

Catharanthus roseus-mediated zinc oxide nanoparticles against photocatalytic application of phenol red under UV@ 365 nm

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***Catharanthus roseus* leaf extract has potential efficiency for the formation of biosynthesized zinc oxide (ZnO) nanoparticles against dye degradation with various time intervals. The leaves of *C. roseus* were utilized as reducing agent for the formation of metal precursors into metal oxide nanoparticles. *C. roseus*-mediated ZnO nanoparticles were confirmed by various analytical techniques such as UV-Vis, FT-IR, XRD and morphological studies by SEM and TEM. Results show that green synthesized ZnO nanoparticles are directly proportional to reaction time. The phytoconstituents present in leaf extract of *C. roseus* play a major role in ZnO nanoparticles formation by acting as a reducing agent.**

Keywords: Biological synthesis, *Catharanthus roseus*, leaf extract, zinc oxide nanoparticles.

In the emerging field of nanotechnology, nanoparticles (NPs) are considered as fundamental building blocks by the researchers¹. Size, shape and surface morphology of synthesized NPs play a vital role in various applications². Biologically synthesized NPs are cost-effective, non-toxic and environmentally benign³. Several physical and chemical methods are reported for the synthesis of zinc oxide (ZnO) NPs, which have mostly toxic to the environment⁴. Bio-nanomaterials have gained much attention especially in metal and metal oxide synthesis, which are potent in yielding uniform sized nanoparticles and also eco-friendly in nature^{5,6}. ZnO NPs are multi-tasking metal oxide⁷. They display specific electrical and optical properties which can be utilized for several applications⁸ such as sensing gas molecules⁹, solar coatings¹⁰, disease-resistant antibiotics¹¹ and UV degradation¹². ZnO NPs have a band width of 3.3 and 60 meV of energy binding with huge excitation¹³. Among several metal oxides that are studied with respect to anti-bacterial activity, ZnO

NPs are found to be toxic enough to result in apoptosis of various disease-causing pathogens¹⁴. However, their stability during harsh condition decreases its toxicity, increases the application as photocatalyst and food industries¹⁵⁻¹⁸. *Citrus aurantifolia* extract¹⁹, *Aloe vera* leaf extract²⁰ and milky latex of *Calotropis procera*²¹ are used as biomaterials for ZnO NPs synthesis. The secondary metabolites present in the plant extract promote and stabilize the NP formation²² by acting as capping agent to prevent agglomeration²³. The present study was designed in a simple, cost-effective, eco-friendly manner to synthesize ZnO NPs at an ambient condition using *C. roseus* leaf extract as reducing and stabilizing agent.

Experimental procedure

Plant collection

Fresh leaves of *C. roseus* (L.) G. Don were collected from Arcot (12°56'N; 79°24'E), Vellore district, Tamil Nadu, India. Collected leaves were subjected to authentication process in Tamil Nadu Agriculture University, Coimbatore (ref. no. BSI/SRC/5/23/2013-14/Tech.1117)²⁴ and kept in the herbarium until further study.

Resources required

Zn(O₂CCH₃)₂ and methanol were procured from Sisco Research Laboratory (SRL-India), phenol red dye was obtained from Hi-media (India) and used without further purification. Dye degradation study was carried out in U Wave-1000 Microwave-UV-US synthesis/extraction reactor.

Preparation of the extract

C. roseus leaves were collected, washed and air-dried under dark conditions. Leaves were ground into small

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pieces using a motor. Soxhlet extraction process was used to remove hydrocarbons from the plant material with petroleum ether followed by methanol. The solvents were distilled using a water baths; further the collected solvents were utilized as capping or reducing agent for the formation of metal NPs.

Synthesis of ZnO NPs

About 100 ml of 1 mM zinc acetate solution was made by adding double-distilled water. Then 80 ml zinc acetate was added to methanolic extract of 20 ml and placed in a stirrer at 60°C. Formation of ZnO NPs was examined at every 1 h with the help of UV-Vis spectroscopy.

Characterization

The synthesized metal oxide NPs using plant mediated bio-reductant and NPs formed were examined through UV-Vis spectrometer (Schimadzu model UV-1800). Using the Fourier transform infrared spectroscopy (FT-IR), the functional group of the secondary metabolites identified. X-ray diffractometer (XRD), atomic force microscopy (AFM), dynamic light scattering (DLS), Zeta potential, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were studied during the nanoparticle analysis.

Dye degradation

Photocatalytic degradation was carried out with biologically synthesized ZnO NPs. Dye degradation was done using 2 ml eppendorf in which 1 ml (1×10^{-4} M) of toxic dye, i.e. phenol red was added to 0.25 mg of ZnO NPs. The ZnO NPs with dye were kept in the presence of UV irradiation light source @ 365 nm wavelength and various aliquots were collected in different time intervals. After each incubated time interval, samples were centrifuged at 1000 rpm. Supernatant was collected and monitored by UV-Vis spectrometry to estimate the residual dye.

Results and discussion

ZnO NPs that are formed were monitored using UV-Vis spectrometry at every 1 h interval. The effect of time was observed in UV-Vis band. At 3 h interval we can clearly visualize a high absorbance band. As time increases, the intensity of the colour (green) fades out and become pale which confirms the conversion of metal salt to metal oxide nanoparticles. The obtained results indicate that the time duration for optimization of reaction for ZnO NPs formation is 3 h (Figure 1).

Using FTIR result the functional group has been identified. The peaks around 1091 and 3458 cm^{-1} are due to O-H stretching and deformation (Figure 2). The peaks at 1639 and 621 cm^{-1} correspond to Zn-O stretching and deformation vibration.

The crystalline patterns of the synthesized ZnO NPs were identified using XRD spectrophotometer and also matched with JCPDS data of 89-1397. With the help of Scherrer formula, the synthesized ZnO NPs were confirmed to be in crystalline form (Figure. 3). Using full width at half maxima (FWHM), the average particle size was calculated to be 38 nm. Figure 3 indicates the peak (***) of compounds that may act as secondary metabolites.

$$\text{Particle size } P = k\lambda/\beta\cos\theta,$$

where k is the constant derived by Scherrer's formula (0.94), λ the value obtained from Bragg's equation of ($2d\sin\theta = n\lambda$), λ is wavelength, β the full width at half maximum and θ is the diffraction angle.

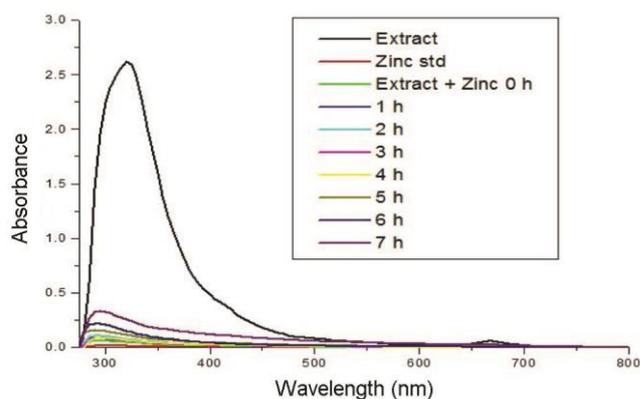


Figure 1. UV-visible spectrum of ZnO nanoparticles.

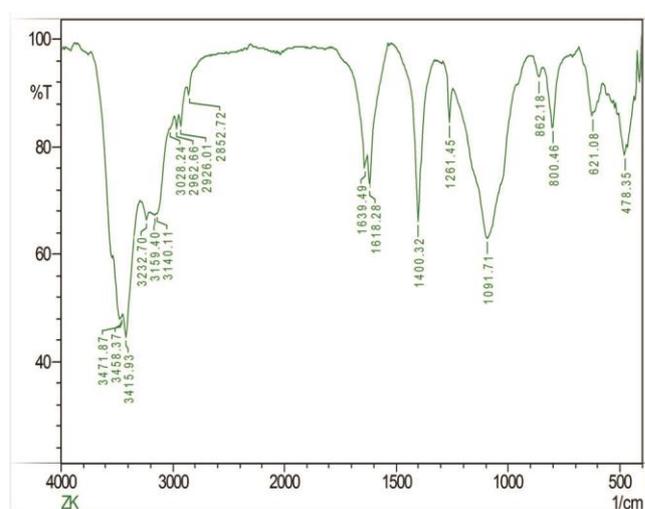


Figure 2. FT-IR of ZnO nanoparticles.

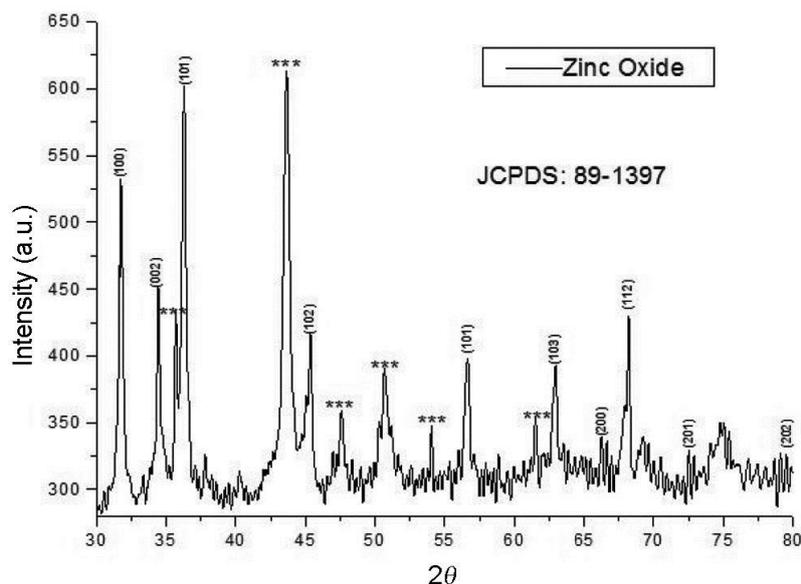


Figure 3. XRD pattern of ZnO nanoparticles.

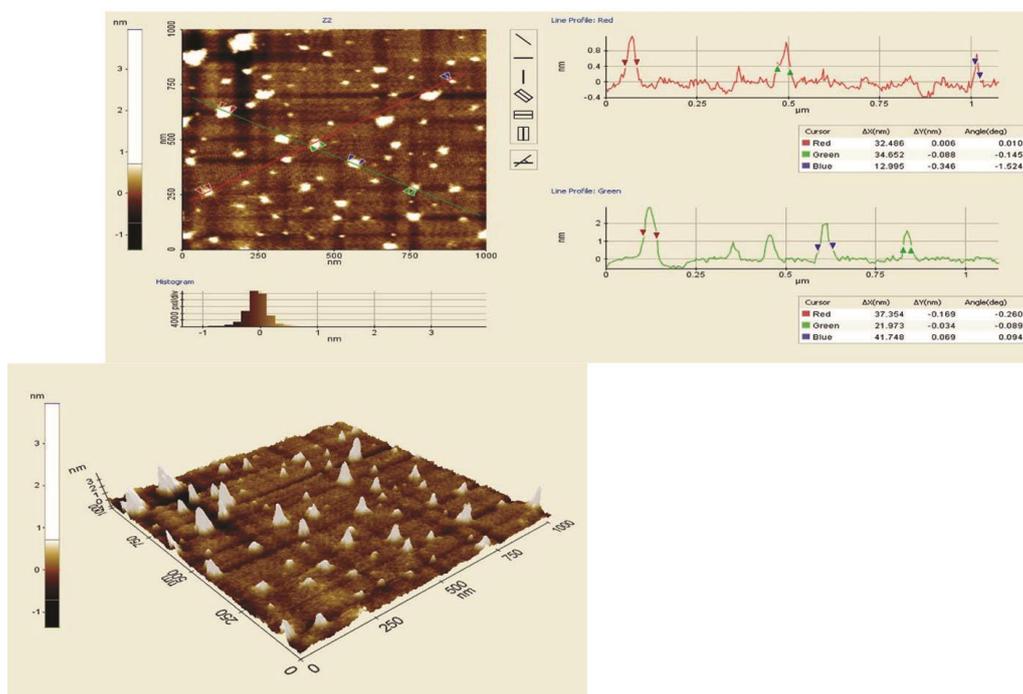


Figure 4. AFM 2D and 3D images of ZnO nanoparticles.

AFM was used for morphological analysis of green synthesized ZnO NPs. The size and shape were calculated by AFM measurements (Figure 4). The average particle size of ZnO NPs was 21.97 nm.

The size of synthesized NPs was measured using DLS and zeta potential was found using nano ZS series (Malvern). DLS is used for measuring the average mean particle size known as ‘z-average’ diameter (d_z)²⁵. At room temperature measurement was done for 5 min to obtain

z-average particle size of ZnO NPs. The hydrodynamic diameter of the synthesized ZnO NPs was 287.0 (nm) z-average particles (see [Supplementary material online](#)). The zeta potential of the methanolic synthesized metal oxide nanoparticles was -50.5 mV.

SEM analysis reveals the shape of the ZnO NPs and EDAX analysis confirms the elemental composition of the metal oxide NPs. The photomicrographs of SEM analysis of ZnO NPs were around 98–110 nm (see

[Supplementary material online](#)). The EDAX image shows the peaks with elemental composition as 84.75% of the zinc and 15.25% of the oxides.

The synthesized ZnO NPs were further subjected to TEM which resulted in a size of 10–50 nm (Figure 5 a). The image was recorded by dissolving the synthesized ZnO NPs in ethanol and a small drop was placed in a copper grid surface for analysis. The selective area electron diffraction (SAED) shows that there is uniform distribution of the particles (concentric set of rings) (Figure 5 b).

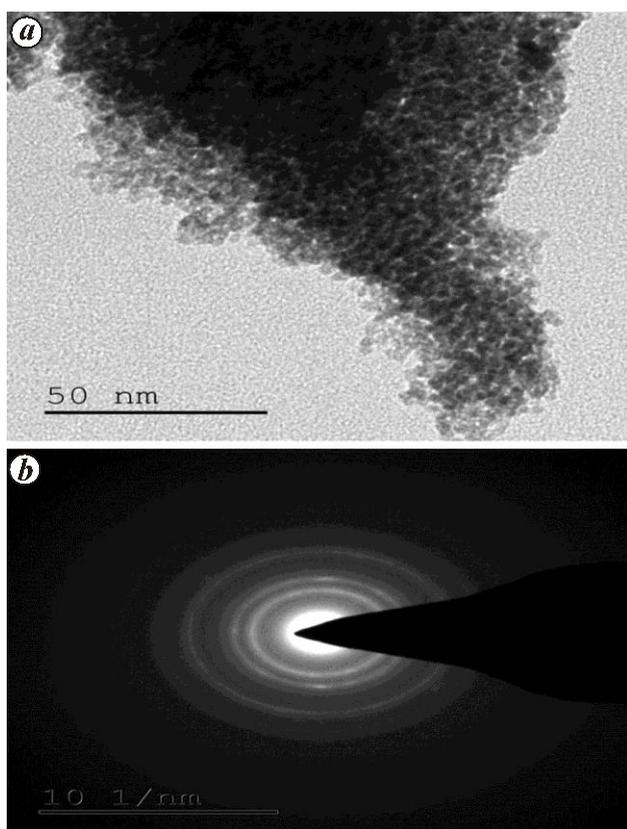


Figure 5. a, TEM; b, SAED patterns.

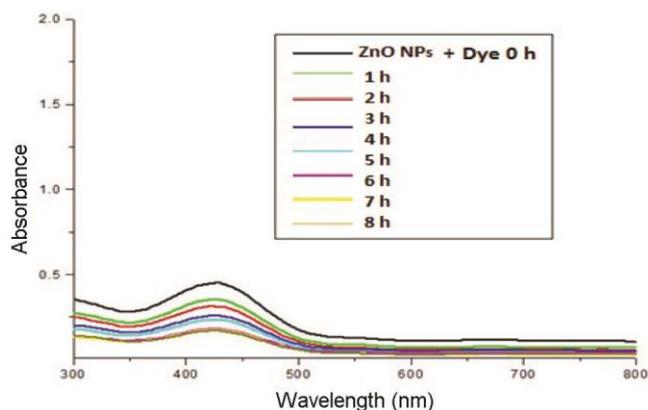


Figure 6. Dye degradation using ZnO nanoparticles.

The dye degradation process was carried out using optimized ZnO NPs with phenol red dye. One millilitre of phenol red dye was mixed with 0.25 mg of synthesized ZnO NP dispersions with different aliquots at various time intervals and kept under UV irradiation light source @ 365 nm wavelength. The absorbance range was taken from 200 to 800 nm (Figure 6). At the eighth hour, clear surface plasmon resonance (SPR) was observed. Thus the optimum duration for effective dye-degradation is 8 h.

Conclusion

In this study, *C. roseus* leaf methanol extract was used for the synthesis of ZnO NPs from zinc acetate. It is an eco-friendly approach to reduce chemical toxicity and biological method was adopted using methanol extract as reducing agent that reduces $[\text{Zn}(\text{OAc})_2]$ to ZnO NPs. The average particle size was found to be 38.2 nm. The secondary metabolites that are present in the plant material may be responsible for the formation of ZnO NPs by acting as a reducing agent. The optimized time for synthesis of ZnO NPs was 3 h. Further, dye degradation study was carried out using phenol red. It was found that ZnO NPs effectively degrade the dye at an optimum duration of 8 h taking into account.

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