Green synthesis, characterization and catalytic applications of zinc oxide nanoparticles

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Abstract
Zinc oxide nanoparticles UV rays filtering properties, semiconducting property, unique antimicrobial and wound healing property are of greater significance which make it a worthy catalyst in several synthetic and photochemical aspects. Hence it is planned to synthesize Zinc Oxide nanoparticle in an ecofriendly and greener path by using Solanum xanthocarpum berry extract. The bio-synthesized nanoparticles were characterized by XRD, SEM with EDX, TEM, FT-IR, PL and DRS techniques. The green synthesized ZnO nanoparticle was studied for its ability towards photodegradation of Methyl green dye (MEG) under various parameters along with the UV - light radiation at 365nm.

The mechanism of dye degradation in UV–light explained higher photocatalytic activity of catalyst. The catalyst was found to be stable and reusable without appreciable loss of catalytic activity up to four cycles. The study was further extended to electrochemical study from DSSCs and CV analysis which revealed marked increase in current by bio derived ZnO nanoparticles.

Keywords: Solanum xanthocarpum berries, methyl green, photodegradation, electrochemical activity.

Introduction
Among diverse metal oxides, ZnO nanoparticles have attained a remarkable place because of its outstanding antimicrobial, wound healing, application in dye sensitized solar cells (DSSC), UV filtering properties (cosmetics), valuable catalytic (organic synthesis) and photochemical degradation activity. It is from several years back, plants and different natural sources have come up as a low cost, energy-efficient, eco-friendly and non-toxic approach for the synthesis of nanomaterials. The green synthesized nanoparticles were found to have the advantage of polydispersity, dimensional stability in turn to its lesser synthesizing cost.

It was found that the combination of nanoparticles utilizing plants or parts of plants can demonstrate much valuable over other organic procedures by dispensing with the detailed procedures of maintaining cell cultures which can further be correctly scaled up for large nanoparticles synthesis.

Several studies have been made and are available in literature regarding the greener synthesis of ZnO nanoparticles with Zn(CH$_3$CO)$_2$.2H$_2$O as a precursor and extracts prepared from several parts of plants as medium for example, Corriandrum Sativum, Calotropis procera, green coloured Caulerpa peltata, red coloured Hypnea valencia and brown coloured Sargassum myriocystum, squeezed orange, Calotropis procera latex, aqueous leaf extract of Acalypha indica, and Calotropis gigantea leaf extract.

India is one of the crude material-delivering countries of South Asia. Phytochemical studies of Solanum xanthocarpum revealed that various parts of this plant are found to contain alkaloids, phenolics, flavanoids, sterol, saponins and their glycosides. All of these were found to have a wide variety of therapeutic values. Solanum xanthocarpum upon extraction provides natural organic substance solanocarpidine and a sterol, carpesterol.
Root was found to contain one of the constituents of Dasamulasava. Seeds are used as diuretic. Juice of berries is found to be good for treating sore throat. A decoction of the plant is used as a cure for gonorrhea and it as well said to promote conception in females. Respiratory diseases like kasa roga (hack) and tamkwasa (bronchial asthma) were also found to be cured by this Solanum xanthocarpum which is popularly called as kantakari in south India. In Chhattisgarh, it is considered as a most vital herb for traditional healers in treatment of more than 100 common diseases by itself or in combination with other nearby and striking herbs. They are of numerous applications in many fields including biological, inorganic and analytical Chemistry.

It is because of the better yield and excellent selectivity utilization of heterogeneous catalysts in numerous organic synthetic reactions becoming trending, moreover it is because of the possible reason that they can perform an environmentally benign synthesis. Major factors might be large surface area offered, less coordinating sites, huge atom efficiency, simple product purification and good reusability. Different morphologies and a wide range of particle sizes for ZnO have led to diverse investigations in academic and industrial societies.

In this present examination we prepared ZnO nanoparticles by a green and minimal cost technique utilizing berries of Solanum xanthocarpum. This technique is actually favorable for preparation of very much described nanoparticles without usage of cruel, poisonous and costly chemicals. In addition, this method is considered to be more significant since it is cost suitable. Other than the green synthesis, it is to explore the catalytic action of ZnO nanoparticle against the Methyl green dye (MEG) because of its enhanced photocalysis in presence of UV radiation and study the electrochemical activity of these bioderived ZnO nanoparticles using DSSCs and Cyclic voltammograms.

**Material and Methods**

**Materials:** Materials used for the synthesis of ZnO nanoparticles are Zinc nitrate [Zn(NO₃)₂·2H₂O], Methyl green (MEG) dye, Isopropanol (2 mL), Acetic acid (1 mL) and all chemicals were purchased from Merck, India and used without further purification.

*Solanum xanthocarpum* is a herbal plant which was found in cultural lands and waste lands. *Solanum xanthocarpum* berries were collected in and around Chidambaram, Cuddalore district, Tamil Nadu, India. *Solanum xanthocarpum* berries were washed, shade dried and finely powdered. 100g powder was suspended in 250 ml of water for two hours and then heated to 60-65°C for 30 minutes. The extract was collected separately and the processes were repeated thrice with the residual powder, each time the extract was collected. The collected extracts passed through a fine cotton cloth. The filtrates were evaporated at 40-50°C under reduced pressure. The dark semisolid material (yield-14%) obtained was stored at 0-4°C for further usage. The chemical structure of methyl green dye and *Solanum xanthocarpum* berry is shown in the figure 1a and 1b.

**Preparation of ZnO nanoparticles by chemical and greener methods:** Chemical synthesis of ZnO nanoparticles is done by the precipitation technique. 5 grams of Zinc nitrate was added along with the solvents Isopropanol (2 mL) and Acetic acid (1 mL). The mixture was rapidly stirred at room temperature and distilled water was added drop wise to obtain precipitate. Then the precipitate was collected and dried in an oven at 100ºC for 12 hours. It was then air dried and calcined at 400ºC for 2 hours in order to obtain the ZnO nanoparticle.

Bio-derived ZnO nanoparticles were prepared by heating 20 ml of aqueous solution containing 5 gms of Zinc nitrate in a stirrer hotter, when the temperature reaches 60ºC, 50 ml of the Solanum xanthocarpum berry extract was added to the Zinc nitrate solution with constant stirring. This mixture is then bubbled until it condensed to yellow colored paste. The paste thus obtained was collected carefully in a ceramic crucible which was further heated to 400ºC in an air heated furnace for 2 hours. A light white shaded powder was obtained and it was meticulously accumulated and stuffed for characterization and used as a nanocatalyst. The material was pounded into particles of desirable size in mortar with a pestle to get better sized nanoparticles for further studies. Scheme of preparation of bioderived ZnO Np’s is shown in figure 2.

**Characterization:** Ultraviolet and visible (UV-vis) absorbance spectra were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length. HR-SEM and EDX evaluation experiments were performed on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25ºC. XRD spectrum was recorded on the XPERT PRO model X-ray diffractometer from Pan Analytical instruments operated at a voltage of 40 kV and also a current of 30 mA with Cu Ka radiation.
The nanoparticles size and structure verifications were done by HR-TEM making use of Philips CM200. Each spectrum was recorded with an acquisition time of 18s. PL spectra at room temperature were recorded using a Perkin-Elmer LS 55 fluorescence spectrometer. UV spectral measurements were done using a Hitachi-U-2001 spectrometer.

Ultraviolet and visible (UV-vis) absorbance spectra were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length.

The Photovoltaic properties were characterized by the photo current voltage (I-V) curve under illumination of A.M.1.5 (100Mw/cm²). Cyclic voltammetry (CV) measurements were carried out using CHI 60 AC electrochemical analyzer.

**Photocatalysis:** The photocatalytic activities of the photocatalysts (Chemically synthesized ZnO and bio derived ZnO nanoparticles) were evaluated by the photodegradation of dye. The light source was UV lamp at 365 nm. The reaction was carried out at an ambient temperature (303 K). The experimental solution consists of an aqueous suspensions of dye (40 mL, 1×10⁻⁵ M) and 0.150 g of photocatalyst was loaded in reaction tube of 50 mL capacity and 60 minutes of irradiation in prior, suspension was magnetically stirred in dark to ensure the establishment of an adsorption/desorption equilibrium.

The suspension was kept under constant air-equilibrated condition. At the regular intervals of irradiation time, the suspension was measured spectrophotometrically with a quartz cell with 10 mm of optical path length.

**Results and Discussion**

**Characterization of ZnO nano particles**

**Optical absorption:** UV visible absorption spectra were examined by dispersing nano catalyst in highly pure state at room temperature. Figure 3 shows the UV absorption spectra of plant mediated synthesized ZnO, a peak was observed at a wavelength of 370 nm. This is in good agreement with the previous work².

**XRD Analysis:** XRD diffraction pattern of bioderived ZnO nanoparticles is shown in figure 4. It is found that there exist strong diffraction peaks with 20 values of 31.73°, 36.23°, 47.48°, 56.58°, 62.83° and 67.88° corresponding to the crystal planes of (100), (101), (102), (110), (103) and (112) respectively.

All diffraction peaks of sample correspond to characteristic hexagonal wurtzite structure of zinc oxide nanoparticles. Similar, X-ray diffraction pattern has been reported in earlier studies¹⁵-¹⁷. Using the Debye-Scherrer formula \( L = 0.89 \lambda / \beta \cos \theta \) where \( L \) is the crystalline size (nm), \( \lambda \) is the wavelength (nm), \( \beta \) is the full width at half maximum intensity (FWHM-in radian), and \( \theta \) is the Bragg diffraction angle (°), the average crystalline size of bio-derived ZnO NPs is found to be 20 nm. Diffraction patterns corresponding to impurities are found to be absent. This proves that pure ZnO nanoparticles were synthesized from the Sx berry extract.

**Fig. 3:** Uv-visible spectra of bio-derived ZnO NP

**Fig. 4:** XRD of bio derived ZnO nanoparticles

**HR-SEM with EDX analysis:** The surface morphology and size of the bio-synthesized zinc oxide nanoparticles were analysed using a High-Resolution Scanning Electron Microscope (HR-SEM) image.

ZnO nanoparticles in individual as well as number of aggregates were seen clearly from the HR – SEM image¹⁸. The chemical purification and their stoichiometry were tested by EDX studies. Figure 5a shows that particles are predominantly spherical in shape and are aggregated into larger particles with no well-defined morphology. As shown in figure 5b, zinc and oxygen are the only elementary components of the prepared nanoparticles.

**HR-TEM analysis:** High-resolution transmission electron microscope measurements of bio derived ZnO nanoparticles are shown in figure 6a. It is established from the figure that presence of particles is also depicted from HR-TEM
micrographs of the mixed nanomaterial of 50 nm in size and spherically shaped, hexagonal structure. Figure 6b represents an image profile, figure 6c represents the plot profile of bioderived ZnO nanoparticles and figure 6d indicates the particle size distribution (0.725 nm) with a selected particle area highlighted.

**Fig. 5a:** 29 HR- EM of bio derived ZnO NP’s

**Fig. 5b:** 29 EDX analysis of bio derived ZnO NP’s

**Fig. 6a:** HR-TEM of Bio-derived ZnO NP’s

**Fig._6b:** Image_profile_of_ZnO_NPs

**Fig. 6c:** Plot profile of ZnO NPs

**Fig. 6d:** Particle size distribution

**FT-IR analysis:** FT-IR spectrum of ZnO nanoparticles from *Solanum xanthocarpum* berry extract shows a band at 619 cm\(^{-1}\) assigned to the stretching vibration of (Zn–O) bond. The broad band with low intensity at 3422 cm\(^{-1}\) is due to vibration mode of (OH) group, indicating the presence of water in trace adsorbed by the ZnO nanoparticles. Figure 7 shows FT-IR of bio-derived ZnO nanoparticles.
**PL analysis:** The photoluminescence spectra of chemically synthesized ZnO nanoparticles and bioderived ZnO nanoparticles from *Solanum xanthocarpum* berry extract were shown in the figure 8a and 8b. As photoluminescence occurs due to electron–hole recombination, its intensity is proportional to the rate of electron–hole recombination. The recombination of electron and hole pairs releases energy in the form of PL emission. In the case of bioderived ZnO nanoparticles, low electron and hole recombination rate imply a lower luminescence emission intensity and there by higher photocatalytic activity[19,20].

**UV-Visible DRS Spectrum:** The UV-visible DRS Spectrum of chemically synthesized ZnO and biosynthesized ZnO nanoparticles shows that Zn$^{2+}$ ion covalently interact with the synthesized ZnO nanoparticles and decrease its band gap. Bio-synthesized ZnO nanoparticles caused a red shift in absorption edge. The analysis was made with the diffused reflectance spectroscopy and the results obtained were transformed in to the Kubelka-Munk function F(R) to hole. From the plot of modified Kubelka – Munk function vs the energy of the absorbed light (E), the band gap energy was obtained. The plot is shown in figure 9 a and b.

\[
\frac{(F(R)E)^{1/2}}{2R} = \frac{(1-R)^{1/2}}{2R} \nu
\]

Plot results obtained indicate that band gap energy of the chemically synthesized ZnO NP’s and biosynthesized ZnO NP’s are 3.44 eV and 3.2 eV correspondingly. The lower band gap energy is found to be more supportive for higher photocatalytic activity[21].

**Effect of solution pH:** The photo degradation of MEG dye is obtained by using bio-derived ZnO nanoparticles between the pH of 3 – 9 under UV- light irradiation at 365 nm shown in figure 10a. It shows MEG dye degradation as a function of irradiation time under acidic and alkaline conditions. The pH of dye solution was adjusted with dilute NaOH and HCl.
It was observed that increase in pH from 3 was found to increase the removal efficiency of MEG dye up to a pH of 7 and further increase in pH tends to decrease the removal efficiency by the bioderived ZnO nanoparticles. From this, it is inferred that the pH of the solution also affects the degradation of MEG dye. Above pH 9, the photocatalytic degradation of MEG was found to decrease rapidly. Thus, it was observed that higher photocatalytic degradation is observed at pH 7.

**Photodegradation of MEG with artificial UV light:** The photodegradation of MEG in aqueous medium in the presence of catalytic loading (0.150g) and atmospheric air is studied using multi lamp photoreactor with mercury UV lamps of wavelength 365 nm. The reference wavelength of MEG reaction solution is 665 nm. Originally, the dye concentration (1x10^{-4} M) was dark blue in color after catalyst loading with the UV-light irradiation, the color of the solution becomes colorless within 60 minutes.

![Figure 9a and 9b: UV-Vis DRS analysis Plot of Kubelka Munk versus energy of the light absorbed of the Chemically synthesized ZnO nanoparticle and bio-derived ZnO nanoparticle](image)

At a time interval of 20 minutes, the absorbance is recorded. The comparative study of the photocatalytic activity of chemically synthesized ZnO and bio-derived ZnO nanoparticles for photodegradation as well as decolourization of MEG by varying pH from 3 – 9 is shown in figure 10a. The Bio-derived ZnO NP’s exhibited higher photocatalytic activity for MEG under UV-light irradiation compared to that of Chemical synthesized ZnO inferred from the figure 10b.

![Figure 10a: Effect of pH](image)

**Fig. 10a:** Effect of pH

**Fig. 10b:** Photodegradation study of MEG under UV-light irradiation at 365 nm by Bio-derived ZnO nanoparticles

**Effect of catalyst loading:** Different catalyst loading of Bio-derived ZnO nanoparticles on MEG in the range of 0.100 g, 0.150 g and 0.200 g, is shown in figure 11a. The results revealed that the increase of catalyst loading increases the degradation rate due to increased catalytic surface area which enhances number of active sites.

On increasing the weight of catalyst loading, the degradation was found to be low; this may be due to the aggregation of Bio-derived ZnO nanoparticles that cause a decrease in the number of active sites, increase the cloudiness and light scattering of Bio-derived ZnO nanoparticles. This tends to decrease the passageway of irradiation through the sample.

The catalyst loading of 0.150 g showed optimum activity when compared to other catalyst loadings.

**Effect of concentration change of MEG:** MEG dye of two different concentrations (1 x 10^{-4} and 2 x 10^{-4}M) was treated
with the bio-derived ZnO nanoparticles and investigated for photocatalytic degradation under UV light irradiation at 365 nm. The photodegradation results were plotted and the plot thus obtained was expected to show high degradation because of increased concentration (2 x 10^{-4}M) of MEG dye i.e. more molecules of MEG will be available for degradation.

However, on increasing the concentration above 1 x 10^{-4}M, the reaction rate was found to decrease. This might be because of the increased number of MEG dye molecules may act as a filter for the incident light, preventing a sufficient intensity of light from reaching the dye molecule in the bulk of the solution\textsuperscript{26,27}. So the photodegradation of MEG was best in lesser concentration of the order of (1x10^{-4}M), in comparison to the high concentration (2x10^{-4}M) of it. The comparison of the effect of MEG dye concentration change is shown in figure 11b.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure11.png}
\caption{(a) Effects of catalyst loading\hspace{1cm} (b) Effect of BMEG D dye change under UV-light irradiation at 365 nm by Bio-derived ZnO nanoparticles}
\end{figure}

**Reusability of the catalyst:** One of the best and renowned advantage of nanomaterial is stability and reusability. The reusability of Bio-derived Zinc Oxide nanoparticles towards photodegradation was tested by using them in four successive cycles of MEG photodegradation under UV- light irradiation at 365nm. The results are shown in figure 12. For I and II cycles in 60 minutes, 100% degradation was achieved, but for III cycle it was 98 %. Anyhow there is no considerable loss in activity of the catalyst up to III and IV cycles i.e. the catalyst is found to be stable and reusable.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure12.png}
\caption{Stability and Reusability on MEG dye degradation B BMEG D 3D 1x10-4 M % 2C 40 mL pH 3D7% 3B catalyst loading % 3D 0.150 g and UV-light irradiation for % 3D 60 min by Bio-derived ZnO nanoparticles}
\end{figure}

**Mechanism for photocatalytic effect of Bio-derived ZnO nanoparticles:** On the basis of these observations, a tentative mechanism for photocatalytic degradation of methyl green dye is proposed as follows:

1\textsuperscript{MEG}_0 + h\nu \rightarrow 1\textsuperscript{MEG}_1 \tag{2}

1\textsuperscript{MEG}_1 + ISC \rightarrow 3\textsuperscript{MEG}_1 \tag{3}

ZnO NP’s + h\nu \rightarrow e^- + h^+ \tag{4}

- OH + h^+ \rightarrow \cdot OH \tag{5}

\cdot OH + 3\textsuperscript{MEG}_1 \rightarrow \text{Leuco MG} \tag{6}

\text{Leuco MEG} \rightarrow \text{Products} \tag{7}

Methyl green absorbs radiation of desired wavelength and it forms excited singlet state, it undergoes intersystem crossing (ISC) to give its more stable triplet state.

Bio-derived ZnO nanoparticles from Sx also utilize this light to excite its electron from valence band to the conduction band. The semiconductor generates \cdot OH radical because of the abstraction of an electron from OH\textsuperscript{-} ion by a hole (h\textsuperscript{+}) present in the valence band of semiconductor. This hydroxyl radical in turn will oxidize methyl green to its leuco form, which may ultimately result in the formation of degraded products. It was confirmed that the \cdot OH radical participates as an active
oxidizing species in the degradation of methyl green as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger (2-propanol)\textsuperscript{21}. The mechanism of this dye degradation may involve the following reaction as shown in scheme 4.

\[
\text{Organic dye} + \text{OH}^- \rightarrow \text{Mineral acids} + \text{CO}_2 + \text{H}_2\text{O}
\]

**Cyclic voltammogram (CV):** Chemically synthesized ZnO and bioderived ZnO nanoparticles are used to modify electrode by construction through the mechanical attachment\textsuperscript{24}. Figure 13 shows the cyclic voltammogram of unmodified/modified glassy carbon electrode on the electrochemical oxidation/reduction potential.

The glassy carbon electrode was made with prepared photocatalyst, it gives enrichment or decrement in the cycles. The mashed amid chemically synthesized ZnO modified glassy carbon electrode (GCE), upon investigation showed that the electrochemical oxidation of KCl is an irreversible process with a suitable peak [anodic current and the (Epa) peak potential of 0.0233 V and \(i = 1.627 \times 10^{-5} \text{A}\)]. In the bio-derived ZnO nanoparticles modified glassy carbon electrode, the results proved to be a well-defined reducing glassy carbon electrode showing that electrochemical redox reaction of KCl is a reversible process [enhanced anodic current and the (Epa) peak potential of 0.350 V, and \(i = 3.334 \times 10^{-5} \text{A}\)].

Bio-derived ZnO nanoparticles modified glassy carbon electrode had larger adsorption–desorption and high electrochemical reaction than that of chemically synthesized ZnO nanomaterial modified glassy carbon electrode. GCE modified by metal ion and carbon materials is created to achieve better results in comparison to a bare GCE\textsuperscript{28,29}. The result thus suggests that the occurrence of Zn metal oxide nanoparticles could increase current and improve the relative electron transferred by Bio-derived ZnO nanoparticles.

**Photovoltaic properties:** Fig. 14 shows the photo current voltage (J-V) characteristics of the dye Sensitized Solar cell (DSSCs). The chemically synthesized ZnO and Bio-derived ZnO nanoparticles to act as photoelectrode are coated on Fluorine doped Tin oxide (FTO) plate as glass substrate. The routine solar cell is fabricated with chemically synthesized ZnO and bio-derived ZnO nanoparticles separately along with Ruthenium dye (535-bisTBA, N719).

From the data, it is clear that bio-derived ZnO nanoparticles based cell give the most brilliant performance with the use of dye as sensitizer resulting with highest value of short-circuit current density, \(J_{sc} (3.5 \text{ mA/cm}^2)\), open-circuit voltage, \(V_{oc} (500 \text{ mV})\), fill-factor, FF (0.94) and efficiency, \(\eta (1.7\%)\). It is observed that the effectiveness of bio-derived ZnO doped photoelectrode based cell is much higher than chemically synthesized ZnO\textsuperscript{30-32}.

**Conclusion**

In summary, we have developed a new green, simple, and efficient methodology for the synthesis of Schiff base derivatives with high product yield and excellent selectivity, using biologically synthesized Zinc oxide using berry extract of *Solanum xanthocarpum* as a cheap and effective catalyst.

Biologically synthesized ZnO nanoparticles are unique catalyst among all other reported catalysts considering conversion percentage, environmental safety, stability, reaction time, catalyst mole percentage, and reusability. The mild reaction conditions, easy work-up and clean reaction profiles render this approach as an interesting alternative to the existing methods.
The photodegradation efficiency was analyzed by the chemically synthesized ZnO and bio derived nanoparticles employing various experimental parameters such as effect of pH (increases and then decreases), the catalyst loadings of 0.150 g loading showed optimum photocatalytic activity when compared to others. Concentration 1x10⁻⁴M has high photocatalytic activity than that of 2x10⁻⁴M and catalysis was stable and reusable on the degradation of MEG dye. The bioderived ZnO NP’s were employed in photovoltaic property of the Dye Sensitized Solar Cells (DSSCs) and a high activity was observed. The cyclic voltammogram (CV) result showed increase of current and improved relation of electron transfer compared to that of chemically synthesized Zinc oxide nanoparticles.

References
10. Neelapu Neelima, Naikwadi Gajanan Devidas, Muvvala Sudhakar and Jadhav Kiran V., Preliminary phytochemical investigationon the leaves of Solanum xanthocarpum,


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