



BIOMEDIATED SYNTHESIS OF ZNO NANOPARTICLES (ZNONPS) FOR PHOTOCATALYTIC APPLICATION

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Abstract— In this paper, we have worked on synthesis of ZnO nanoparticles (ZnONPs) by biological method and its application as a photocatalyst also has been investigated. Sechium edule extract exhibited quick formation of ZnONPs at near room temperature. X-ray diffraction patterns of synthesized ZnONPs and ZnO as a reference compound were well in accordance. FTIR spectra of ZnONPs displayed similar stretching vibration of Zn-O, however, the intensity was somewhat less except the surface -OH group. The photocatalytic activity of ZnONPs was tested for oxidative cleavage of a cationic dye under the spectrum of visible light.

Keywords— ZnONPs, Biosynthesis, Photocatalyst

I. Introduction

Zinc oxide (ZnO) is a wideband gap semiconductor of IIVI group with band gap energy of 3.37 eV and binding energy of 60 meV. ZnO has several favourable properties like high electron mobility, good transparency and high temperature luminescence. These have made ZnO an attractive precursor in different applications include gas sensors [1], nano generators [2], luminescent material [3], solar cells [4], optoelectronics [5], biosensors [6], photodetectors [7], photocatalyst [8] antibacterial material [9] and catalyst [10].

There are several methods for synthesis of ZnONPs such as vapor phase transparent [11], wet chemical [12], direct precipitation [13], chemical microemulsion [14], hydrothermal

[15], solvothermal [16], microwave assisted combustion [17], chemical [18] and sonochemical [19] processes. Almost all the processes either suffer from utilization of corrosive & costly chemicals or high energy consumption.

Currently, green synthesis of nanoparticles is gaining importance due to its inexpensive, simplicity and environmental-friendly nature. Biosynthesis of ZnONPs by plants such as maffle leaves [20], calotropis procera [21], aloe barbadensis miller [22] and bacteria [23] have been reported in literature very recently. Chayote squash also known as Sechium edule, is an abundantly grown local vegetable in the north eastern part of India. It is popularly eaten by the local people and the price is relatively cheaper. Chayote contains a large amount of natural antioxidants and amino acids along with polyphenolic compounds, like phenylalanine and tyrosine [24]. It could be a potential reducing agent due to presence numerous -OH groups [25].

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II. Experimental Section

A. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (purity, 99.5% w/w), KBr (purity, 99.5% w/w) and Brilliant green (BG) dye (purity, 90% w/w)

were obtained from Merck, India., ZnO (purity, 98.0% w/w) was procured from Loba Chemie, India. Ethanol (purity, 98% v/v) was purchased from Changshu Yangyuan Chemical, China. Deionized water (DI) (Millipore, filtration unit (USA), model: Elix-3) was used to prepare all solutions and reagents.

B. Biosynthesis of ZnONPs

Sechium edule was collected from the local market. Its peel was removed, washed properly and cut into small pieces (10 mm×10 mm). 150 g chayote pieces were taken in 200 mL distilled water and heated at 60 °C for 24 h. The solution was cooled to room temperature and filtered using filter paper (Prefilter AP25, Millipore, India). Later, Zn(NO₃)₂·6H₂O was added at 0.378 :100 (Zn²⁺: extract, g/mL) in bioextract under constant agitation on a magnetic stirrer (M/s Tarson, India, model: MC-02). The agitation was continued for 5 h at 60 °C, allowed to room temperature cooling and the supernatant was partly discarded to avoid loss of ZnONPs. The black solid product obtained was centrifuged twice at 4500 rpm for 15 min after through washing using ethanol and dried at 80 °C for 8h.

C. Analytical techniques

The X-ray diffractometer of M/s Bruker, Germany, model: D8 Advance, was employed to record the diffractogram of ZnONPs, ZnO and Zn(NO₃)₂·6H₂O. FTIR spectra were acquired using the spectrometer of M/s Shimadzo, Japan, model: IR affinity-1. BG dye concentration was determined by colorimetric method using a UV-Vis Spectrophotometer of M/s Thermo Scientific, India, model: UV 2300.

D. Catalytic activity test of ZnONPs

The photocatalytic activity of the ZnONPs was investigated through the degradation of BG dye which was monitored through UV-Vis spectroscopy. 0.1 g/L catalyst was dispersed in 20 mg/L BG aqueous solution in the ultrasonic bath for 15 min and it was then kept in dark for 45 min to equilibrate dye adsorption at natural pH. A sample of about 5 ml was taken to determine the initial dye concentration prior to illumination of light. The reaction mixture was stirred in a 200 ml cylindrical borosilicate glass vessel in room temperature (25±2°C) under a visible light lamp of 200 W of source Bajaj (model: L-1699276, India) equipped on the top of the reactor (about 20 cm above solution). The

reaction mixture was withdrawn at different intervals for a total time of 120 min and analyzed for dye concentration and then returned into the reaction vessel. Prior to analysis, the solutions were filtered to remove the catalyst particles.

III. Results and Discussion

A. X-ray diffractogram

Figure 1 represents the X-ray diffraction pattern of bare ZnONPs, ZnO and Zn(NO₃)₂·6H₂O. The diffraction peaks located at 31.8°, 34.5°, 36.3°, 47.6°, 56.7°, 62.9°, 68.1°, and 69.2° have been keenly indexed as hexagonal wurtzite phase of ZnO [26, 27] with lattice constants $a = 0.324$ nm and $c = 0.521$ nm (JPCDS card number: 36-1451) [28]. It also confirms the synthesized ZnONPs was free of impurities as it does not contain any characteristics XRD peaks other than ZnO peaks. The synthesized ZnO nanoparticle diameter was calculated using Debye-Scherrer formula [29] as in (1).

$$d = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where, θ is the Bragg diffraction angle, 0.89 is Scherrer's constant, λ is the wavelength of X-rays, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane (100) (Figure 2). The average particle size of the sample was found to be 48.86 nm which is derived from the FWHM of more intense peak corresponding to (100) plane located at 31.8° using Scherrer's formula. Similar results were also reported for biosynthesized ZnONPs using poncirus trifoliata [30] and calotropis procera extract [31].

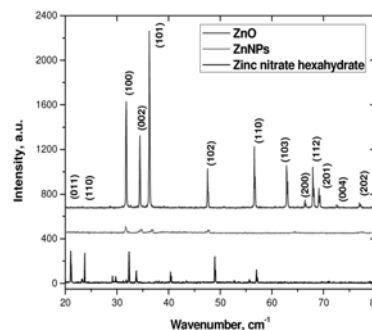


Figure 1. XRD patterns of ZnO, ZnONPs and bare zinc nitrate hexahydrate.

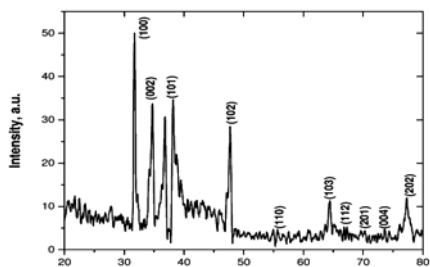
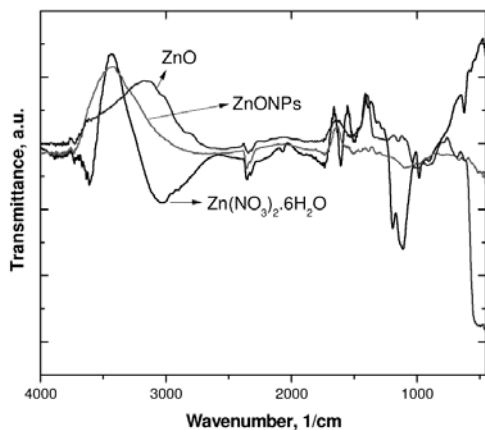


Figure 2. XRD patterns of ZnONPs.

B. FTIR spectra of ZnONPs

The FT-IR spectra in Figure 3 shows the functional groups present in bare $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ZnO and synthesized ZnONPs. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ showed a broad band between 3952 and 2408 cm^{-1} including N-H stretches at 463 and 1383 cm^{-1} . Similar groups were noted for both ZnO and ZnONPs. The -OH group observed at 3640 cm^{-1} in the ZnO also existed in the ZnONPs spectrum at 3610 cm^{-1} , probably due to atmospheric moisture [33]. The peaks at 682 nm and 525 cm^{-1} are related to the stretching vibrations of Zn-O bonds. There were fine structures at 463, 1332 and 1714 cm^{-1} due to hydrogen bonding of NH_3



FTIR spectra of ZnONPs, ZnO and bare zinc nitrate hexahydrate.

C. Photocatalytic activity of ZnONPs

The photocatalytic efficiency of ZnONPs for the cleavage of BG dye is shown in Figure 4. It can be observed that with ZnONPs, BG dye was removed, by adsorption, by about 34% after 15 min of sonication followed by 45 min of equilibrium period. Irradiation of light initiate cleavage of preadsorption dye and it is quite reasonable that degradation efficiency was calculated with respect the initial dye of 20 mg/l.

There was about 72% decomposition at 120 min (inset figure).

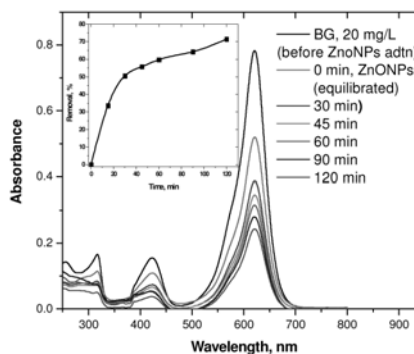


Figure 3. BG dye decolourization with exposure time using ZnONPs. Experimental conditions: initial BG dye concentration 20 mg/l, ZnONPs dose 0.1 g/L, agitation speed 270 rpm and temperature 30°C. Inset: percentage BG removal with exposure time.

IV. Conclusions

Chayote squash extract could effectively form ZnONPs from a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at near room temperature. The X-ray diffraction peaks confirmed formation of hexagonal wurtzite crystal of ZnO. The average particle size of ZnONPs was calculated as 48.86 nm using Debye-Scherrer formula which was as per the earlier reports. The characteristic stretching vibrations of Zn-O bonds appeared at 682 nm and 525 cm^{-1} . The photocatalytic degradation under visible light spectrum gave upto 72% BG dye decomposition at natural pH in 120 min. However, a systematic study is needed in order to optimize the fabrication condition for better size control and formation of ZnONPs.

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