



## Synthesis, structural and optical properties of Mn doped ZnO nanoparticles and their antibacterial application

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### ABSTRACT

In the present investigation,  $Mn_xZn_{1-x}O$  ( $x = 0.05, 0.075$  and  $0.1\%$ ) nanoparticles have been synthesized by simple precipitation method. Their structural, morphological and optical properties were examined by using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Energy dispersive X-ray spectroscopy (EDX), High resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Differential scanning calorimetry (DSC) and UV-Visible spectroscopy. The Powder X-ray diffraction studies confirmed that the manganese doped ZnO have a single phase nature with hexagonal wurtzite structure and Mn successfully incorporated into the lattice position of Zn in ZnO lattice. The FESEM and HRTEM images are coincided with each other for aggregation of particles in nature. The elemental analysis of doped samples has been evaluated by EDX. The antibacterial activity of Mn doped ZnO nanoparticles has also been examined.

### Keywords

ZnO, Precipitation method, Nanoparticles, Band gap, Antibacterial activity.

### Academic Discipline And Sub-Disciplines

Physics

### SUBJECT CLASSIFICATION

Nano technology

### TYPE (METHOD/APPROACH)

Precipitation method.

### 1. INTRODUCTION

In recent years, large number of investigations has focused on transitional metals such as La, Fe, Pd and Mn doped ZnO nanoparticles, due to its direct band gap of 3.37 eV at room temperature with large excitation binding energy of 60 meV [1]. Compared with all other metal oxides, it is abundant in nature and eco - friendly. These characteristics make this material attractive for many applications such as solar cells, optical coatings, photocatalysts, antibacterial activities, electrical devices, active medium in UV semiconductor lasers and gas sensors [2]. Hence, it has influenced the attention of researchers and scientists to develop ZnO in the field of science and technology.

Compared with pure ZnO nanoparticles, transition metal doped ZnO nanoparticles enhances the visible light absorption by generating energy states within the band gap, which act as intermediate steps for electrons in their transitions between the valence and conduction bands due to photoexcitation [3-5]. Doping of 3d transition metal Mn into the ZnO lattice tailors the various properties of ZnO. Further, it has been reported that Mn doping with an optimal concentration narrows the band gap of ZnO thus extending the absorption into the visible light region [6]. ZnO nanoparticles uniformly doped with Mn have advantages as dilute ferromagnetic semiconductor with characteristic luminescence [7].

Now-a-days microbial contamination is a serious issue in healthcare and food industry, so that the development of antimicrobial agents and surface coatings has been attracting and increasing attention in recent years. It has been recognized that toxicity of nanoparticles are generally high. Therefore, developments of nanoparticles with antimicrobial properties are of considerable interest [2].

Mn doped ZnO nanoparticles have been synthesized in several forms (Thin film, bulk and nanoparticles) by RF sputtering, Pulsed laser deposition (PLD), Chemical vapour deposition (CVD) and simple sol-gel method [8-12]. They, herein report the synthesis of different concentration of Mn doped ZnO nanoparticles by precipitation method. The characterization of  $Mn_xZn_{1-x}O$  ( $x = 0.05, 0.075$  and  $0.1\%$ ) nanoparticles were accomplished by X-ray diffraction, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Differential scanning calorimetry (DSC) and UV-Visible absorbance spectroscopy methods. The antibacterial activity of the various concentrated (0.05, 0.075 and 0.1%) Mn doped ZnO nanoparticles have also been examined.



## 2. EXPERIMENTAL

### 2.1. Physical measurements

The synthesized samples were recorded using powder X-ray diffractometer XPERT PRO X-RAY with the CuK $\alpha$  radiation source ( $\lambda=1.5406$  nm). The morphology of the samples was recorded using Scanning electron microscope JSM-6701F-6701 and particle size was recorded using transmission electron microscope TECNAI G2 Model. The elemental analysis was carried out by using energy dispersive X-ray spectroscopy (EDX). The composition quality of the synthesized material is characterized by Fourier transform infrared Thermo Nicolet 6700 FT-IR spectrophotometer in the range of 400 to 4000  $\text{cm}^{-1}$ . The Raman spectra have been recorded with a JASCO NRS 3300 spectrophotometer. Differential scanning calorimetry (DSC) performed using thermal analysis system DSC Q20 V24.10 Build 122, and studies the phase variations during crystallization. The absorbance spectra have been recorded in UV-visible spectrometer JASCO V-670. The *in vitro* antibacterial screening against *Staphylococcus aureus* and *Escherichia coli* for the nanoparticles have been carried out by agar disc diffusion method.

### 2.2. Preparation of Mn doped ZnO

ZnO nanoparticles have been prepared using the required precursors by precipitation method. An aqueous solution of 0.3M zinc acetate dihydrate  $\{\text{Zn}[\text{CH}_3(\text{COO})]_2 \cdot 2\text{H}_2\text{O}\}$  is dissolved in 50 ml distilled water and stirred for about 30 minutes at room temperature. After the reaction time, add drop by drop 50ml of 0.75M sodium hydroxide (NaOH) solution. The solution mixture was stirred for 4 hours at room temperature. After 4 hours the deposited precipitate is centrifuged and washed with distilled water and ethanol several times. The samples are then suspended in ethanol and allowed to age for 2 hours without stirring. After centrifugation, the samples then dried in oven at 70°C for 2 hours. Then, the prepared ZnO nanoparticles are placed in the middle of muffle furnace in silica crucible. The samples have been annealed at 450°C for an hour.

Similarly for Mn doping, the required amount of manganese nitrate ( $x = 0.05, 0.075$  and  $0.1$  %) was added into the zinc acetate dihydrate with 100 ml water and stirred for about 30 minutes at room temperature. In that solution, 50 ml of 0.75 mole sodium hydroxide solution was added drop wise, the obtained solution is aged, centrifuged and annealed in a similar way as mentioned above.

### 2.3. Determination of antibacterial activity

The antibacterial activities of the prepared samples were evaluated using agar disc diffusion method. The microorganisms used for this study were *Staphylococcus aureus* and *Escherichia coli*. 7 mm filter paper discs were impregnated with 20 mL of each of the different dilutions. The discs were allowed to remain at room temperature until complete diluents evaporation and kept under refrigeration until ready to be used. Discs loaded with samples were placed onto the surface of the agar. Then, the diameters of the inhibition zones were determined in millimeters.

## 3. RESULTS AND DISCUSSION

### 3.1. XRD analysis

The phase formation of  $\text{Mn}_x\text{Zn}_{1-x}\text{O}$  is confirmed by X-ray powder diffraction spectroscopy (Fig.1a). The pattern shows strong and sharp peaks, which confirm the hexagonal wurtzite structure of ZnO. Interestingly, the XRD pattern of Mn doped samples show no much change when compared with the pattern of un-doped sample, which confirms that there is no additional phase formation but there is a small shift to larger angle compared to pure ZnO diffraction pattern. For Mn doping the average crystallite size increases as 18, 25 and 26 nm for 0.05, 0.075 and 0.1 % Mn doped ZnO nanoparticles respectively.

The average crystallite size are calculated using the Scherrer's formula,

$$d = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where  $d$  is the average crystalline size,  $\lambda$  is the wavelength of radiation used;  $\theta$  is the Bragg angle and  $\beta$  is the full width at half maxima (FWHM).

When doping concentration increases, the dopants enhance the agglomeration of particles and hence crystallite size increases. The increase in crystallite size subsequently reduces the band gap, which causes the red shift of absorption band [13]. The diffraction peaks at  $2\theta$  (degree) of 31.91, 34.50, 36.33, 47.64, 56.71, 63.01, 68.01 and 69.25 are respectively indexed to (100), (002), (101), (102), (110), (103), (112) and (201) planes of ZnO. They are in good accordance with the JCPDS card No. 75-0576.

The high intensity peaks such as (100), (002) and (101) showed in Fig. 1b indicates that the preferential orientation for the nanoparticle along the c-axis. There is no trace of manganese related phase was detected up to 0.075% of Mn doped ZnO nanoparticles. This indicated that the Mn ions substituted Zn sites without changing the crystal structure of ZnO without

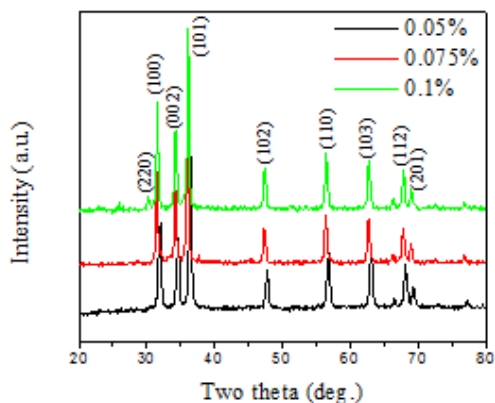


Fig 1a: XRD patterns of Mn doped (0.05, 0.075 and 0.1%) ZnO nanoparticles

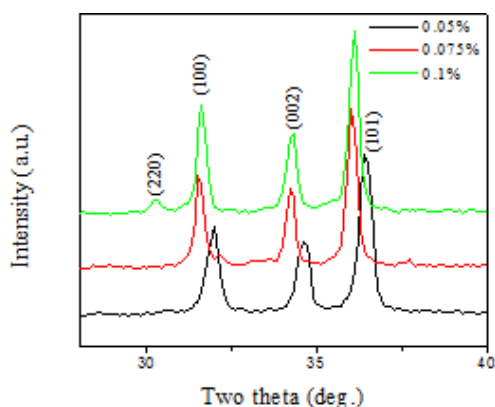


Fig 1b: Shifting of XRD peaks to higher degrees with increasing of Mn concentration

any precipitated phase or clustering. However with 0.1% of Mn doping, the appearance of an additional peak at  $30.24^\circ$  may assigned to  $Mn_3O_4$ . That is to say, not all the stoichiometric  $Mn^{2+}$  has entered the ZnO lattice, the rest of  $Mn^{2+}$  has been oxidized into manganese oxide [14]. The incorporation of  $Mn^{2+}$  into ZnO lattice is evidenced by the shrinkage or the expansion of the lattice parameters of ZnO in response to the transition metal dopant up to 0.075% Mn after which both a and c parameter show increase. This increase is accounted for the fact that ionic radius of  $Zn^{2+}$  ( $0.74\text{\AA}$ ) is smaller than that of  $Mn^{2+}$  ( $0.83\text{\AA}$ ). Such change in lattice parameters is indicative of the incorporation of Mn ions inside the ZnO lattice [7].

### 3.2. Field emission scanning electron microscopy

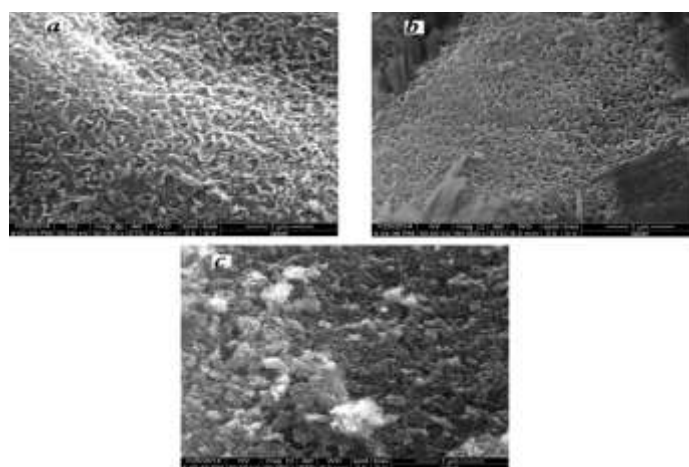


Fig 2: FESEM images of (a) 0.05% (b) 0.075% (c) 0.1% Mn doped ZnO nanoparticles

The surface morphological properties of the nanoparticles were analyzed by using FESEM (Fig.2) pattern of different concentrations of Mn doped ZnO nanoparticles. The amount and kind of dopant plays an important role on the surface properties and it is clearly identified from FESEM patterns [15]. At lower concentration, the  $Mn_xZn_{1-x}O$  nanoparticles are merged and appear as rice like grains. When the doping concentration increases, well-formed nanoparticles are appeared on the surface with nanorod like structures. Whereas in the case of 0.1% Mn doped ZnO, the morphology of particles significantly changes from rods to merging like granules [16]. The incorporated Mn in Zn lattice sites, changes the nanorod morphology to bound grains. The small particles are agglomerated and bound one another to form spherical shape of Mn doped ZnO nanoparticles due to the increase of doping concentration.

### 3.3. Energy dispersive X-ray spectroscopy

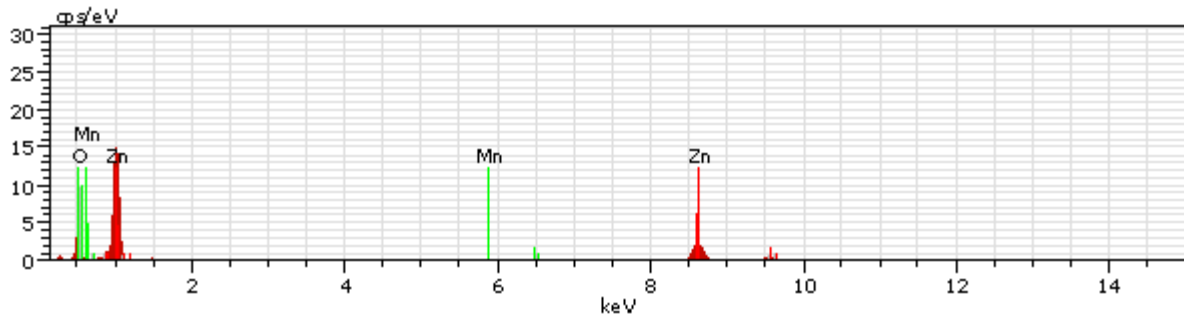


Fig 3: EDX analysis of  $Mn_xZn_{1-x}O$  ( $x=0.1\%$ ) nanoparticles

The Energy dispersive X-ray spectroscopy of the Mn doped ZnO nanoparticles was recorded to confirm the presence of Mn, Zn and O (Fig.3). The spectra showed that the atomic ratio of Zn, Mn and O is 8.60:0.32:91.08. This confirms the presence of Mn in the ZnO particles with wt% less than the nominal values of Mn in ZnO. Manganese is different from other transition metals when substituted in an  $A^{II}B^{VI}$  matrix, since it forms stable phases over a wide range of compositions. It appears that the ease with which manganese substitutes for the group II elements in the zinc blende and wurtzite structures results from the fact that the 3d orbitals of Mn are exactly half filled [14].

### 3.4. High resolution transmission electron microscopy

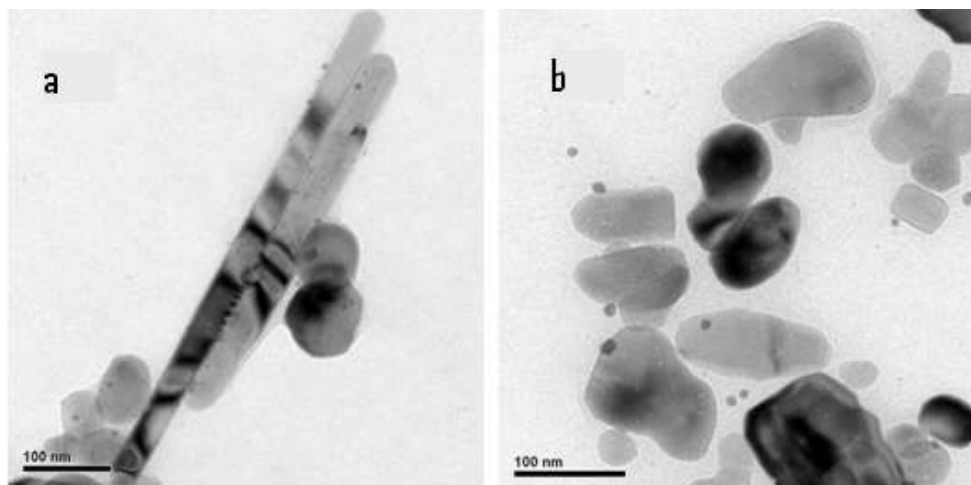
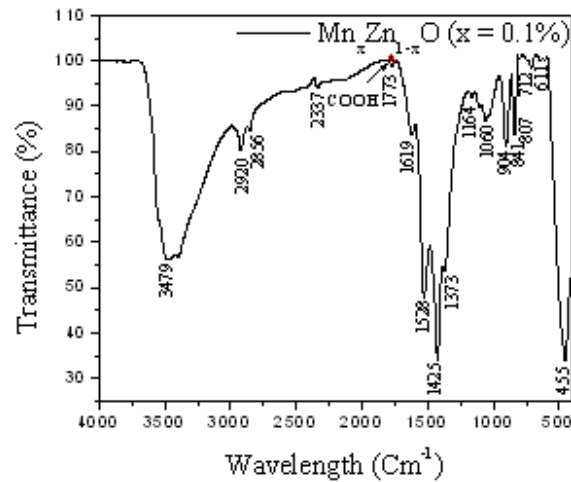


Fig 4: HRTEM images of (A) 0.075% (B) 0.1% Mn doped ZnO nanoparticles

The high resolution transmission electron microscope (HRTEM) image reveals that the size and morphology of Mn doped ZnO nanoparticles. Figure 4a (0.075%) shows the composed of polyhedral particles, which have a slight tendency to aggregate as nanorods [17]. Figure 4 (b) shows 0.1% Mn doped ZnO nanoparticles and the average size of the particle is found to be approximately 23.52 nm, which is in good agreement with the XRD results.

### 3.5. Fourier transform infrared spectroscopy

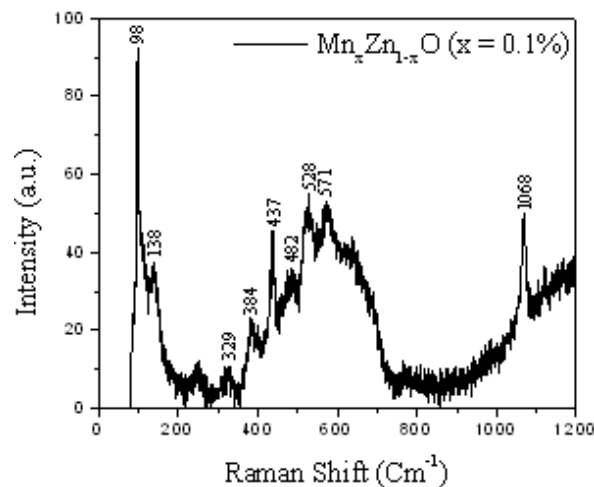
FTIR spectral data gives the information about functional groups present in a system, the molecular geometry, inter and intra molecular interactions. The FTIR spectra of the synthesized  $Mn_xZn_{1-x}O$  ( $x=0.1\%$ ) nanoparticles shown in figure 5. The peak at  $611\text{ cm}^{-1}$  is assigned to Mn - O bending [18]. The peak appeared around  $3479\text{ cm}^{-1}$  is assigned to O - H stretching vibration of  $H_2O$  in Zn - O lattice. The peak around  $1619\text{ cm}^{-1}$  is assigned to H - O - H bending vibration, due to the presence of small amount of  $H_2O$  in ZnO nanoparticles.



**Fig 5: FTIR spectrum of  $Mn_xZn_{1-x}O$  nanoparticles**

The peak around  $2337\text{ cm}^{-1}$  is the existence of  $CO_2$  molecule in air [19]. Peaks observed in the range from  $1200$  to  $1600\text{ cm}^{-1}$  can be attributed to the stretching vibration of  $C = O$  (asymmetric stretching). The peaks at  $2856$  and  $2920\text{ cm}^{-1}$  are due to  $C-H$  bond bending and stretching mode [20]. The above FTIR spectra showed that the  $C = O$  and  $C - O$  stretching vibration bands of  $COOH$  are around  $1773$  and  $1060\text{ cm}^{-1}$  [21,22]. A peak with low intensity at  $712\text{ cm}^{-1}$  can be assigned to the  $ZnO$  stretching mode [23]. The peak at  $841\text{ cm}^{-1}$  is appeared due to  $C - O - C - O$  bonds [22]. The strong peak appeared around  $455\text{ cm}^{-1}$  is due to  $Zn - O$  stretching vibration [24]. The absorption peak at  $807\text{ cm}^{-1}$  is due to the formation of tetrahedral coordination of  $Zn$ . The peak around  $1164\text{ cm}^{-1}$  indicates that the saccharide structure of  $ZnO$  nanoparticles [25]. The peak at  $904\text{ cm}^{-1}$  is due to  $C - O - C$  vibrations [26].

### 3.6. Raman spectroscopy



**Fig 6: Raman Spectrum of  $Mn_xZn_{1-x}O$  nanoparticles**

Raman spectroscopy used to identify the crystal quality, structural defects and disorder formation of the sample. Fig. 6 clearly showed that the prepared sample consists of nine peaks located at about  $98$ ,  $138$ ,  $329$ ,  $384$ ,  $437$ ,  $482$ ,  $528$ ,  $571$  and  $1068\text{ cm}^{-1}$ . In this peaks,  $98$ ,  $138$  and  $384\text{ cm}^{-1}$  are the fundamental phonon modes of hexagonal  $ZnO$  [27, 28, and 30]. The  $528\text{ cm}^{-1}$  peak was attributed to the lattice defects or distortions that are usually found in  $Mn$  doped  $ZnO$  nanoparticles. The peak around  $581\text{ cm}^{-1}$  due to  $ZnO$  ( $A_1(LO)$ ) mode. The peak shifted to lower wavelength  $571\text{ cm}^{-1}$  due to the formation  $Mn$  doping  $ZnO$  [29]. The Raman peaks at about  $329$  and  $1068\text{ cm}^{-1}$  might be due to the  $3E_{2H} - E_{2L}$  and  $A_1(TO) + E_1(TO) + E_{2L}$  multi phonon scattering modes, respectively [30]. The sharpest and strongest peak is observed at about  $437\text{ cm}^{-1}$ , which can be assigned to  $E_{2H}$  mode [31]. The mode  $482\text{ cm}^{-1}$  is related to the vibration of oxygen atom in  $ZnO$  hexagonal wurtzite structure [32].

### 3.7. Differential scanning calorimetry

Differential scanning calorimetry carried out to identify the release of water and  $OH$  groups from  $Mn$  doped  $ZnO$  nanoparticles. Figure 7 showed that the temperature range from  $25$  to  $500^\circ\text{C}$  and an endothermic peak spreading from  $80$  to  $160^\circ\text{C}$ , this reveals that the materials liberate water molecules [23]. The second endothermic peak from  $190$  to  $275^\circ\text{C}$  is due to the elimination of  $OH$  groups from the  $Mn_xZn_{1-x}O$  nanoparticles [33].

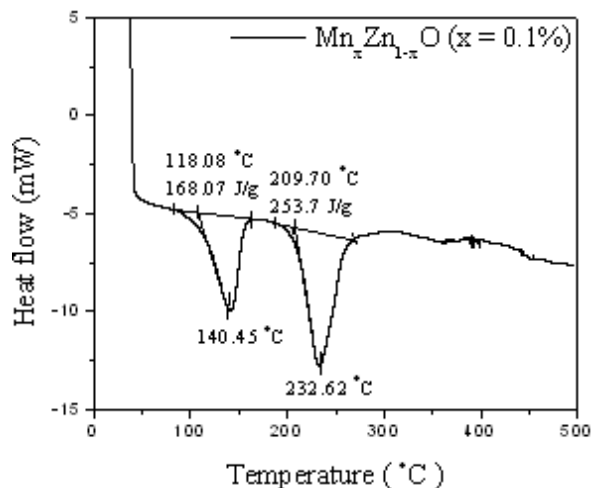


Fig 7: DSC analysis of Mn<sub>x</sub>Zn<sub>1-x</sub>O nanoparticles

### 3.8. UV-Visible spectroscopy

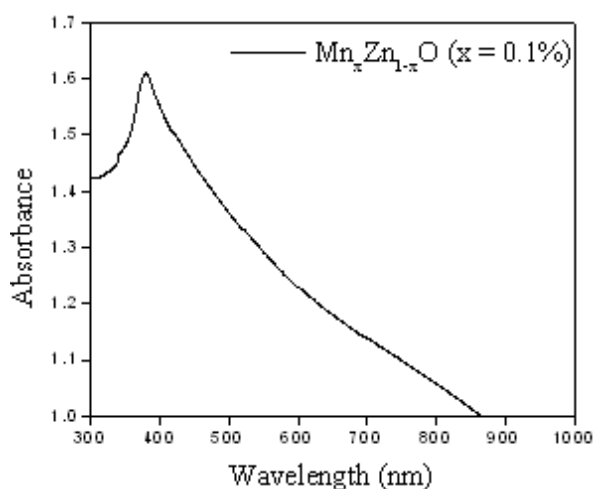


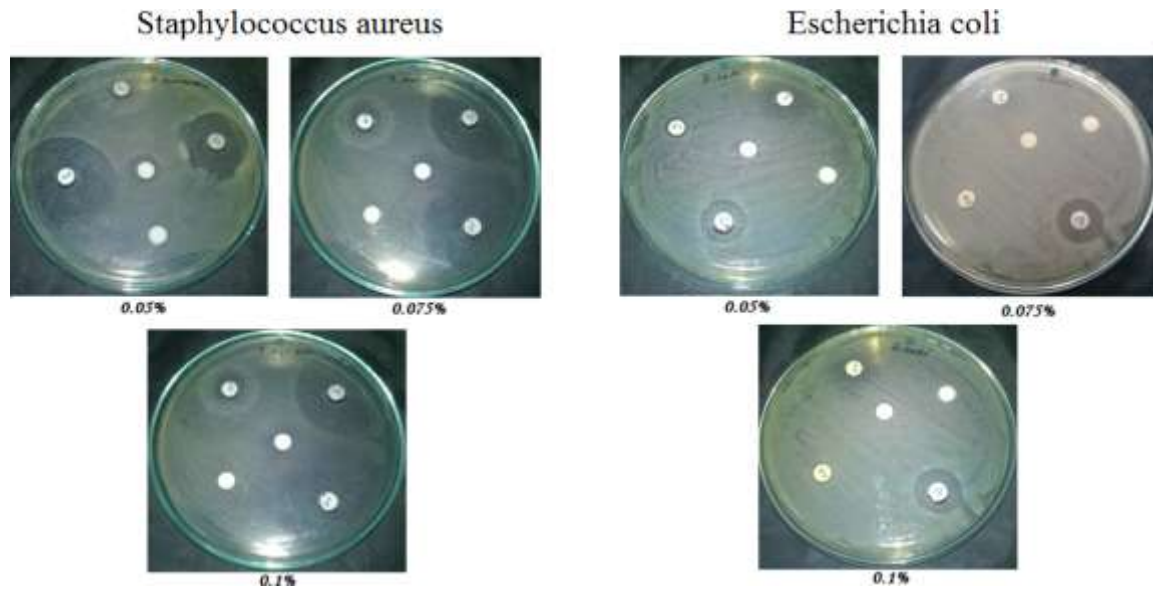
Fig 8: UV - Vis spectrum of Mn<sub>x</sub>Zn<sub>1-x</sub>O nanoparticles

The absorbance spectra of Mn<sub>x</sub>Zn<sub>1-x</sub>O (x = 0.1%) nanoparticles given in figure 8. This figure showed that the absorbance peak at 380 nm. The band gap energy of Mn doped ZnO nanoparticles could be determined using the following formula:  $E_{bg} = hc / \lambda$ , where h is planck's constant ( $4.135667 \times 10^{-15}$  eVs), c is the velocity of light ( $2.997924 \times 10^8$  m/s) and  $\lambda$  is the absorption wavelength in nm [1].

The band gap energy of undoped ZnO nanoparticles has comparatively high rather than band gap energy of doped ZnO (ie 1.9 eV). It may be due to the sp – d spin exchange interaction between the band electrons and localized d electrons of Mn ions substituting in cation sites [34]. Our experimental result indicates red shift in the band gap. This confirms the substitution of Mn in ZnO nanoparticles [35].

### 4. Antibacterial activity

The antibacterial activity of Mn doped ZnO nanoparticles (Sample) along with antibiotics are investigated against pathogenic bacteria such as *Escherichia coli* and *Staphylococcus aureus* using agar disc diffusion method. The diameter of inhibition zones around each disc is shown in figure 9 and the results are tabulated in Table 1. The results showed that, the toxicity of the sample increases with increase in concentration. Though the sample possesses activity, it could not reach the effectiveness of the standard drugs ampicillin and erythromycin. But, the sample moderate increase in inhibition zones were against penicillin.



**Fig 9: Antibacterial activities of  $Mn_xZn_{1-x}O$  nanoparticles**

**Table-1: Zone of inhibition concentration of  $Mn_xZn_{1-x}O$  ( $x=0.05, 0.075$  and  $0.1\%$ ) nanoparticles**

S.No	Antibiotics	Diameter of inhibition Zone (mm)					
		<i>Escherichia coli</i>			Staphylococcus aureus		
		0.05	0.075	0.1	0.05	0.075	0.1
1	$Mn_xZn_{1-x}O$	8	9	10	14	16	36
2	Penicillin (P 10)	8	7	8	14	15	38
3	Ampicillin (A 10)	17	17	17	26	38	39
4	Erythromycin (E 15)	22	22	22	38	36	41

## 5. Conclusion

The Mn doped ZnO nanoparticles have been prepared by precipitation method. The prepared nanoparticles are annealed at 450°C and characterized on the basis of XRD, SEM, HRTEM, DSC and spectral (FT-IR, Electronic, Raman and EDX) data. Also, examined their antibacterial activities and found significant antibacterial activity.

## 6. References

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