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Research Article

COMPARATIVE STUDIES ON GREEN SYNTHESIZED AND CHEMICALLY SYNTHESIZED OF ZnO NANOPARTICLES

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ABSTRACT

ZnO nanoparticles have been synthesized via a simple green and chemically method. The synthesized ZnO nanoparticles were characterized by UV–Vis-diffuse reflectance spectroscopy (UV-Vis DRS), Photoluminescence measurements (PL), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Field emission-scanning electron microscopy (FE-SEM) and Transmission electron microscopy (TEM), respectively. Moreover, the antibacterial activity of synthesized ZnO nanoparticles against *S. aureus*, *S. paratyphi*, *V. cholerae*, and *E. coli* are also screened.

INTRODUCTION

Semiconductor materials in nanodimensions have fascinated the scientific community in the recent past owing to their peculiar physical and chemical properties [1]. Among the semiconductor materials ZnO an important II-VI semiconductor material with a wide band gap of 3.37 eV and a large excitation binding energy of 60 MeV, has been studied extensively because of its potential applications in ultraviolet light-emitting diodes and laser diodes[2], field emission displays[3], solar cells[4], sensors[5,6], varistors [7], and catalysis[8]. Biological methods for NPs synthesis using microorganisms, enzymes, and plants or plant extracts have been suggested as possible eco-friendly alternatives to chemical and physical methods. Thus, there is a need for a new simple and eco-friendly green synthesis processes, those avoids the use of toxic chemicals and high energy inputs. Green synthesis of ZnO has also been reported for antibacterial properties [9].

Mentha (also known as *mint*, from Greek *míntha*) is a genus of plants in the family *Lamiaceae (mint* family). The genus has a subcosmopolitan distribution across Europe, Africa, Asia, Australia, and North America [10]. *Mentha* was originally used as a medicinal herb to treat stomach ache, skin disease, wounds, cuts and chest pains etc.

MATERIALS AND METHODS

Chemicals

All the chemicals used in this study were purchased from Merck and are of analytical reagent grade with 99% purity. The glass wares used in this experimental work were acid washed. Ultra pure water was used for all dilution and sample preparation.

Chemical method

For the preparation of ZnO nanoparticles, 7.43g (0.5 M) of zinc nitrate hydrate dissolved in 50 ml of deionized water was stirred vigorously by magnetic stirrer and 5.63 g (2 M) of potassium hydroxide in 50 ml of deionized water was added drop by drop to the above mixture. The entire was stirred magnetically at 60°C until a white precipitate was formed. The obtained dispersions were purified by dialysis against deionized water and ethanol several times to remove impurities. The yield products were dried in hot air oven at 100°C for 6 h to evaporate water and organic material to the maximum extent. Finally, the obtained product was annealed in a muffle furnace at 400°C for 2 h. The annealed powders were pulverized to fine powders using agate mortar for further characterizations.

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Biological methods

Preparation of the leaf extract

Mentha leaves were collected from Polur, Thiruvannamalai district, Tamil Nadu, and India. The collected leaves subjected to washing several times with distilled water to remove the dust particles. In the preparation of leaves extract, 20 g of fine cut leaves in 250 mL glass beaker mixed with 100 mL of distilled water. Boiling of the mixture for 20 minutes changed the color of the aqueous solution from watery to light yellow. After allowing the extract to cool to room temperature, using a Whatman filter paper broth filtration took place.

Preparation of zinc oxide NPs

For the synthesis of ZnO nanoparticles, 50 mL of leaves extract allowed to boil using a stirrer–heater. Then, 5 gm of zinc nitrate added to the above solution as the temperature reached 60 °C. This mixture further boiled until its color changed into a dark yellow. The obtained paste further transformed to the ceramic crucible and annealed at 400 °C for 2 hours. The finally arrived light white colored powder consumed for different characterizations.

Antimicrobial assay

The synthesized compounds tested for inhibition of the human pathogenic bacteria. Microbial assay carried out by following [11] disc diffusion method. The pathogens namely Salmonella paratyphi, Vibrio cholerae, Staphylococcus aureus and Escherichia coli, were obtained from Raja Sir Muthaiya Medical College, Annamalai University. About 150 CFU/mL of inoculums was swabbed onto MH-agar plates uniformly and allowed to dry in a sterile environment. Sterile disc of 6 mm (HIMEDIA) were loaded with 20 µL of test solution (solvent, leaf extract, and ZnO NPs). Ampicillin (10 mg in 1mL) was used as positive control. The plates were incubated at 25°C for 3 days to measure zone of inhibition. Mean was calculated by performing the experiments in triplicates.

RESULTS AND DISCUSSION

XRD analysis

The X-ray diffraction patterns of ZnO synthesized for leaf extract and chemically synthesized ZnO nanoparticles are shown in Figure 1. From the diffractogram of XRD are very well matched with the hexagonal phase (wurtzite structure) by comparison with the data from JCPDS card No.89-1397 and no indication of a secondary phase or impurity peaks were obtained. The strong and narrow diffraction peaks indicate that the produce has good crystalline structure. The average grain size of the sample was calculated using the Scherer's equation.

$$D = \frac{K\lambda}{\beta Cos\theta}\ \text{Å} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Where D is the average crystallite size in Å, K is the shape factor (0.9), λ is the wavelength of X-ray (1.5406 Å) CuKα radiation, θ is the Bragg angle, and β is the corrected line broadening of the NPs. The calculated crystallite was found to be 33 nm and 35 nm for green and chemically synthesized ZnO nanoparticles respectively.

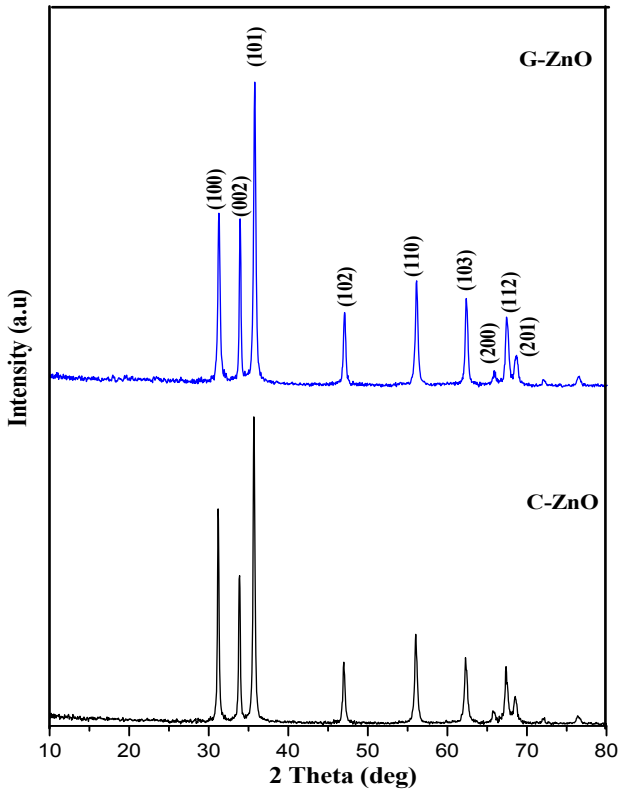

Fig 1 XRD pattern of ZnO nanoparticles.G) Biostabilized ZnO nanoparticles C) Chemically synthesized ZnO nanoparticles

Optical studies

Figure 2a shows the optical absorption spectrum of ZnO NPs synthesized by using leaf extract and chemically synthesized ZnO nanoparticles. The sample has a clear and strongly observed absorption peak below at 400 nm.

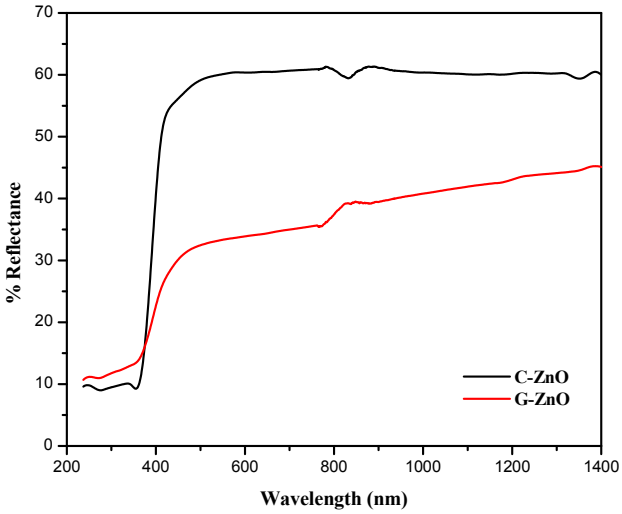

Fig 2a UV–DRS spectrum of ZnO nanoparticles. C) Chemically synthesized ZnO nanoparticles G) Green synthesized ZnO nanoparticles

The band gap energy (E_g) of ZnO was obtained from the wavelength value corresponding to the intersection point of the vertical and horizontal part of the spectrum, using the equations:

$$E_g = \frac{hc}{\lambda}\ eV\ ;\ E_g = \frac{1240}{\lambda}\ eV \quad \ldots\ldots\ldots\ldots\ldots (2)$$

The band gap energy corresponds to the absorption limit and can be roughly evaluated by the above relation. Where, E_g is the band gap energy (eV), h is the Planck's constant (6.626 x 10^{-34} J s), C is the light velocity (3 x10^8 m/s) and λ is the wavelength (nm). From Fig.3a, the absorption edges are positioned at 331 and 358 nm, respectively for green and chemically synthesized ZnO nanoparticles. The band gap of ZnO is found to be 3.74 and 3.46 eV.

Indirect band gap energy (Kubelka–Munk plot)

The reflectance spectra were analyzed using the Kubelka-Munk relation (equation 3). To convert the reflectance data into a Kubelka-Munk function (equivalent to the absorption coefficient) F (R), the following relation was used. Where, R is the reflectance value.

$$F(R) = \frac{(1-R)^2}{2R} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Band gap energy of the samples was estimated from the variation of the Kubelka-Munk function with photon energy. Fig. 2b shows the Kubelka-Munk plots for the ZnO NPs. It is used to determine their band gap energy associated with their indirect transitions. The ZnO exhibits indirect E_g of 3.75 and 3.47 eV for green and chemically synthesized ZnO nanoparticles.

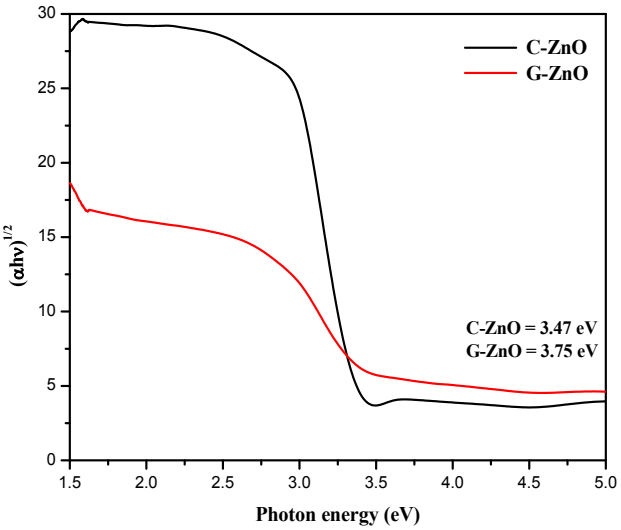

Fig. 2b Plot of indirect band gap energy for ZnO NPs

Photoluminescence (PL) analysis

Photoluminescence (PL) studies were performed to emphasize its emission properties as shown in Fig. 3. The photoluminescence of ZnO sample suggested three emission bands, including two blue bands at 402 and 469 nm, probable green band at 529 nm have been observed from the prepared ZnO NPs sample. The blue band at 417, 440 and 462 nm may be in correlation with the defect structures in ZnO crystal. The green bands at 520 nm.

FT-IR analysis

Possible biomolecules responsible for the reduction of ZnO and capping agent of bioreduced ZnO NPs and chemically synthesized ZnO nanoparticles through particular bond vibration peaks identified from defined wave numbers in FT-IR technique.

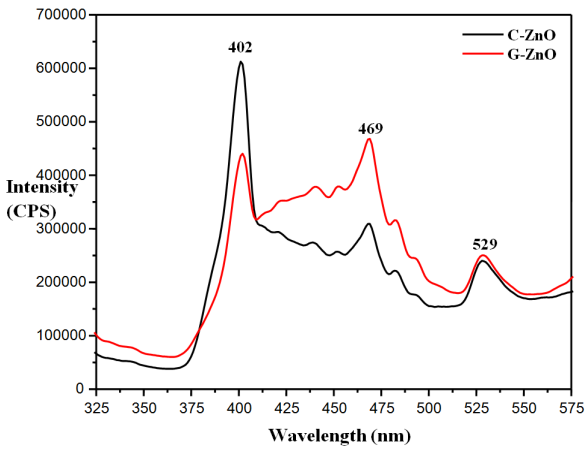

Fig 3 Photoluminescence spectrum of ZnO nanoparticles .C) chemically synthesized ZnO nanoparticles G) Green synthesized ZnO nanoparticles

The FT-IR spectra of control leaf extract (before reaction without Zn $(NO_3)_2$ and synthesized ZnO (after reaction with Zn $(NO_3)_2$ are shown in Fig. 3. The absorption bands at 3402, 2929, 2358, 1649, 1029 and 671 cm^{-1} in leaf extract wound be shifted into 3398, 2926, 2368,1653, 1024, 445 $cm^{1}$and 2360,507 cm^{-1} in chemically and green synthesized ZnO nanoparticles. Whereas the stretching of ZnO NPs were found around 400-800 cm^{-1}. The FT-IR spectra showed the presence of bonds due to C–H stretching (around 2924 cm^{-1}). The band at 1029 cm^{-1} corresponds to C-N stretching vibration of amine [12]. The bands incidence at 1030 cm^{1} illustrates the chemical bonding, crystal structure and relative intensities of the IR bands of the carbonate [13].

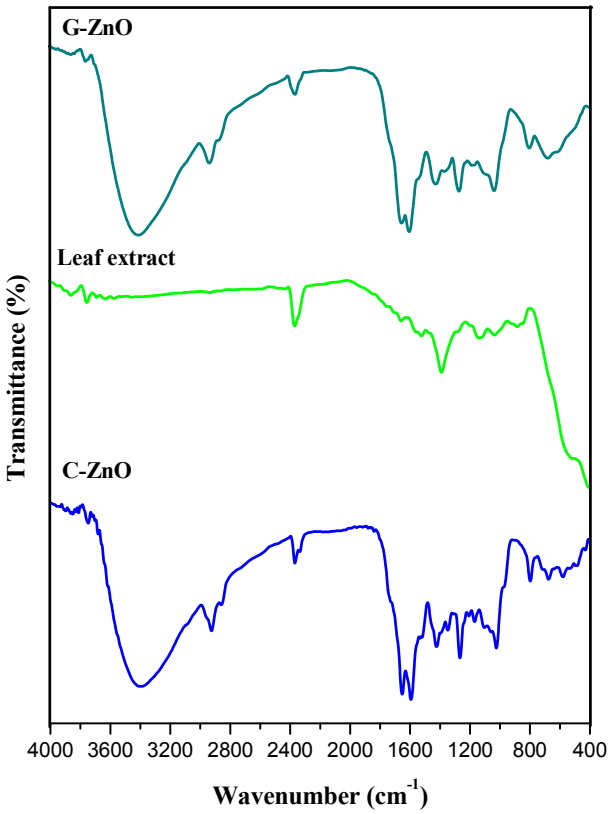

Fig 4 FTIR spectrum of ZnO nanoparticles. C) Chemically synthesized ZnO nanoparticles, Leaf Extract, G) Green synthesized ZnO nanoparticles

Therefore the synthesized ZnO NPs were surrounded by proteins and metabolites such as terpenoids having functional groups. From the analysis of FTIR studies, we confirmed that the carbonyl groups from the amino acid residues and proteins has the stronger ability to bind metal ions ,indicating that the proteins could possibly from the metal NPs (i.e.; capping of silver NPs) to prevent agglomeration and thereby stabilize the medium. This suggests that the biological molecules could possibly perform dual functions of formation and stabilization of ZnO NPs in the aqueous medium.

FE-SEM analysis

The synthesized ZnO nanoparticles of broth extract analyzed for their morphology by field-emission scanning electron microscopy (FE–SEM). The images showed the presence of star-like structure. The diameter of the cluster ZnO NPs found to be in the range of 20-40 nm. From the EDX pattern the existence of elements Zn and O is confirmed (Fig. 5a).

analysis displays the optical absorption peaks of ZnO NPs and these absorption peaks were due to the surface plasmon resonance of Zinc oxide NPs. The origin of these elements lies in the biological components; mostly align along with ZnO NPs [14].

TEM analysis

The size and morphology of ZnO nanoparticles analyzed by TEM and SAED pattern obtained from TEM studies are depicted in Fig. 6 (a, b). This image reveals that most of the ZnO NPs are quasi-spherical and rod -like structure. The SAED pattern revealed that the diffraction rings of the synthesized ZnO exhibited Debye-Scherrer rings assigned (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) respectively. Lattice planes of the face centered cubic (fcc) ZnO, indicating that the biogenic NPs The SAED pattern shows the well defined electron diffraction spots, confirming

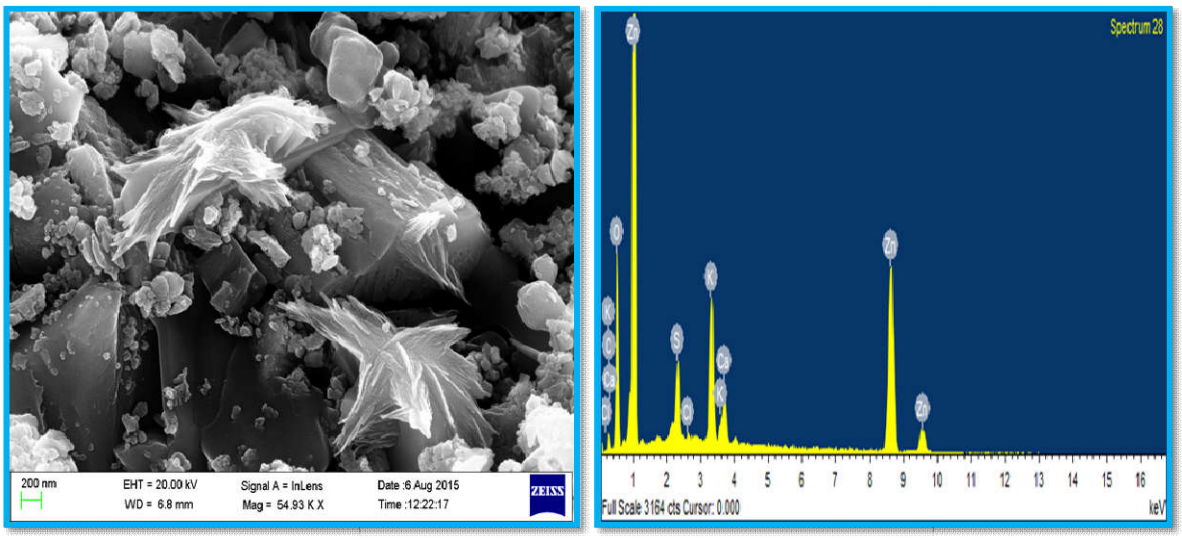

Fig. 5a FE–SEM image and EDX spectrum of Green synthesized ZnO nanoparticles

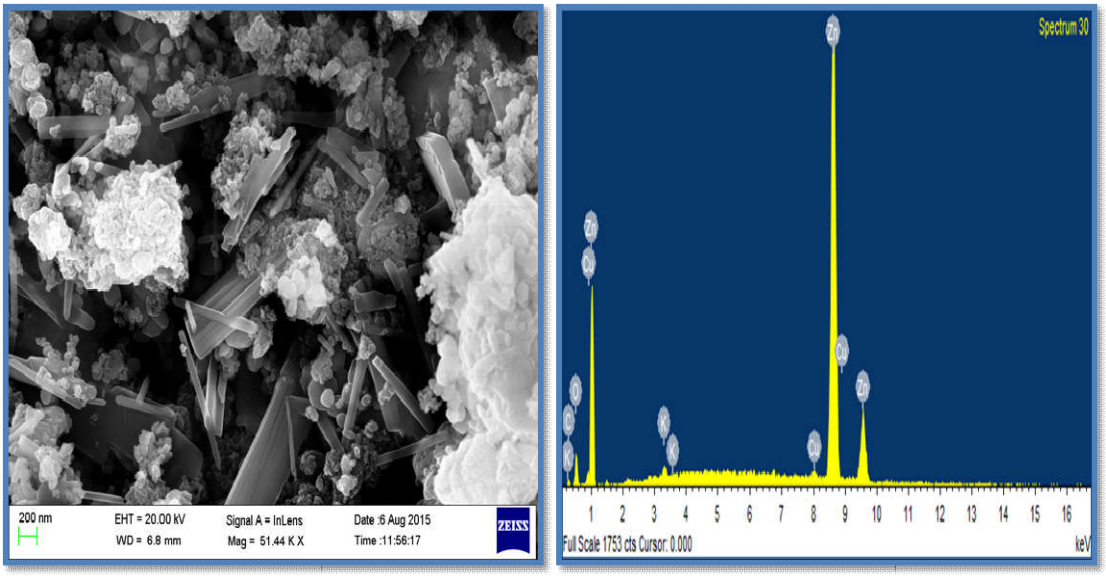

Fig. 5b FE–SEM image and EDX spectrum of chemically synthesized ZnO nanoparticles

The chemically synthesized ZnO nanoparticles images showed the presence of rod-like structure. From the EDX pattern the existence of elements Zn and O is confirmed. The EDX

the nano- crystalline in nature. The particle size determined from TEM analysis is in good agreement with that of the XRD analysis.

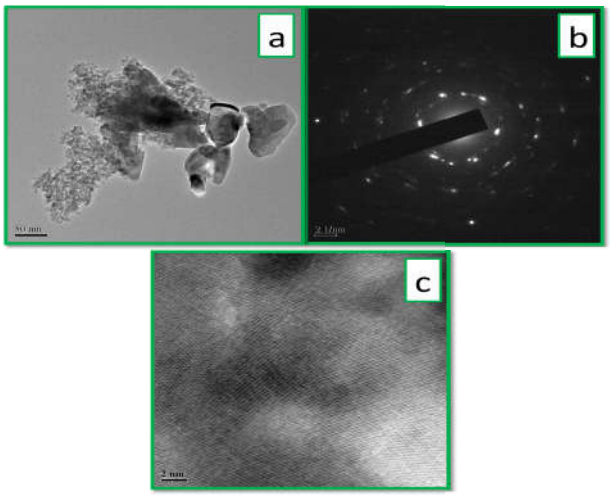

Fig. 6a TEM image ZnO NPs synthesized using leaf extract

(b) Corresponding SAED patterns (c) HRTEM

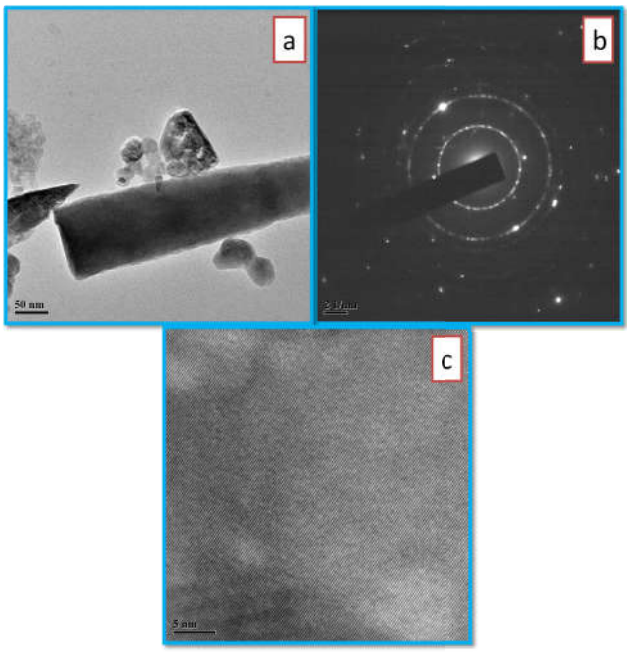

Fig. 6b TEM image of chemically synthesized ZnO NPs

(b) Corresponding SAED patterns (c) HRTEM

Antibacterial activity of ZnO–NPs

The antibacterial activity of green and chemically synthesized ZnO NPs towards various human pathogens was tested by disc diffusion methods and was represented in the Fig. 7a. The antibacterial activity of leaf mediated ZnO was studied against the Gram-negative and the Gram-positive bacteria. As seen in the figure, inhibition zones of 18 mm, 20 mm, 15 mm, 4 mm and 11 mm, 8 mm, 11 mm, 10 mm and were obtained from the synthesized ZnO nanoparticles against *S. paratyphi*, *V. cholerae*, *S. aureus,* and E. *coli,* respectively. In the present study, when compared to leaf extract and solvent, green synthesized ZnO NPs showed a greater significant zone of inhibition. However, when compared to standard tablet, lower antibacterial activity of ZnO NPs was observed in all the bacterial pathogens. The results of the present study are identical with the results reported by other researchers [15-17]. The potential reason for the antibacterial activity of ZnO is that ZnO NPs may attach to the surface of the cell membrane and perturbing the permeability and respiration functions of the cell. Smaller ZnO NPs can have larger surface area available for interaction and may give more antibacterial effect than the larger particles. It is also possible that ZnO NPs not only interact with the surface of membrane, but can also penetrate inside the bacteria.

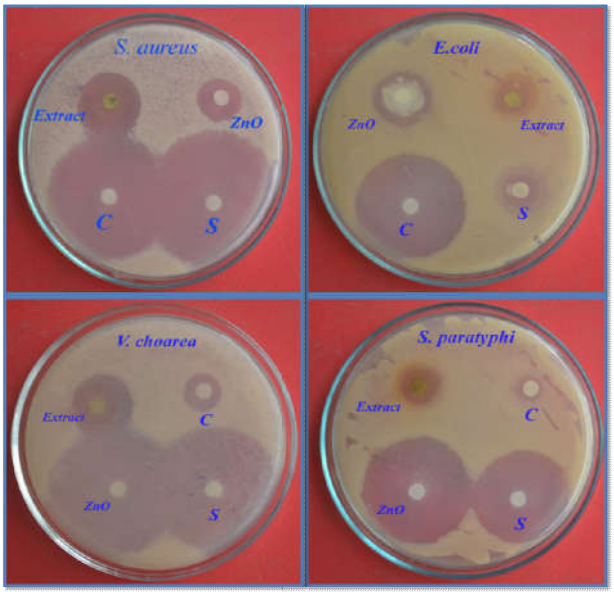

Fig. 7a Zone of inhibition produced by biostabilised ZnO nanoparticles

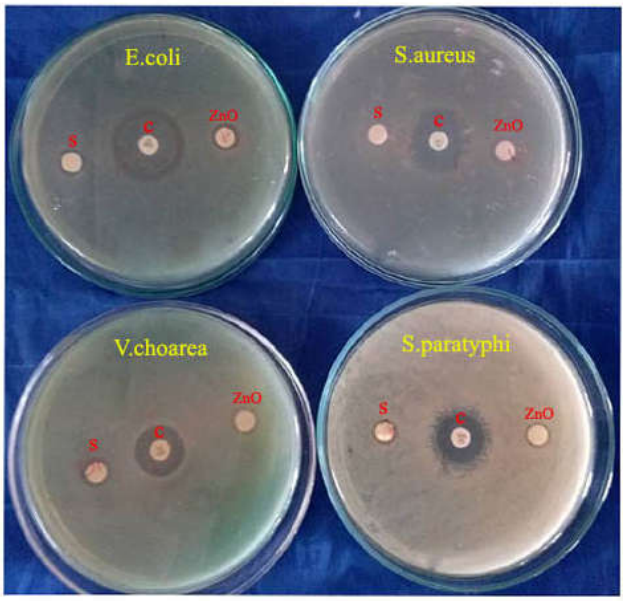

Fig. 7b Zone of inhibition produced by chemically ZnO nanoparticles

CONCLUSION

In this study we have prepared ZnO nanoparticles a) using leaf extract as capping agent and b) chemical method. The structure, morphology and size (dimension) of prepared ZnO NPs were examined by XRD, FT-IR, and FE–SEM and TEM analysis. Leaf extract was found to be lesser in size and more dispersed than the ZnO nanoparticles prepared by chemical method. UV-Vis-DRS studies confirmed the indirect band gap 3.74, 3.46 eV and photoluminescence was found the blue band at 402, and 469 nm. The average grain size lies

between 20-40 nm were obtained from XRD study as well as FT-IR spectra revealed the functional groups of stretching bands for ZnO NPs were found around 800-400 cm^{-1}. TEM study confirmed the diameter of the NPs and the quasi-spherical and rod-like structure. The synthesized NPs was studied for antibacterial activities against the microorganisms both Gram-positive (*S. aureus*) and Gram-negative (*S. paratyphi, V. Choarea, E. coli*) bacteria. Based on these results we conclude that the leaf extract-stabilized ZnO nanoparticles may have potential biomedical applications when compared to chemically synthesized ZnO nanoparticles due to its enhanced dispersibility, stability and surface coatings. Finally, the present study is so helpful and useful to the scientific community for using the ZnO NPs as the potent applications to the semiconducting, pyroelectric, piezoelectric, catalysis, optoelectronics, antidiabetic and antihyperlipidemic activities. Besides, it is inexpensive, stable, safe and eco-friendly without side effects of human beings. Therefore, in the present research was designed to prepare eco-friendly, stable and nontoxic ZnO nanoparticles from the *Mentha* leaf extract.

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