National University of Lesotho International Science, Technology & Innovation Conference & Expo
January 23 – 25, 2018
Maseru, Lesotho
nulistice 2018

Eco-Friendly Synthesis of Zinc Oxide Nanoparticles for Rayon Pulp

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Abstract: Various methods have been employed not just to synthesize but also to improve the size and properties of the Zinc oxide (ZnO) nano particles (NPs) so as to enhance its performance. We report synthesis of ZnO NPs through bio-reduction of zinc-nitrate using neem (*Azadirachta indica*) plant extract. Characterization was done through FT-IR, UV-vis spectroscopy, XRD, AFM and SEM. Peak around 513 cm^{-1} in the FT-IR spectra indicated characteristic absorption of ZnO. UV-Vis absorption spectra showed a typical ZnO profile with peak-wavelength around 352 nm. The SEM images show that ZnO NPs prepared in this study are spherical in shape with smooth surface. The size of the NPs was determined from SEM, as well as AFM pictures, and was estimated to be within 16 – 40 nm. As a potential application, a qualitative analysis of antibacterial activity of ZnO NPs for rayon pulp was also carried out, and the results obtained were found promising.

Keywords: ZnO NPs, Bio-Reduction, Chemical and Physical Methods, Anti-bacterial activity, Rayon

1. Introduction

Today, nanotechnology is operating in various fields of science via its operation for materials and devices using different techniques at nanometer scale. Nanoparticles are a part of nanomaterials that are defined as a single particles 1–100 nm in diameter. From last few years, nanoparticles have been a common material for the development of new cutting-edge applications in communications, energy storage, sensing, data storage, optics, transmission, environmental protection, cosmetics, biology, and medicine due to their important optical, electrical, and magnetic properties.

Nanotechnology concerns with the development of experimental processes for the synthesis of nanoparticles of different sizes, shapes and controlled disparity. This provides an efficient control over many of the physical and chemical properties with various potential applications including pharmaceuticals and medicine.

Recently, ZnO nanoparticles have received considerable attention due to their unique remarkable chemical and physical properties that are distinctive from those of conventional bulk materials. To date, various methods have been adopted for the preparation of ZnO crystallites including sol–gel method, evaporative decomposition of solutions, gas-phase reaction, wet chemical synthesis and hydrothermal discharging gas method. However, these methods usually involve high temperatures and sometimes complicated processes, which might result in impurities in the final products.

Rodrigues-Paez et al. synthesized zinc oxide nanoparticles with different morphologies by controlling different parameters of the precipitation process such as solution concentration, pH, and washing medium.

In the last few decades, with the increase in new antimicrobial fiber technologies and the growing awareness about cleaner surroundings and healthy lifestyle, a range of textile products based on synthetic antimicrobial agents such as triclosan, metal and their salts, organometallics, phenols and quaternary ammonium compounds, have been developed and quite a few are also available commercially. In the present study, ZnO nanostructures have been synthesized by Bio-Reduction of Zinc Nitrate in plant extract method. Zinc nitrate heptahydrate and plant extract were used as precursors to formulate ZnO nanostructures.

Bio-Reduction of Zinc Nitrate in plant extract for synthesis of ZnO nanostructures has many advantages such as fast crystallization, cost efficiency and low waste production. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM), and the purity of the sample was tested by FTIR spectroscopy and UV-Visible spectroscopy. Antimicrobial activity was analyzed using ZnO NPs in rayon pulp. The rayon fabric showed no antibacterial activity against both Gram positive and Gram negative bacteria. The results show excellent antibacterial activity of the ZnO NPs in Rayon pulp samples.

2. Experimental

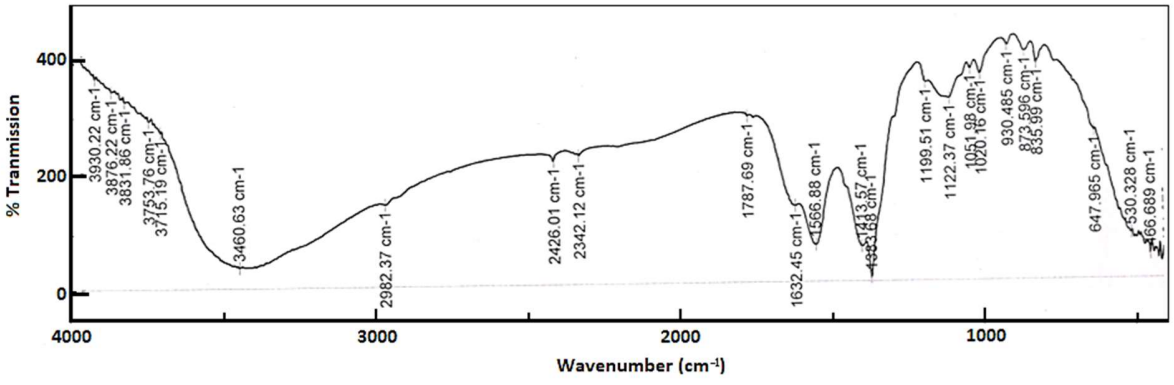
Hot water extraction:

The Neem (*Azadirachta indica*) Leaves were washed with sterile double distilled water to remove the surface contamination and dried in shadow. The dried plant material was cut into in small pieces. 5gm of plant material was taken and mixed with 100 ml of sterile double distilled water and kept in water bath for reflux at 100 ºC for 60 minutes. The obtained reflux solution is then filtered by Whatman No. 1 filter paper. The filtered extract was stored in refrigerator at 20 ºC for further studies.

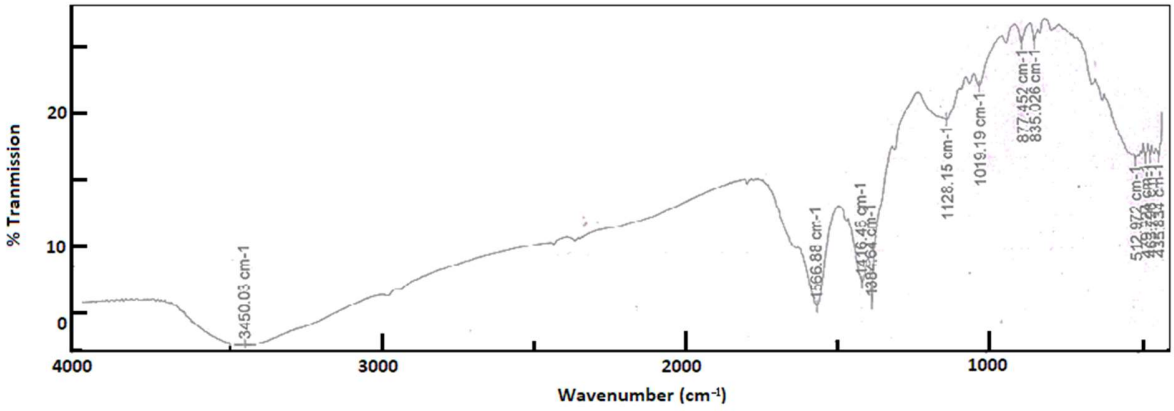
Figure 1. Preparation of ZnO NPs: Change of colour during the course of reaction.

Biosynthesis of ZnO NPs:

The biosynthesis of ZnO NPs, 15 cm^3 of plant extract



(a)



(b)

Figure 2. FT-IR Spectra of (a) Plant extract, and (b) ZnO NPs.

having pH 5 was mixed with 15 ml of 4.0 mM aqueous zinc nitrate solution, at temperature 60 ºC and put for sonaication for 30 Minute. The bio-reduction of the Zinc ions in the solution was monitored periodically by measuring the UV-Vis spectroscopy (200–800 nm) of the solutions. Fig.1 shows colour changes for the preparation of ZnO NPs was observed during the course of the reaction. Initially, the solution is yellow, but over 30 minutes the solution turned Yellowish brown. The formation of a yellowish brown coloured solution indicated the formation of the ZnO NPs. The ZnO NPs obtained was centrifuge and then obtain ZnO NPs were purified by sterile deionized water several times to remove the water-soluble biomolecules such as proteins and secondary metabolites. After that dried ZnO NPs were used to characterize the structure and composition.

Instruments:

FTIR was carried out on a JUSGO unit and XRD measurements were performed on MiniFlex machine with Cu-K_α radiation (λ = 1.54178 Å) at 40 kV and 15 mA, and scan-speed of 04.00 º/min. Electron microscopy was done on Zeiss SEM DSM 960A and Atomic Force Microscopy on a Nanoscope IV unit. The Varian CARRY 500 UV-Vis-NIR Spectrophotometer was used fot UV-Vis spectroscopy.

3. Results and Discussion

Fourier Transform Infra-Red spectroscopy:

Two milligram of ZnO NPs was mixed with 200 mg of potassium bromide (FTIR grade) and pressed into a pellet. The sample pellet was placed into the sample holder and FTIR spectra were recorded in FTIR spectroscopy. To validate again the nature of the synthesized nanoparticles and their purity Fourier Transform Infrared spectroscopy (FTIR) (Jasgo) studies were performed. A reports the typical FTIR spectrum of the pressed powder in the spectral range of 200-4000 cm^{-1}. The IR transmission is plotted so to single out the major absorptions observed at lower wave numbers.

The bands of biosynthesized zinc nanoparticles from plant extract of *Azadirachtaindica* were noticed at 3450.03, 1566.88, 1416.46,1384.64 and 513 cm^{-1} in the FTIR spectrum fig.2 (b), Whereas, bands of plant extract in fig.2 (a) were noticed at 3715-3930, 3460.63, 2982.37, 2426.37,2426.01, 2342.12, 1787.69, 1632.45, 1566.88, 835.99 to 1199.51, 647.95 cm^{-1}. In fig.2(a)the intense broad band at can be assigned to O-H ,N-$H_2$and C = O stretching band. The band in fig.2(a)of plant extract shifted to 3450.03, 1566.88, 1416.46 ,1384.64 and 513 cm^{-1} shows in Fig.2 (b).The absorption band corresponding to 3450.03 cm^{-1} was due to C-H, stretching vibrations of carboxylic acid and hydroxyl

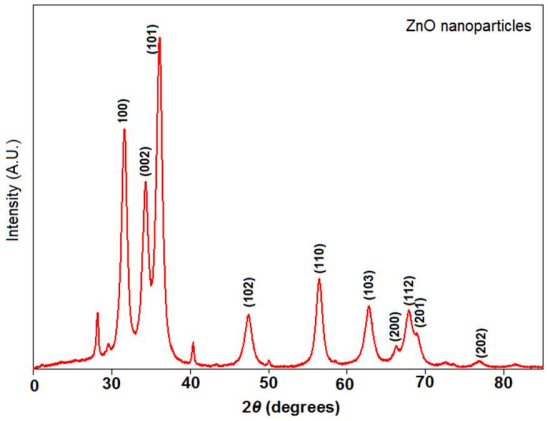


Figure 3. XRD Spectra of ZnO NPs synthesized by from 4.0 mM $ZnNO_3$.

stretch vibrations. Further, at 1019 cm^{-1}, which are sharper and broader for ZnO NPs participates in the reaction. In Fig.2 (b), IR spectra peak shows the bulk ZnO showing a high intensity broad band around 513 cm^{-1} due to the stretching mode of the zinc and oxygen bond. The significant changes in intensity peak due to reduction of Zinc Nitrate to ZnO NPs.

X-ray diffraction analysis of ZnO nanopowder:

The X-ray diffraction (XRD) pattern of the ZnO NPs prepared by bio-reduction is shown in figure 3. Strong peaks in the XRD profile indicate crystalline nature of the synthesized NPs. Prominent diffraction peaks around 31º, 34º, 36º, 47º, 56º, 62º, 66º, 67º and 68º of 2θ, which corresponds to reflections from (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes, were found to match with the JCPDS file 00-079-0206 ($a = b$ = 3.249 Å, c = 5.206 Å) for the hexagonal wurtzite structure of ZnO. Furthermore, the average crystalline size was calculated using Debye–Scherrer equation $d = k\lambda/(\beta\cos\theta)$, where d is the mean crystalline size of the powder, λ is the wavelength of Cu-K_α (λ = 1.54178 Å), β is the full width at half maximum (FWHM) intensity of the peak

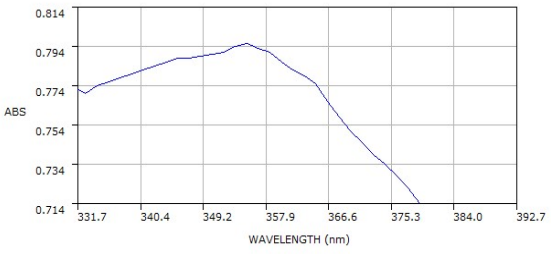


Figure 4. UV-Vis absorption spectra of ZnO NPs with a peak around 350 nm.

in radian, θ the Bragg's diffraction angle and k is dimensionless shape factor (a constant normally taken ~0.9). The average crystallite size of samples was determined to be about 18 nm. Diffraction peaks corresponding to the impurity were not found in the XRD confirming the high purity of the synthesized products.

UV-Vis spectroscopy:

UV-Vis spectroscopy showed a decrease in intensity of the characteristic surface plasmon band in the spectrum for the ZnO NPs, in the range 358-372 nm. As mentioned earlier, the solution turned yellow to yellowish brown indicating the formation of ZnO NPs (Fig.1). UV-vis spectroscopy also showed a broad absorption band centered around 230 nm and a small but sharp peak at 352 nm (Fig.4) corresponding to spherical ZnO nanostructure.

Microscopy results:

Figure 5 shows the SEM image of ZnO NPs. The SEM image was taken at 25,000x magnification. The image shows ZnO NPs are spherical in shape with smooth surface and the size of the particles around 16-36 nm.
Figure 6 shows size and shape of the nanoparticles which obtained directly from tip-corrected AFM measurements, and the shape of the nanoparticles is estimated on the basis of AFM images and line scans. The tip-corrected measured the size of ZnO NPs to be 20-30 nm and spherical in shape.

Anti-microbial activity:

Antimicrobial activity (figure 7) was analyzed using ZnO NPs in rayon pulp. The rayon fabric showed no antibacterial activity against both Gram positive and Gram negative bacteria. The results show the excellent antibacterial activity of the ZnO NPs in Rayon pulp samples which was found to be improving with increase in concentration of ZnO NPs. Antibacterial activity against *S. aureus* was maximum whereas that against *E. coli* was minimum. Further increase in concentration of ZnO NPs show appreciable increase in antibacterial properties against *E. coli* and the optimum concentration for antibacterial property was taken as 0.4 M. In case of ZnO NPs rayon pulp, the unwashed sample showed Maximum antibacterial activity.

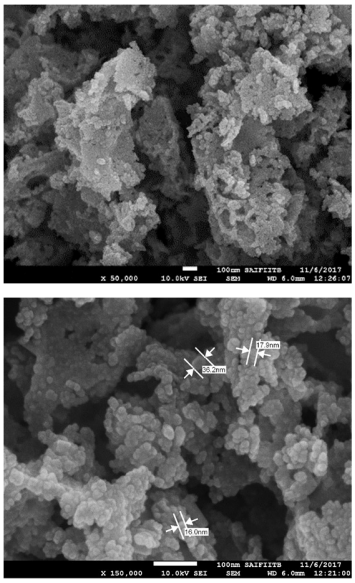


Figure 5. SEM images of ZnO NPs.

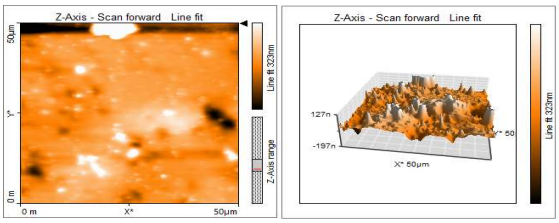


Figure 6. AFM images of ZnO NPs.

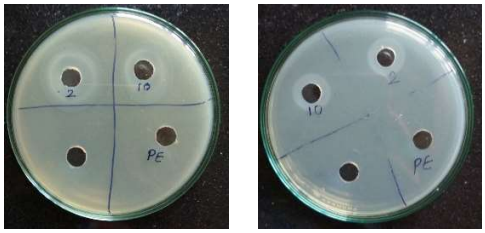


Figure 7. Antimicrobial activity of ZnO NPs with Rayon pulp against *S. aureus* (Left) and *E. coli* (Right).

4. Conclusions

Several approaches have been employed to obtain a better synthesis of ZnO NPs, such as chemical and biological methods. Development of easy, reliable and eco-friendly methods helps increase interest in the synthesis. Recently, synthesis of ZnO NPs using plant extracts has attracted attention of many materials scientists. We have presented a report on rapid biological synthesis of ZnO NPs using plant extract, which provides an environmental friendly, simple and efficient route for synthesis of NPs. The ZnO NPs were obtained through a homogeneous phase reaction between zinc nitrate and plant extract solution having various concentrations with pH 5 under constant sonication time and temperature. FTIR showed a peak around 513 cm^{-1}, which is characteristic absorption of zinc oxide bond. This confirmed the formation of zinc oxide nanoparticles. X-ray diffraction further confirmed the formation of a hexagonal wurtzite phase structure of ZnO, which is the most stable form at

ambient conditions. The average crystalline sizes estimated using the Debye–Scherrer equation was about 16 nm. Particle size measured from AFM was around 20 - 36 nm for the mostly spherical NPs. SEM image also showed that most of the NPs are spherical in shape formed within a diameter range of 10 - 40 nm. Finally, the antibacterial activity of the ZnO NPs in Rayon pulp samples was tested and was found to be improving with increase in concentration of the NPs.

5. References

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