



Preparation and Characterization of Ag doped ZnO nanoparticles and its Antibacterial Applications

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ABSTRACT

In the present investigation, $Ag_xZn_{1-x}O$ nanoparticles ($x = 0.05, 0.075, \text{ and } 0.1\%$) have been successfully synthesized by precipitation method. The synthesized $Ag_xZn_{1-x}O$ nanoparticles were characterized by X-ray diffraction analysis (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 and UV-visible spectrophotometer. The XRD studies revealed that the Ag doped ZnO nanoparticles in hexagonal wurtzite structure. The FESEM and HRTEM images show that the presence of aggregated nanoparticles. The EDX spectrum confirmed the present metals in $Ag_xZn_{1-x}O$ nanoparticles which indicated the purity of the sample. The FTIR and Raman spectrum indicates that the present functional groups and crystalline quality of Ag doped ZnO nanoparticles. The optical properties were measured by using UV-Vis Spectrophotometer. The antibacterial activity of the samples are examined and also compared with standard drugs.

Keywords

Antibacterial activity, Nanoparticles, Precipitation method, Silver, ZnO nanoparticles.

Academic Discipline and Sub-Disciplines

Physics

SUBJECT CLASSIFICATION

Nano technology

TYPE (METHOD/APPROACH)

Precipitation method.

1. INTRODUCTION

Nanomaterials are considered as excellent adsorbents, catalysts and sensors by reason of their large specific surface area and high reactivity. In recent years, the application of nanoparticles are developed in different fields such as cell labeling, drug targeting gene delivery, micro electronics, solar cells, electroluminescent devices, detergent and cosmetics. Due to their abilities, nanoparticles have been further investigated for reduce microbial infections and prevent bacterial colonization. Hence the nanoparticles are called as "a modern medicine" [1].

Among the metal oxides, ZnO is unique due to its dual semiconducting and piezoelectric properties. In addition, it has direct wide band gap 3.37 eV at room temperature and large exciton binding energy of 60 meV [3]. ZnO nanoparticles have also been studied for their industrial applications such as photocatalytic, luminescent, pigments, components for the pharmaceutical, cosmetic and metal protective coatings [2]. Due to the high electron mobility, transparency and tunable magnetic property, it has been become a key material for applications in laser diodes, solar cells, gas sensors, dilute magnetic semiconductors, spintronics and optoelectronic devices [4].

The main objective of synthesis is to produce particles only in nanorod structure for various toxicity and biological application studies. There are different doping agents like P [5], N [6], as [7], Li [8], Sb [9-12], and Ag [13]. Among these, we took Ag as a doping agent because of simple link matrices and their behavior becomes important to surface states in nonmaterials. Silver nanoparticles exhibit unique physicochemical properties that facilitate their use in a variety of applications. The nano structured Ag is highlighted with the purpose of use in the environment and human health [14]. The large number of chemical methods such as hydrothermal [15], precipitation [16], sol-gel [17] and thermal decomposition [18] have been widely used to synthesize Ag doped ZnO nanoparticles. Among these chemical methods, precipitation method is a common method that can be used for large scale production with low cost, low temperature, environmental safety and simple equipments.

In the present work, we reported that the synthesis and characterization of silver doped ZnO nanoparticles by precipitation method. Also, its antibacterial activity of the various concentrated (0.05, 0.075 and 0.1%) Ag doped ZnO nanoparticles have also been examined.

2. EXPERIMENTAL

2.1. Physical measurements

The synthesized nanoparticles were recorded by powder X-ray diffractometer (XPRT PRO X-RAY) with the CuK α radiation source ($\lambda=1.5406$ nm). The morphology of the nanoparticles was recorded by field emission scanning electron microscopy (JSM-6701F-6701). Compositional analysis of the sample was recorded with the help of energy dispersive X-ray spectroscopy (JEOL Model JED – 2300). The particle size was determined by high resolution transmission electron microscopy (Philips TECNAI F20). The FTIR spectrum was recorded using FTIR spectrometer (THERMO NICKOLET-6700). The Raman spectrum was recorded by Raman spectroscopy (JOBIN YVON HORIBA HR 800 UV) and to study the crystallinity of the sample. The optical properties were carried out using UV – vis spectrophotometer (JASCO V- 670). The antibacterial activity of the nanoparticles was carried out using agar disc diffusion method against *Staphylococcus aureus* and *Escherichia coli*.

2.2. Preparation of Ag doped ZnO

ZnO nanoparticles have been prepared using the required precursors by precipitation method. An aqueous solution of 0.3M zinc acetate dihydrate $\{Zn[CH_3(COO)]_2 \cdot 2H_2O\}$ 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 is 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 Ag doping, the required amount of silver 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 agar disc diffusion method is used to determine the antibacterial activities of the silver doped ZnO nanoparticles. A suspension of each sample of tested microorganisms diluted earlier to $10^{-1}, 10^{-2}$ and 10^{-3} (1 ml of 108 cells / ml) was spread on a solid agar medium. Filter paper discs (4 mm in diameter) were soaked in 5 μ l of the sample and placed on the inoculated plates and allowed to dry for 15 min, then incubated at 37°C for 24 h. The diameters of the inhibition zones were measured in millimeters.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The phase and crystal structure of Ag doped ZnO ($Ag_xZn_{1-x}O$, where $x = 0.05, 0.075$ and 0.1%) nanoparticles are confirmed by X – ray diffraction analysis and the pattern is recorded in the range from 20° to 80° shown in the figure 1. It has been found that all the major diffraction peaks perfectly indexed with the hexagonal wurtzite structure of ZnO and the phase is well matched with JCPDS card no. 75 – 0576 (Phase: Hexagonal, Lattice: Primitive, space group: P63mc (186), $a=0.324$ nm, $c=0.519$ nm). In this pattern, the peaks are detected at angles 2θ of $31.9^\circ, 34.5^\circ, 36.3^\circ, 47.7^\circ, 56.7^\circ, 63.0^\circ, 66.5^\circ, 68.1^\circ, 69.0^\circ, 72.7^\circ$ and 77.3° corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) respectively.

The pattern of Ag doped ZnO nanoparticles has been revealed three additional diffraction peaks at 2θ of $38.3^\circ, 44.4^\circ, 64.6^\circ$ and associated with the metallic Ag fcc phase (JCPDS card no.04-0783). The appearance of Ag peaks clearly indicated that the formation of silver as second phase clusters [19]. The decrement of the peak position value is observed when a doping element with a larger ionic radius than Zn^{2+} is replaced at the substitution sites of the ZnO crystal lattice. The Ag^+ ion (1.22 Å) has higher ionic size than Zn^{2+} ion (0.74 Å), probably substituting Zn^{2+} ions. Therefore, the increment of the peak position suggested that the Ag ion has occupied the interstitial sites of ZnO, which is consistent with the reported data [20]. Since, Ag acts as an amphoteric dopant and having a tendency to occupy both substitution Zn and interstitial sites. However, it has been predicated theoretically that the incorporation of Ag^+ ions at the interstitial sites is a difficult proposition due to their high formation energy, ~ 3 eV [21].

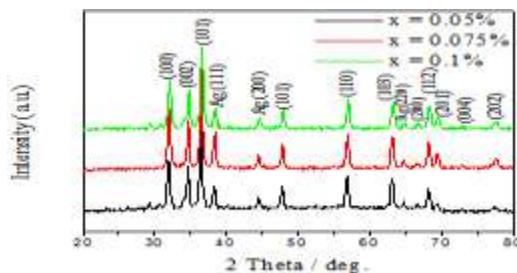


Fig.1: XRD patterns of $Ag_xZn_{1-x}O$ nanoparticles

The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye - Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \text{-----} [2]$$

Where D is the average crystallite size, λ is the wavelength, β is the Full width at half – maximum and θ is the Bragg angle. The calculated average crystallite sizes are 18.19 nm, 21.63 nm, and 21.93 nm for the concentrations 0.05, 0.075 and 0.1% of Ag doped ZnO.

3.2. Field emission scanning electron microscopy

The surface morphology of the prepared Ag doped ZnO nanoparticles are investigated by FESEM analysis shown in the figure 2. The FESEM images revealed that the formation of homogeneous and uniformly distributed Ag doped ZnO nanoparticles. The average grain size is found to decrease with the increase of Ag doping, which suggests that the aggregation of particles are much less in this method of preparation. Due to adding Ag into ZnO nanoparticles, the morphology varies from nanorods to spherical nanoparticles. In the morphological variation, the Ag doping may be strongly influenced on the growth rate of ZnO [22, 23].

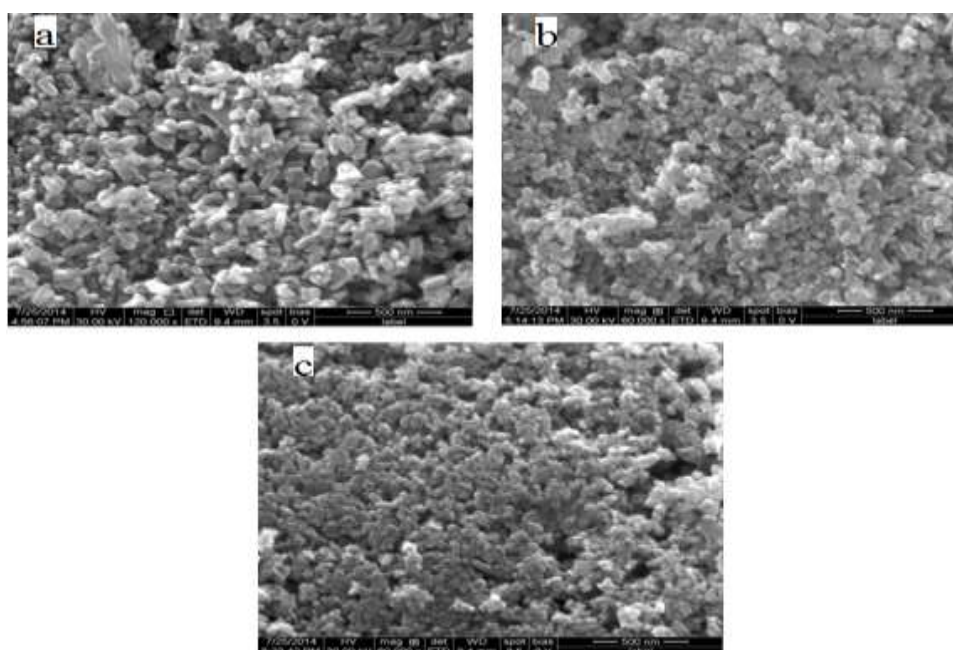


Fig.2: FESEM images of $\text{Ag}_x\text{Zn}_{1-x}\text{O}$ ($x= 0.05, 0.075$ and 0.1%) nanoparticles

3.3. Energy dispersive X-ray spectroscopy

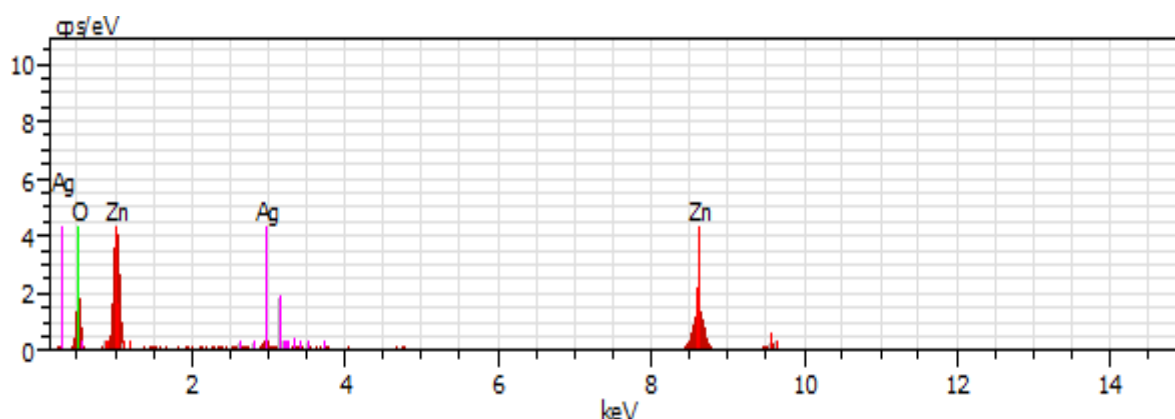


Fig.3: EDX pattern of $\text{Ag}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.075\%$) nanoparticles

The energy dispersive X – ray spectrum recorded in figure 3 and confirmed that the presence of silver, zinc and oxygen metals in the sample. In figure 3, the present peaks clearly showed that the silver, zinc and oxygen metals were pure [24]. The spectrum showed the atomic ratio of Zn, Ag and O is 64.03:1.84:34.13.

3.4. High resolution transmission electron microscopy

The morphology and particle size of $\text{Ag}_x\text{Zn}_{1-x}\text{O}$ was further characterized by HRTEM which showed the direct information about the distribution of metal oxide on the surface. Figure 4(a) shows the interplanar lattice spacing of the planes and it is found to be 2.127 Å corresponding to (200) plane of hexagonal ZnO. Fig. 4(b) shows the average particle size is in the range of 20.31 nm, which is in good agreement with the XRD results.

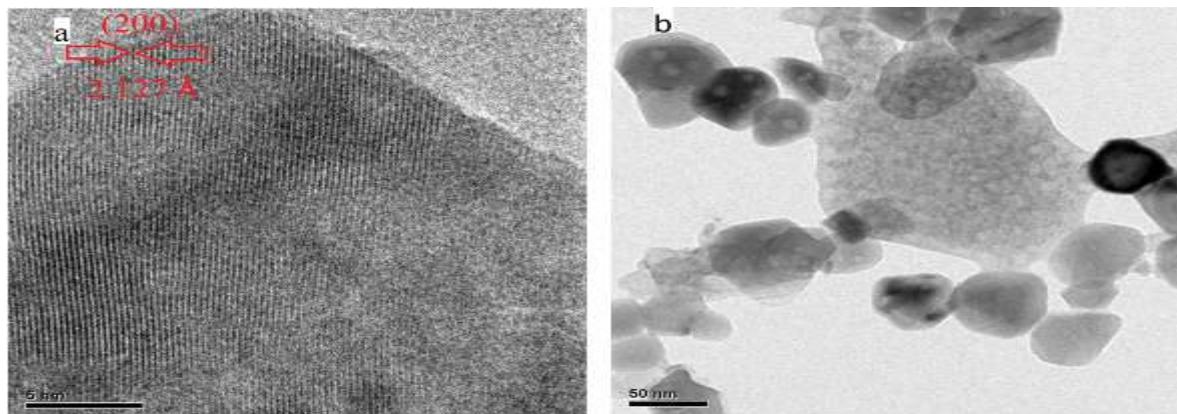


Fig.4: HRTEM images of $\text{Ag}_x\text{Zn}_{1-x}\text{O}$ ($x = 0.075\%$) nanoparticles

3.5. Fourier transform infrared spectroscopy

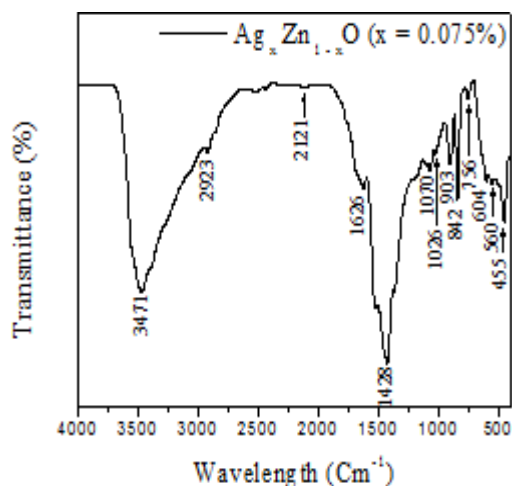


Fig.5: FTIR spectrum of $\text{Ag}_x\text{Zn}_{1-x}\text{O}$ nanoparticles

The FTIR has been used to study the nature of the bonds present in the prepared samples. The FTIR spectrum of Ag doped ZnO nanoparticles recorded in the range 4000 – 400 cm^{-1} are shown in the figure 5. The peaks observed in the range from 400 to 700 cm^{-1} can be attributed to ZnO stretching modes [25]. The peak around 1626 cm^{-1} is appeared due to the hydroxyl group of absorbed H_2O molecules. The peaks around 1070 and 1428 cm^{-1} may be assigned to the C – O – C and O – H bonds owing to the deformations of the C – OH groups [26]. The wide intense peak at 3471 cm^{-1} can be assigned to O – H group stretching vibrations due to the bound H_2O molecules present on the surface of the Ag doped ZnO nanoparticles [27]. The 842 cm^{-1} peak may be appeared by reason of the C – O – C – O vibrations [28]. The peaks 903 and 2121 cm^{-1} are appeared due to C – O – C vibrations and the result of CO_2 and CO physisorption [29]. The peaks around 2923 and 1026 cm^{-1} can be assigned to C – H stretching vibrations and the aromatic C=C stretching mode [30, 4]. The peak at 756 cm^{-1} is appeared due to the chemical bonding, crystal structure and relative intensities of the IR bonds of the carbonate [31].

3.6. Raman spectroscopy

The Raman spectrum has been used to study the crystallization, structural disorder and defects in nanostructures. The Raman spectrum of Ag doped ZnO nanoparticles recorded in the range 0 – 1200 cm^{-1} shown in the figure 6. The Raman peak at 487 cm^{-1} appeared only for Ag doped samples due to the interfacial surface phonon mode. The peak at 237 cm^{-1} can be assigned to the radial effect of Ag atoms in the spectrum [32]. The 565 cm^{-1} peak appeared due to $A_1(\text{LO})/E_1(\text{LO})$ polar branches for doped samples. Due to the incorporation of Ag ions into ZnO lattice, the $A_1(\text{LO})/E_1(\text{LO})$ peak is widened and shifted to lower energy. Such widen and shifting in the phonon mode can be

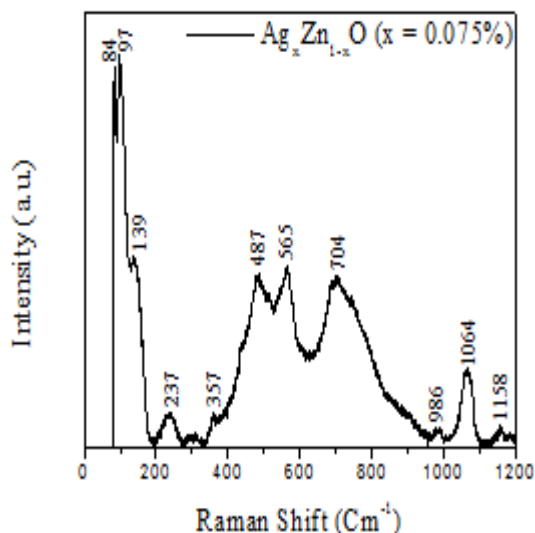


Fig.6: Raman spectrum of $Ag_xZn_{1-x}O$ Nanoparticles

attributed to the contribution of $A_1(LO)/E_1(LO)$ branch outside the Brillouin zone centre and this phonon mode is assigned to the defect complexes having oxygen vacancy (VO) and zinc interstitial (Zn_i) in ZnO. The Raman peaks 139 and 1158 cm^{-1} can be assigned to the second order phonon mode ($2E_{2L}$) and the multi phonon process [3]. The peaks 357 and 704 cm^{-1} may be appeared to the Ag doped ZnO composite related vibrational modes [32]. The peak around 1064 cm^{-1} can be attributed to the multi phonon scattering modes $A_1(TO) + E_1(TO) + E_{2L}$. The peaks 84 and 97 cm^{-1} can be assigned the fundamental phonon modes (E_{2L}) of hexagonal ZnO. The unidentified peak is appeared at 986 cm^{-1} [33, 34].

3.7. UV-Visible spectroscopy

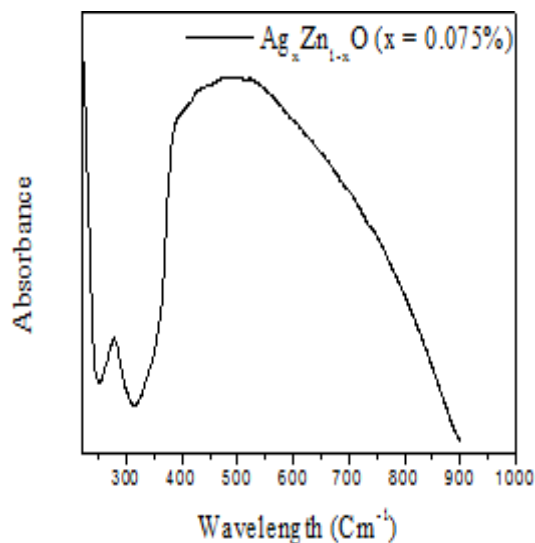


Fig.7: UV-Vis spectrum of $Ag_xZn_{1-x}O$ Nanoparticles

The optical spectrum of Ag doped ZnO nanoparticles is shown in figure 7 and recorded in the wavelength range from 225 to 900 nm. The band gap energy of Ag doped ZnO nanoparticles have been calculated from this formula: $E = hc / \lambda$, where h is planck's constant ($4.135667 \times 10^{-15} eV$), c is the velocity of light ($2.997924 \times 10^8 m/s$) and λ is the absorption wavelength. This spectrum exhibits the absorbance peak at 317 nm which is shifted towards the lower wavelength (i.e. below the band gap wavelength of 365 nm, $E_g = 3.4 eV$ of bulk ZnO) or known as blue shift. The band gap energy is obtained to be 3.9 eV. No extra peak related with impurities is found in the above spectrum and confirmed that the prepared nanoparticles are pure.

4. ANTIBACTERIAL ACTIVITY

The antibacterial activity of silver doped ZnO nanoparticles (Sample) along with standard antibiotics are investigated against pathogenic bacteria such as *Escherichia coli* and *Staphylococcus aureus* using agar disc diffusion method. The inhibition zones diameter of each disc is measured in figure 8 and the values are tabulated in Table 1. The values show 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 increase in inhibition zones were against penicillin.

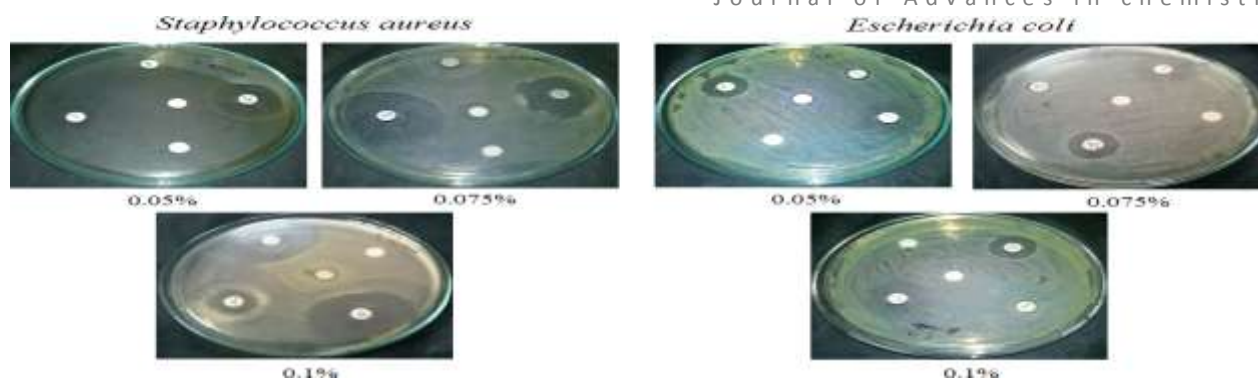


Fig.8: Antibacterial activities of the $Ag_xZn_{1-x}O$ nanoparticles against *S.aureus* and *E.coli*.

Table-1: Zone of inhibition values of $Ag_xZn_{1-x}O$ ($x = 0.05, 0.075$ and 0.1%) nanoparticles

S.No	Antibiotics	Diameter of inhibition Zone (mm)					
		<i>Escherichia coli</i>			<i>Staphylococcus aureus</i>		
		0.05	0.075	0.1	0.05	0.075	0.1
1	$Ag_xZn_{1-x}O$	9	10	11	9	10	12
2	Penicillin	7	8	9	15	16	17
3	Ampicillin	17	18	19	22	26	36
4	Erythromycin	20	21	22	17	32	41

5. CONCLUSION

$Ag_xZn_{1-x}O$ ($x = 0.05, 0.075$ and 0.1%) nanoparticles have been synthesized by precipitation method. The synthesized nanoparticles are successfully characterized by XRD, FESEM, EDX, HRTEM, FTIR, Raman analysis and UV-vis analysis. The crystallite size of $Ag_xZn_{1-x}O$ nanoparticles are calculated to increase with increase in Ag content, without changing the wurtzite hexagonal single phase structure of ZnO. From SEM results, Ag doping significantly influences the grain size and morphology of ZnO nanoparticles. In the UV-visible absorption spectrum of Ag doped ZnO, the calculated band gap is 3.9 eV. $Ag_xZn_{1-x}O$ nanoparticles show an effective antibacterial agent for gram positive bacteria.

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