



GREEN SYNTHESIS OF PURE ZnO AND La DOPED ZnO NANOPARTICLES AND THEIR STRUCTURAL, OPTICAL AND ANTIBACTERIAL STUDIES

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ABSTRACT

Zinc oxide (ZnO) and La doped ZnO nanoparticles (NPs) were successfully synthesized by green method through *Gymnema sylvestre* plant leaf extract. The synthesized ZnO and La doped ZnO NPs have been characterized by X-Ray diffraction (XRD), UV-vis spectroscopy, Fourier transform infra-red (FT-IR) spectroscopy, Field emission scanning electron microscopy (FESEM) and Elemental analysis (EDAX). The ZnO and La doped ZnO nanoparticles were found to be crystalline having a single phase as confirmed by XRD and FESEM. It has been observed that the increase in the concentration of La from 0.01M to 0.03M in ZnO increases the crystallite size from 38 to 42 nm and accordingly its band gap varies from 2.7 to 2.8 eV. After treatment morphology of materials was changed from hexagonal shaped. Besides, this study determines the antibacterial efficiency of the synthesized ZnO and La doped ZnO NPs against G+ bacteria (*S. aureus*, *S. pneumonia*) and G- bacteria (*K. pneumonia*, *E. coli*).

KEYWORDS: Zinc Oxide, *Gymnema sylvestre*, Nanoparticles, La doped ZnO, antibacterial.

1. INTRODUCTION

Metal nanoparticles have been intensively studied in the past decade. Nanosized materials have been an important subject in basic and applied sciences. Biological systems have well organized and controlled physiological processes. This may be used in the nanoparticle synthesis, is rapidly gaining importance. Nanomaterials of different shapes and sizes have attracted considerable attention because of their unique physicochemical properties compared to the bulk materials. There are a considerable number of opportunities to fully utilize in modern clinical technology the new concepts and phenomena that have appeared in the field of NPs research.^[1]

Zinc oxide is a unique and key inorganic material that has attracted extensive research due to its characteristic features and novel applications in wide areas of science and technology. It has multiple properties like semiconducting, piezoelectric, pyroelectric, catalysis and optoelectronics.^[2, 3] ZnO is an n-type semiconductor with wide direct band gap energy (3.37 eV) and large excitation binding energy (60 meV) at room temperature. Nano sized ZnO has been extensively used in many fields such as solar cells^[4], gas sensors^[5], photocatalytic, antibacterial, electrical and optical devices^[6], electrostatic dissipative coatings^[7], degradation of environmental pollutants^[8,9], and biomedical application such as antibacterial agents in lotions, mouthwashes,

ointments and surface coatings to prevent microbial growth.^[10] Among them *G. sylvestre* belongs to *Asclepiadaceae* family. It is a traditional Indian medicinal plant used for diabetes mellitus in Siddha and Ayurveda. This is widely used for treatment of asthma, eye complaints and snake bites.^[11] This leaf extract contains a large number of bioactive compounds such as alkaloids, flavonoids, phenols, saponins (*Gymnemic acid*) and tannins.^[12] Vijaya Kumar et al.,^[13] have reported that *gymnemic acid* has been a good reducing agent in the preparation of metal oxide nanoparticles. In the present work, ZnO and La doped ZnO NPs have been prepared by green synthesis method. The synthesized NPs were analysed for their structural, optical and antibacterial properties.

2. Experimental Method

2.1. Synthesis of ZnO and La doped ZnO (X = 0, 0.01, and 0.03M) nanoparticles

ZnO and La doped ZnO nanoparticles were prepared by green synthesis method using zinc nitrate and lanthanum nitrate as metal precursors (Zn and La respectively) and *Gymnema sylvestre* plant extract as reducing and capping agent. 15 g of finely chopped *Gymnema sylvestre* leaves were weighed, then 150 ml of double distilled water was added and boiled at 60 °C for 15 minutes, the obtained extract was filtered using Whatman -1 filter paper and the filtrate was collected in 250 ml Erlenmeyer flask. Thereafter, 0.3M Zn (NO₃)₂·6H₂O solution was added

into 150 ml of *G. Sylvestre* leaves extract and it was stirred constantly at 80 °C for 6 hours. A dull yellow colour precipitate was obtained, further the precipitate was dried at 120 °C for 6 hours. The obtained ZnO powder was annealed at 700 °C for 6 hours.

The same procedure was followed for the preparation of the La concentration levels ($X=0.01$ and $X=0.03M$). Similarly, in the case of the La-doped samples 0.003M and 0.009M La $(NO_3)_2 \cdot 6H_2O$ was added into Zn $(NO_3)_2 \cdot 6H_2O$ solution and stirred well at room temperature. Thereafter, 150 ml of *G. Sylvestre* leaves extract was added slowly to the above solution and stirred constantly at 80 °C for 6 hours. A dull yellow colour precipitate was obtained, further the precipitate was dried at 120 °C for 6 hours. Thus, La doped ZnO nanoparticle was obtained. The obtained nanoparticles were annealed at 700 °C for 6 hours.

2.2. Characterization Studies

The phase purity of the synthesized NPs were determined by X-ray diffractometer (Model: X'PERT PRO PAN analytical). The morphological features of the sample were measured by Field emission scanning electron microscopy (Model: Carl Zeiss 55) with EDAX (Ultras). The vibrational frequency was measured by Fourier transform infra-red spectroscopy (Perkin-Elmer). The absorption spectrum of the sample was measured on Perkin-Elmer (Lambda 35).

2.3. Antibacterial activity

Antimicrobial activity of ZnO and La doped ZnO nanoparticles were done by agar well diffusion method against gram positive (*S. aureus*, *S. pneumonia*) and gram negative (*K. pneumonia*, *E. coli*) pathogenic bacterial strains on Muller-Hinton agar, according to the Clinical and Laboratory Standards Institute (CLSI).^[14] The media plates (MHA) were streaked with bacteria 2-3 times by rotating the plate at 60 °C angles for each streak to ensure the homogeneous distribution of the inoculums. Then the agar plates were swabbed with 100 mL each of overnight cultures of *S. aureus*, *S. pneumonia*, *K. pneumonia*, and *E. coli* using a sterile L-shaped glass rod. Using a sterile corkborer, wells (6 mm) were created in each petri plate. Varied concentrations of La doped ZnO NPs (1 mg/ml, 3 mg/ml and 5 mg/ml for both G+ and G- both bacteria) were loaded onto the petri plates. The plates were incubated for 24 h at 37 °C, for bacteria. After the incubation period, the diameter of the zone of inhibition (DZI) was recorded. Amoxicillin (Hi-Media) was used as the positive control against G+ and G- bacteria respectively to compare the efficiency of the test samples.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction studies

The X-ray diffraction peaks of pure ZnO and La doped ZnO NPs are shown in Fig. 1. The XRD peaks are located at angles (2θ) of 31.729, 34.390 and 36.209, corresponding to the (100), (002) and (101) planes of the

ZnO NPs, respectively. Similarly, other peaks found at angles (2θ) of 47.485, 56.514, 62.827, 67.86, 69.13, 72.55 and 77.01 correspond to the (102), (110), (103), (112), (201), (004) and (202) planes of the ZnO NPs, respectively. The ZnO NPs exhibits hexagonal wurtzite structure with the p6₃mc space group. This is also confirmed by the JCPDS data (Card no. 36-1451). It is worthy to mention that there is no secondary phase observed in $X=0.01M$ doped ZnO samples because of the ionic radii of La (1.061 Å). Furthermore, increasing the concentration of La^{3+} ions, one additional peak located at $2\theta = 28.941$ (JCPDS No 75-1900), which indicates the partial oxidation of La^{3+} during the synthesis and the formation of La_2O_3 .

The average crystallite size was calculated using Scherrer formula given in Eq. (1).

$$\text{Average crystallite size (D)} = \frac{0.9 \lambda}{\beta \cos \theta} \quad \text{--- (1)}$$

Where D is the crystallite size, λ is the wavelength (1.5406 Å CuK α), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM). The average crystallite sizes of undoped and La-doped ZnO nanomaterials were calculated to be 37 nm ($x = 0M$), 38 nm ($x = 0.01M$), and 42 nm ($x = 0.03M$), respectively. Thus, the particle size increases because of La doping in ZnO nanostructures. This increase in the crystallite size is due to distortion in the ZnO matrix by La^{3+} dopant ions, which increases the rate of growth of ZnO.

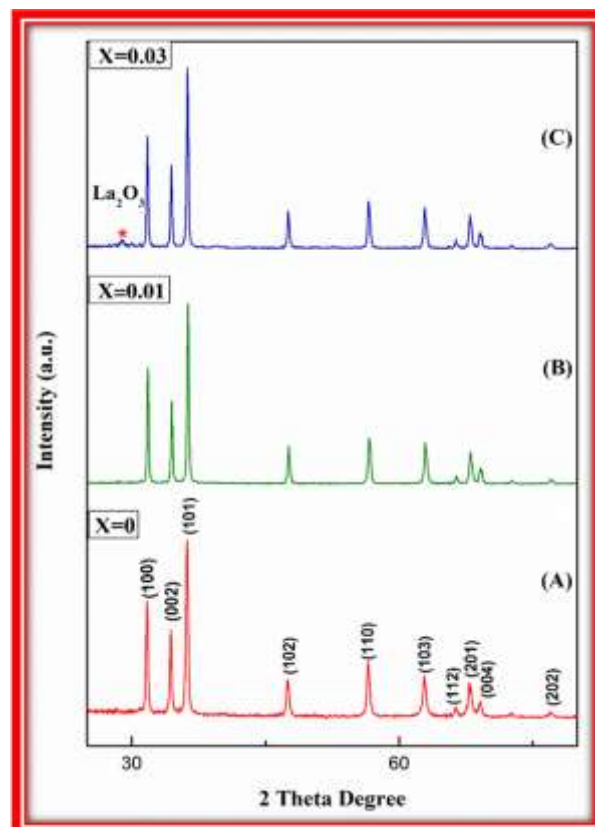


Fig. 1. Powder XRD pattern of ZnO and La doped ZnO NPs a) $X = 0$ b) $X = 0.01$ and c) $X = 0.03$ NPs.

3.2. Field Emission Scanning Electron Microscopy (FESEM) studies

The surface morphology of ZnO and La doped ZnO ($X = 0.0, 0.01, 0.03M$) materials was examined by FESEM analysis and showed in Fig. 2. FESEM images clearly indicated the hexagonal like morphology of

nanoparticles with the average thickness of 38nm, 42nm and 47nm, for ZnO and La doped ZnO NPs respectively. Furthermore, Fig.2 shows that as the La concentration increases, particle size of the samples is found increased. This is also confirmed by the XRD results.

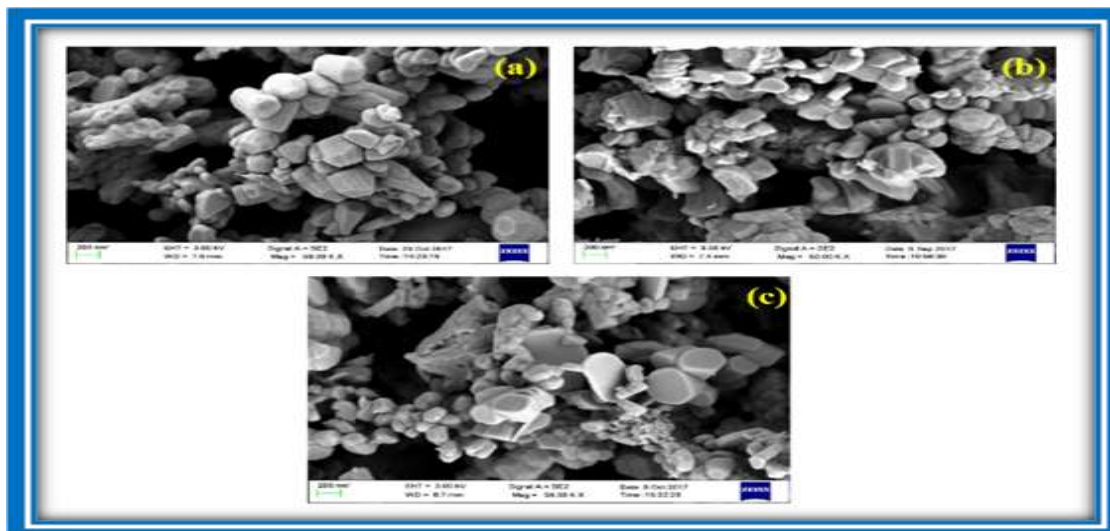


Fig 2: FESEM images of ZnO and La doped ZnO NPs (a) $X = 0$, (b) $X = 0.01$, and (c) $X = 0.03$ NPs.

3.3. Energy dispersive X-ray (EDAX) analysis

The chemical purity and elemental composition of the ZnO and La doped ZnO materials were investigated by Energy Dispersive X-ray analysis (EDAX), is shown in Fig. 3. In the doped samples, for the La concentration of $X = 0.01$ and $X = 0.03M$ are observed at 2.55%, and

7.42% respectively. In the pure ZnO, the chemical composition of Zn and O are found as 77.08% and 22.92% respectively. The EDAX results showed the presence of Zn, O and La. The prepared NPs are made of these elements. This may be La^{3+} ions incorporated with Zn^{2+} ion in the ZnO matrix.

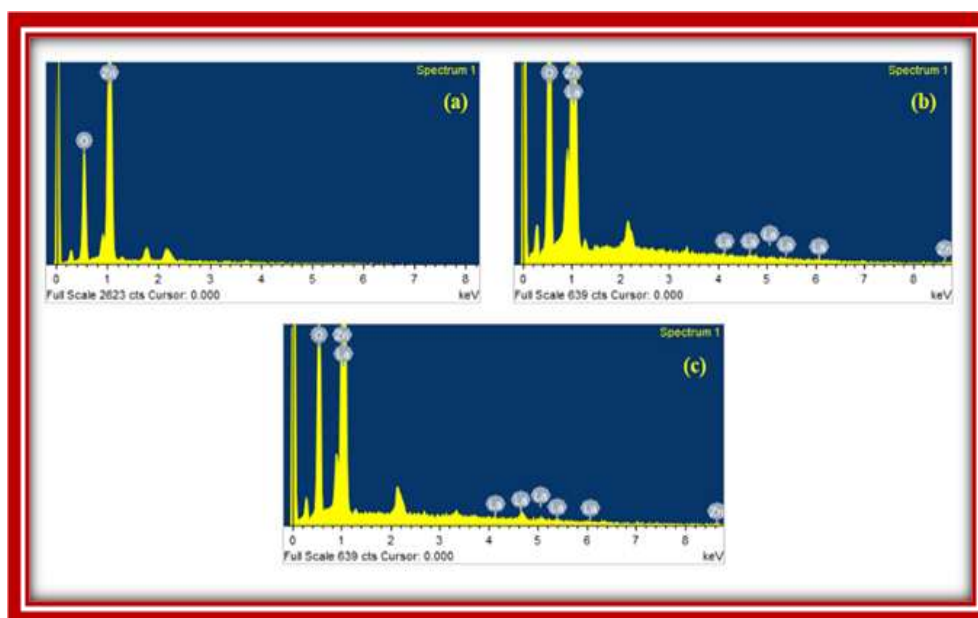


Fig 3: EDAX spectra of ZnO and La doped ZnO NPs. (a) $X = 0$, (b) $X = 0.01$, and (c) $X = 0.03$ NPs

3.4. Fourier transform infrared (FT-IR) spectroscopic studies.

The FT-IR spectra of ZnO and La doped ZnO ($X = 0, 0.01$ and $0.03M$) NPs are shown in Fig. 4. The

synthesized pure and La doped ZnO NPs were analyzed by FT-IR in the range from 400 to 4000 cm^{-1} at room temperature. The FT-IR spectra contains several characteristic bands. The Zn-O stretching band is

observed at 467 cm^{-1} for La doped ZnO NPs and La-O stretching is found at 621 cm^{-1} . This may be due to the formation of La_2O_3 on the surface of the NPs. The corresponding effect are also reflected in XRD studies.

The asymmetric C=O stretching bands appear at 1570 cm^{-1} and asymmetric C-H bands are observed at 2978 cm^{-1} for ZnO and La doped ZnO NPs.

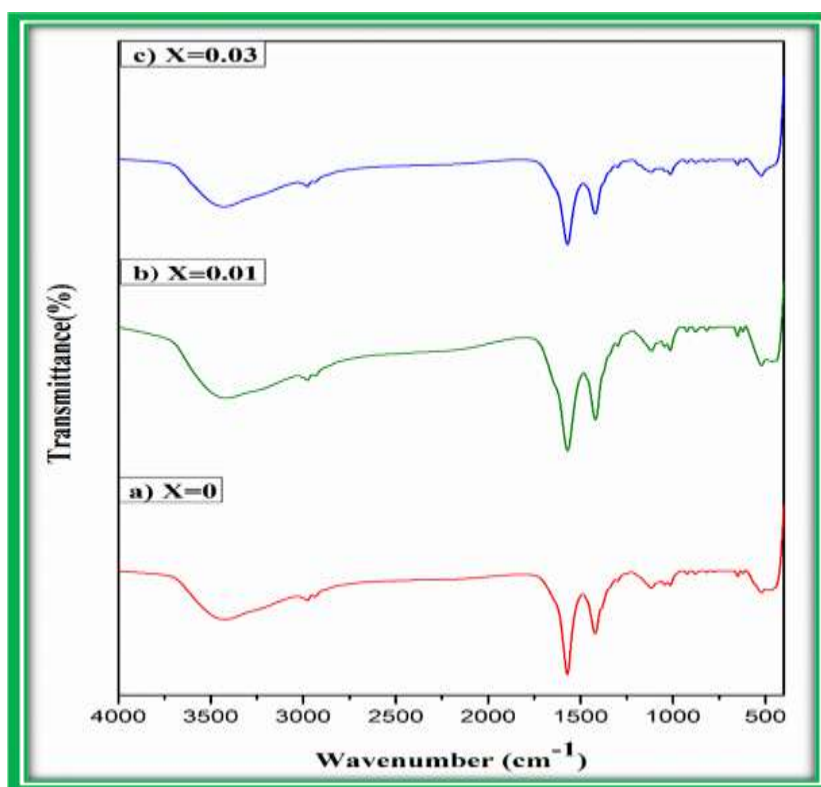


Fig 4: FT-IR spectra of ZnO and La doped ZnO NPs.
(a) $X = 0$, (b) $X = 0.01$, and (c) $X = 0.03$ NPs

3.5. UV-Vis absorption spectroscopy.

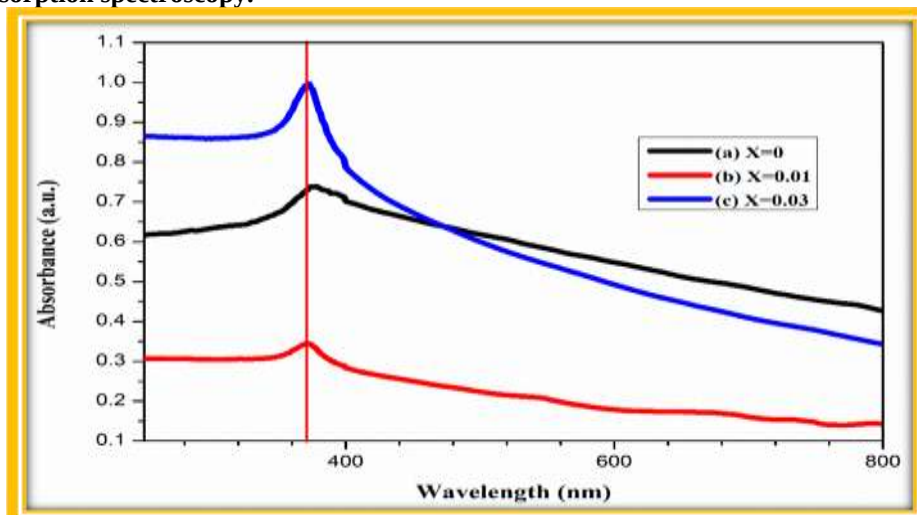


Fig 5: Absorption spectra of ZnO and La doped ZnO NPs.
(a) $X = 0$, (b) $X = 0.01$, and (c) $X = 0.03$ NPs

The optical properties of ZnO and La doped ZnO NPs materials with various doping concentrations were investigated by UV-Vis absorption spectra, are shown in Fig.5. From the absorption spectra, the absorption peaks are found at 377 nm for pure ZnO NPs, whereas the peaks are observed at 370 nm and 372 nm for $X=0.01$

and $X=0.03\text{M}$ La doped ZnO NPs respectively, which can be attributed to the photo excitation of electrons from valence band to conduction band.^[15]

The absorption band gap (E_g) is usually achieved with the aid of the following equation.

$$\alpha = \frac{k(h\nu - E_g)^{n/2}}{h\nu} \text{----- (2)}$$

Where k is a constant, E_g is the band gap and n is a constant equal to 1 for direct gap semiconductors and 4 for indirect band gap semiconductor materials.

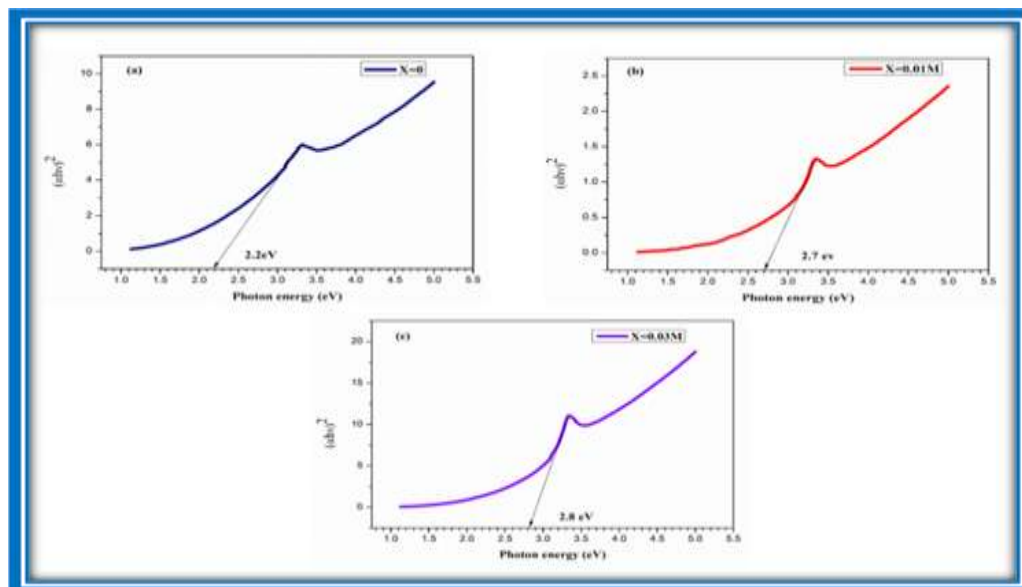


Fig 6: Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ of ZnO and La doped ZnO NPs. (a) X = 0, (b) X = 0.01, and (c) X = 0.03 NPs

From fig 6, it was noted that the lanthanum doping concentration had significant effects on the band gaps of synthesized ZnO and La doped ZnO NPs. When the doping concentration of lanthanum changes from 0 to 0.03 M, the value of E_g is increased from 2.2 to 2.8 eV, which may be due to Zn site in ZnO was occupied by a La atom and two main effects were observed: (1) The

impurity bands closer to the lower edge of the conduction band, which was created by substituted La and (2) The obtained band-gap exhibit narrow, due to the strong orbital coupling between La and O. The results illustrated that La doping concentration plays vital role in tuning the band gap of the synthesized ZnO and La doped ZnO NPs.

3.6. Antibacterial Activities.

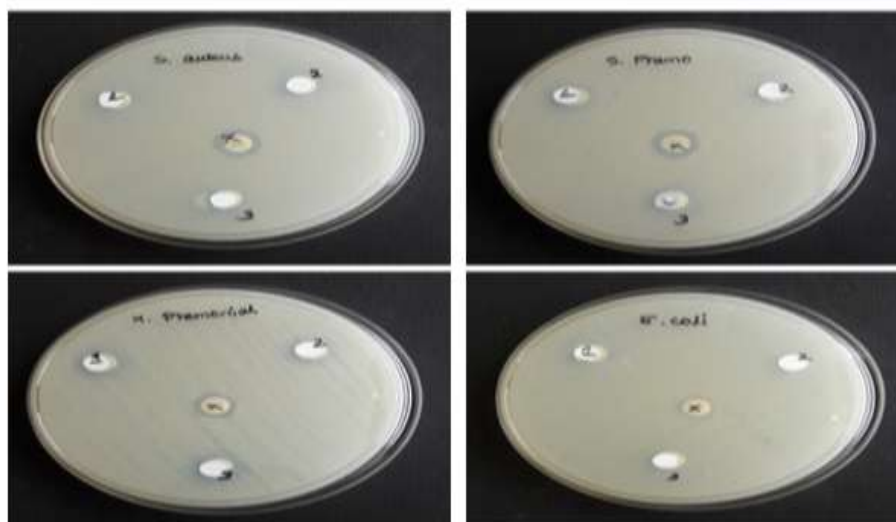


Fig 7: a) *S.aureus*, b) *S.pneumonia*, c) *K.pneumonia* and d) *E.Coli* bacteria medium i) X = 0, ii) X = 0.01 and iii) X = 0.03.

In the present work, the antibacterial activities of ZnO and La doped ZnO NPs are shown in fig.7. The antibacterial activities of synthesized ZnO and La doped ZnO NPs were tested against the human pathogens like

Gram positive (*S.aureus* and *S.pneumonia*), and Gram negative (*K.pneumonia* and *E.Coli*) bacteria with reference to Amoxicillin. The antibacterial activity values are listed in Table 1. From the results, the zones

were increased with respect to the La dopant concentration against the tested bacteria. To compare the Gram positive and Gram negative bacteria, the observed inhibition zone was higher in gram positive bacteria which may be due to the difference in their cell wall structure of chemical composition. From these zone

measurements, it could be stated that La doped ZnO NPs have higher antibacterial property when compared to pure ZnO NPs. The antibacterial activity of NPs may either directly interact with the microbial cells or produce secondary products that cause damage.

Table 1: Antibacterial activities of ZnO and La doped ZnO NPs for against human pathogens
Antibacterial activities of samples were determined as zone of inhibition (in mm).

Samples	<i>S.aureus</i>	<i>S.pneumonia</i>	<i>K.pneumonia</i>	<i>E.Coli</i>
Amoxicillin	1	0.8	0.7	0.8
x=0	0.9	0.7	0.8	1.1
x=0.01	1	0.6	0.8	0.9
x=0.03	1.1	0.7	0.7	0.7

4. CONCLUSIONS

In summary, ZnO and La-doped ZnO (X= 0, 0.01 and 0.03M) nanoparticles have been synthesized by green synthesis method. From XRD measurements, it was confirmed that the particle size of the synthesized ZnO and La doped ZnO NPs increases with increasing La concentrations and possess hexagonal wurtzite structure. In addition, the hexagonal like morphology was revealed by FE-SEM analysis. The elemental composition was confirmed by EDAX analysis. Using the recorded FT-IR spectra, the various vibrational frequencies were assigned for the ZnO and La doped ZnO samples. The band gap energies of doped nanoparticles were increased from 2.2 eV to 2.8 eV with increasing the lanthanum doping concentration. The antibacterial studies performed against a set of bacterial strains showed that the La doped ZnO NPs synthesised by green method possessed more antibacterial property.

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