and the size range was found out around 87.2 nm rendering 3D profile. However, maximum surface particle size of the ZnO NPs affirmed within 45 nm. The (AFM) images were also used for the analysis of the fractal behaviour of the deposited and annealed films. Roughness, porosity and fractal dimension were evaluated by AFM image.

3.6 Photocatalytic activity

Photocatalytic activity of the biosynthesized ZnO Nps was evaluated by dye degradation of MB under sun light irradiation. Dye degradation was visually detected by gradual change in the colour from deep blue to colourless dye solution (depicts the Fig. 6). The characteristic absorption peak was found at 657 nm for pure methylene blue dye solution. The dye degradation in presence of bio synthesized ZnO nanoparticles was verified by the decrease of the

peak intensity at 657 nm during 3.30 hrs exposure in solar light shown in Fig. 7. the dye degradation (%) was calculated by using the following equation and its variant with the time of sun light exposure as shown in fig. 8.

$$\text{Dye degradation (\%)} = [C_0 - C_t / C_0] \times 100 \quad \text{----- (2)}$$

Where C_0 is the initial concentration of MB solution and C_t is the concentration of the dye solution after “t” hours in the sun light irradiation. All dye concentration absorption peaks at 657 nm were measured by UV – Vis spectroscopy.

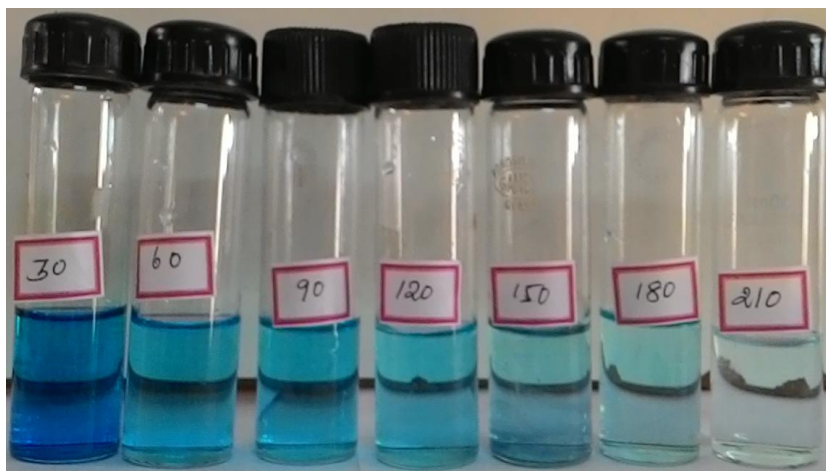


Fig. 6. Gradual change in dye colour from blue to colourless denotes dye degradation

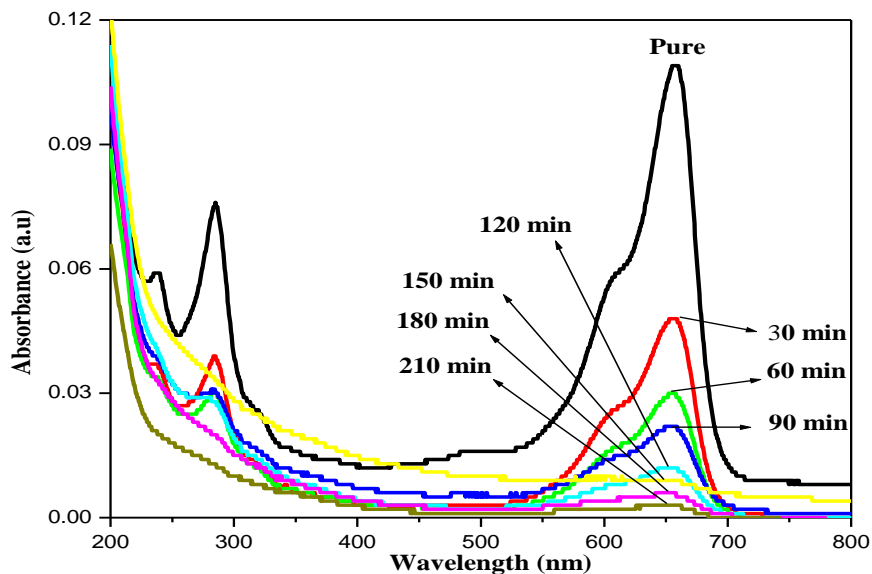


Fig. 7. Photocatalytic degradation of MB using ZnO nanoparticles synthesized from *P. Pyrifolia*.

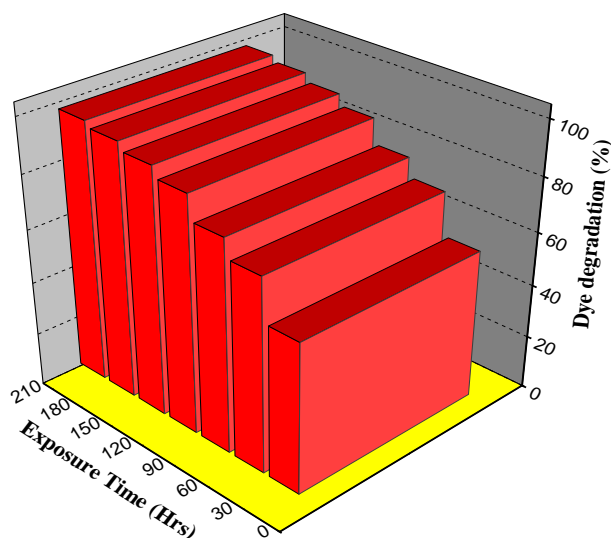


Fig. 8. 3D bar graph depicts the variation of dye degradation at different exposure time

IV. CONCLUSION

The bio synthesized metal oxide nanoparticles has emerged as a low cost, simpler and better choice than physical and chemical methods as it is fast, clean and friendly with environment. The synthesized ZnO Nps from zinc nitrate solution using *P. Pyrifolia* leaf extract and the biosynthesized ZnO Nps were found to be almost spherical in shape with particle size around 45 nm. The photocatalytic study concludes that these bio – ZnO Nps have efficiency to dye degrade MB under solar irradiation. Therefore, they can find application in water treatment plants and textile industries.

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