JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

CHEMICAL MEDIATED SYNTHESIS OF CuO -ZnO NANOCOMPOSITE AND ITS ANTIBACTERIAL ACTIVITY AGAINST HUMAN PATHOGENS

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Abstract: In the field of environmental science, metal oxide nanocomposite has gained a great attention for both theoretical and experimental aspects of their upgradation because of their wide range of practical applications such as catalysts, sensor, biomedicine and optoelectronics. Among all nanocomposites, Copper oxide –Zinc oxide (CuO-ZnO) has attracted more research due to their excellent tunable catalytic, electrical, optical, magnetic properties and environmental-friendly nature. In the present study, CuO-ZnO nanocomposite (NC) was synthesized by using simple chemical precipitation technique, followed by oven drying in the temperature range of 60-70˚C. The synthesis was monitored by UV–Vis spectroscopy, which confirmed the formation of the nanoparticles by showing peaks above 250 nm and a red shift was observed in the spectra of the nanocomposite. The structural evaluation of the nanomaterials using Fourier transform infra-red spectroscopy showed the presence of carboxylic group on their surface, indicative of their role as stabilizing agents. The X-ray crystallographic studies showed the cubic structure with estimated crystallite size of 30.42 nm for CuO–ZnO nanocomposite. The heterostructure of Synthesized CuO-ZnO NC was examined by SEM analysis. Well diffusion method was opted to inquire the antimicrobial ability of nanocomposites against different bacterial strains such as *Escherichia coli* (−) and *Staphylococcus aureus* (+). CuO-ZnO NC possessed good antimicrobial activity against the both selected strains as proved from zone of inhibitions. Furthermore, CuO-ZnO NC showed more sensitive to gram negative bacteria than gram negative bacteria.

***Keywords* - CuO-ZnO nanocomposite, Chemical Precipitation method, XRD, SEM, Antibacterial activity.**

1. Introduction:

A nanocomposite is a matrix to which nanoparticles have been added to improve a particular property of the material and the properties of nanocomposite was differ from individual atoms, molecules and bulk material [1]. The main advantages of nanocomposites are high surface area/volume ratio, improved mechanical and optical properties. Nanocomposite offers opportunities on completely new scales for solving obstacles ranging from medical, pharmaceutical industry, food packaging, water treatment electronics and energy industry [2, 3]. In pharmaceutical application nanocomposite directed against Gram + and Gram – microbes have been described in which bacterial targeting was recognized by electrostatic interaction connecting the negative charge microbial membrane and positive charge residues on the composite surface [4]. Several nanocomposites such as ZnO- TiO2, CuO – NiO- ZnO, WO3-TiO2, ZnO-SnO2, CuO-TiO2, TiO2-MgO, and ZnO-CuO have already successfully synthesized [5]. Among them CuO-ZnO nanocomposite has gained more attention due to its photocatalytic activity, magnetic properties [6] humidity [7] and gas [8] sensing ability. ZnO NPs (n-type 3.37eV) and CuO NPs (P-type 1.2 eV) can be applied in cancer therapy, cosmetic creams and industrial catalysts. ZnO NPs are widely employed due to the production of reactive oxygen species (ROS) and their unique electrostatic behavior, which can prevent DNA damage but Cu ions released from the surface of CuO NPs have insufficient toxicity against the other cancer cells [9,10,11].There are numerous methods are used to involve the nanocomposite synthesis such as Chemical co precipitation method, sol-gel, bubble electro spinning, bubbfil spinning, chemical vapour Deposition method, wet chemical method, thermal decomposition method, electrospinning, Thermal oxidation, Microwave synthesis, hydrothermal method, Complex –directed hybridization, directly heating brass in air [12], perfume spray pyrolysis method [13] and Carbothermal evaporation method [14] etc. Among all methods chemical co precipitation method is simple, easily available and cost effective [15]. The aim of this work is to synthesize CuO-ZnO by chemical precipitation method and investigate their antibacterial potentials against human pathogenic bacteria such as Escherichia coli (−) and Staphylococcus aureus (+). The synthesized CuO-ZnO NC was characterized using physicochemical techniques such as UV-Visible, FTIR, XRD and SEM to investigate their crystalline nature, size, morphology and optical properties of nanocomposite.

2. Experimental

2.1 Materials and methods:

The CuO–ZnO nanocomposite were synthesized firstly by mixing 400 mL of 10 mM $ZnSO_4 \cdot 5H_2O$ with 10 mL of the sodium citrate and 10 mL of 1 M NaOH. It was heated with continuous stirring for about 4 h, after which 400 mL of 2 mM $Cu(CH_3COO)_2 \cdot H2O$ was added to the solution and heated at 70 °C for another 5 h. The solution was centrifuged, washed and the formed nanocomposite was dried in an oven at 60 °C for 24–48 h [16].

2.2 Characterization tools:

The UV-Visible absorption spectra of CuO-ZnO nanocomposite was measured by using Beckman - model NO.Du-50, Fullerton Spectrophotometer. FTIR spectra were studied by using Perkin Elmer Spectrum Express version 10,300 using KBr pellet method. The crystalline nature was analyzed by powder X-ray diffractometer using X'Pert PRO PAnalytic, Philips PW 3050. The morphological character of the nanocomposite was examined by SEM JEOL-JSM 64000LV.

2.3 Antibacterial Activity:

The antibacterial activity of CuO-ZnO nanocomposite was tested against human pathogenic bacteria such as (*Staphylococcus aureus* ATCC33591 (Gram +ve) and *Escherichia. Coli* ATCC10536 (Gram -ve) by well diffusion method.

3. Results and discussion:

3.1. UV-Visible spectroscopy:

The UV-Visible absorption of the synthesized CuO NPs, ZnO NPs and CuO-ZnO NC was recorded in the range of 200-800 nm. The absorption spectra and the optical bandgap of CuO NPs, ZnO NPs and CuO-ZnO NC were presented in Fig 3.1, 3.1.2 and 3.1.3. The absorption band obtained at 261 nm attributed to the charge transfer transition from O^{2-} to Cu^{2+}, which confirms the existence of CuO nanoparticles [17], whereas the observed peak at 360 nm indicates the formation of ZnO nanoparticles. The UV- Visible absorption spectra of CuO-ZnO NC was observed at 261 nm and a minor peak at 365 nm [18]. According to the optical absorption spectral data, the bandgap energy of the CuO-ZnO nanocomposite was determined by using Tauc Plot method. The required equation was

$$\boxed{(\alpha h\nu)^n = B\,(h\nu - E_g)} \qquad \textbf{(1)}$$

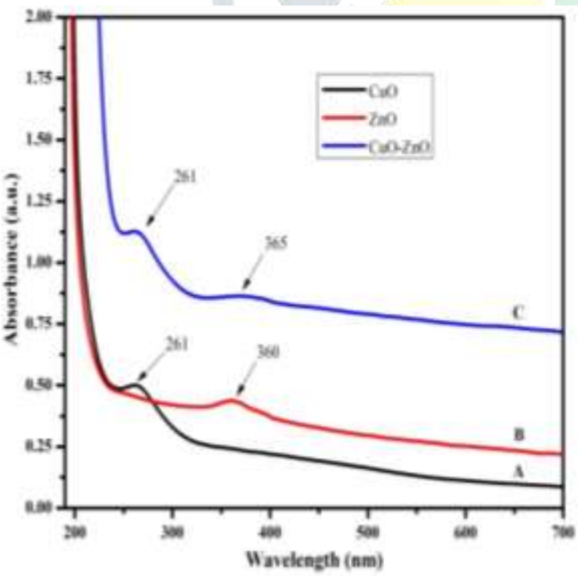
Where, ***h***- Plank's constant

v - Photon frequency.

B- Proportionality constant correlated to the specific material,

α – Linear absorption coefficient

n can be 2 for a direct transition or can be 1/2 for an indirect transition [19]. From the Tauc plot the indirect bandgap energy of CuO nanoparticles is about 1.9 eV [20] and the direct bandgap energy of ZnO nanoparticles is 3.3 eV [21,22]. The direct bandgap energy of CuO-ZnO nanocomposite was found to be at 2.55 eV. This required value was lies between the band gap energy of CuO and ZnO nanoparticles which is also relatively lower than that of ZnO (3.3 eV). The bandgap energy of ZnO decreased from 3.3 eV to 2.55 for CuO-ZnO NC [5].



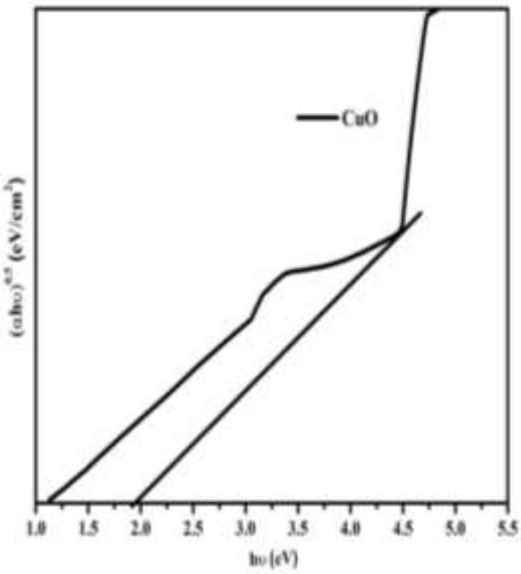


Fig.3.1. UV-Visible spectra of CuO NPs (A) ZnO NPs (B) and CuO-ZnO NC (C)

Fig: 3.1.2. Indirect bandgap energy of CuO

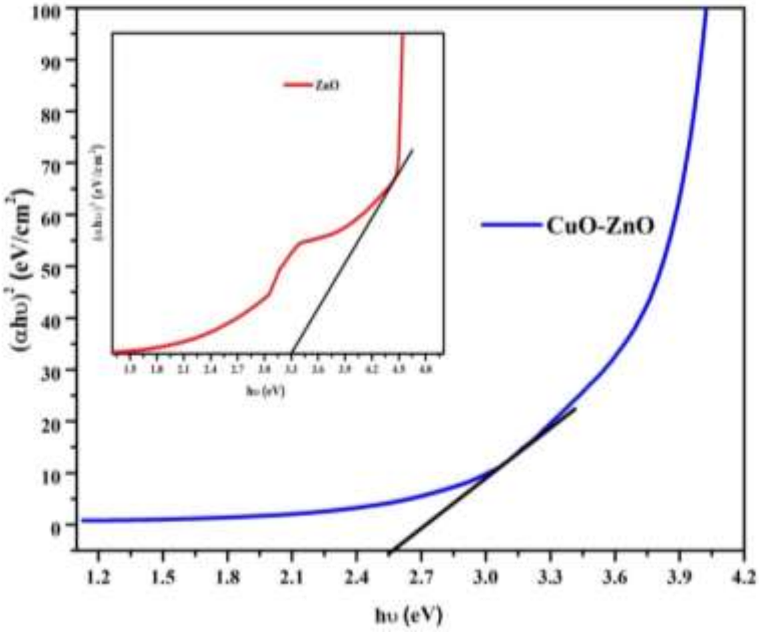


Fig: 3.1.3 Optical direct bandgap energy of CuO-ZnO NC and ZnO NPs

3.2. FTIR spectroscopy:

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was used to examine the chemical composition and functional group of CuO NPs, ZnO NPs and CuO-ZnO NC. Fig.3.2 shows the IR spectra of CuO NPs, ZnO NPs and CuO- ZnO NC and the functional groups of the samples were recorded under the wavenumber of 4000-400 cm^{-1}. The absorption band observed at 415,433 and 455 cm^{-1}were attributed to the Zn-O stretching mode vibration for samples B and C. The Cu-O stretching vibration represented by absorption band at 429, 517, 605 cm^{-1} for samples A and B. The O-H stretching mode vibration could be observed at 3600 – 3100 cm^{-1} for sample a, b and c as shown in fig. 3.2 which confirms the presence of hydroxyl groups. The low intensity peaks obtained at 2921 and 2852 cm^{-1} are corresponding to symmetric and asymmetric stretching frequency of C-H in CH_3 groups respectively. The symmetric stretching of COO^- and C-O was observed at 1417 and 1116 cm^{-1}. These fundamental peaks were appeared may be due to citrate used in the synthesis of CuO-ZnO nanocomposite [13, 23, 24].

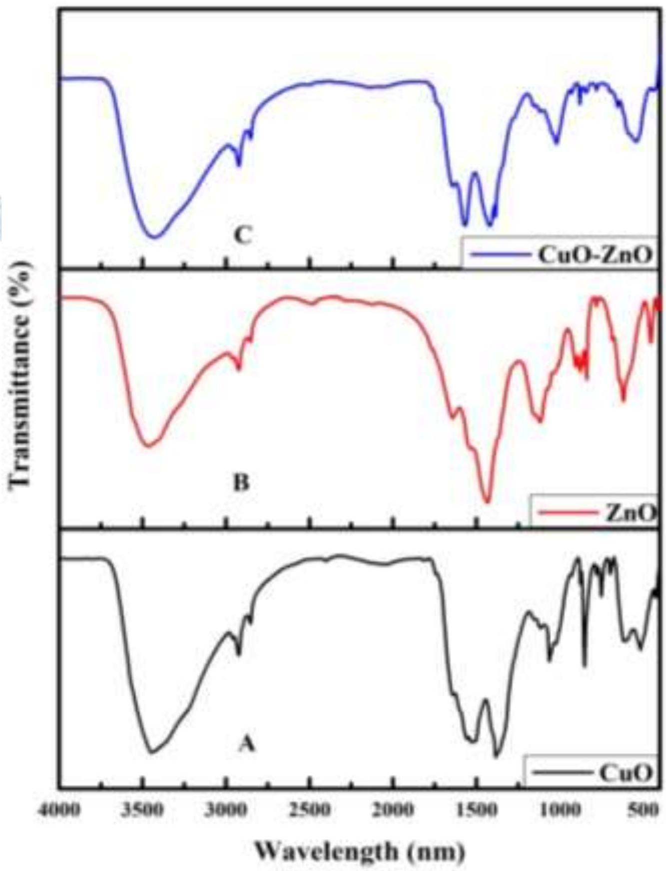


Fig.3.2. FT-IR Spectra of CuO NPs (A) ZnO NPs (B) and CuO-ZnO NC (C)

3.3 XRD Analysis:

The average crystallite size has been calculated by using Debye –Scherrer formula

$$\boxed{D = 0.9\lambda / \beta \cos\Theta} \qquad (2)$$

Where **D** - the particle size,

λ - the wavelength of the incident x-ray beam,

Ө - the Bragg's diffraction angle,

β - Full width at half maxima (FWHM) of the CuO-ZnO nanocomposite peak.

The average size of the CuO-ZnO NC was found to be 30.42 nm. The X-ray diffraction of synthesized CuO-ZnO nanocomposite shows the peak at 2θ position of 18.63 (103), 20.04 (210), 25.60 (123), 27.13, (222) 30.32 (115), 31.48 (230), 32.97 (321), 38.45 (234), 45.22 (430), 48.67 (046), 50.36 (440), 53.24 (446), 56.26 (444), 65.98 (545), and 75.05 (472) are found to be relative to FCC structure of CuO. The reflections at the 2Ө position with corresponding planes were 35.31 (111), 43.13 (200), 61.21 (220) attributed to the FCC, cubic structure of ZnO. All the peaks in XRD patterns has been well labeled according to standard JCPDS card 77-0191 of ZnO and JCPDS 77-1898 of CuO. High intensity peaks shows the good crystalline nature of CuO- ZnO NC [25, 26, 27, 28].

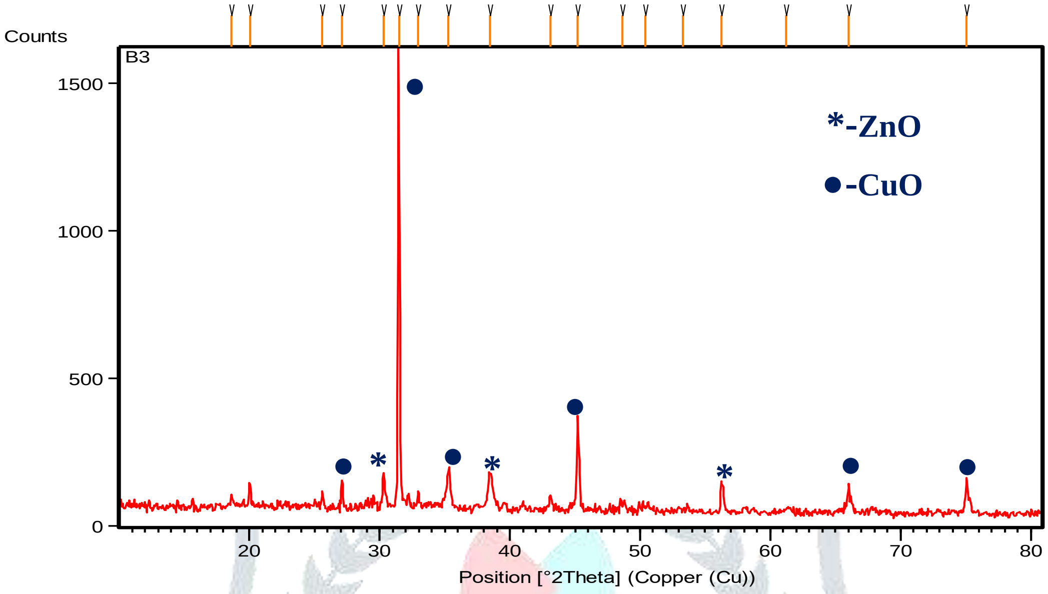


Fig.3.3. XRD pattern of the CuO-ZnO nanocomposite

3.4. SEM Analysis:

The surface morphology of synthesized CuO-ZnO nanocomposite was examined by SEM analysis. Fig.3.4. (a), (b), (c), (d) depicts the SEM images of heterostructure CuO-ZnO nanocomposite. Two morphological features were observed in the prepared CuO-ZnO NC, such as needle and cubic shape also the slight agglomeration phenomenon was observed in the SEM micrographs [5]. Due to the growth in high intensity forms agglomeration moreover ZnO nanoparticles were incorporated with CuO nanoparticles to produce the ZnO-CuO heterostructure [13, 29, 30].

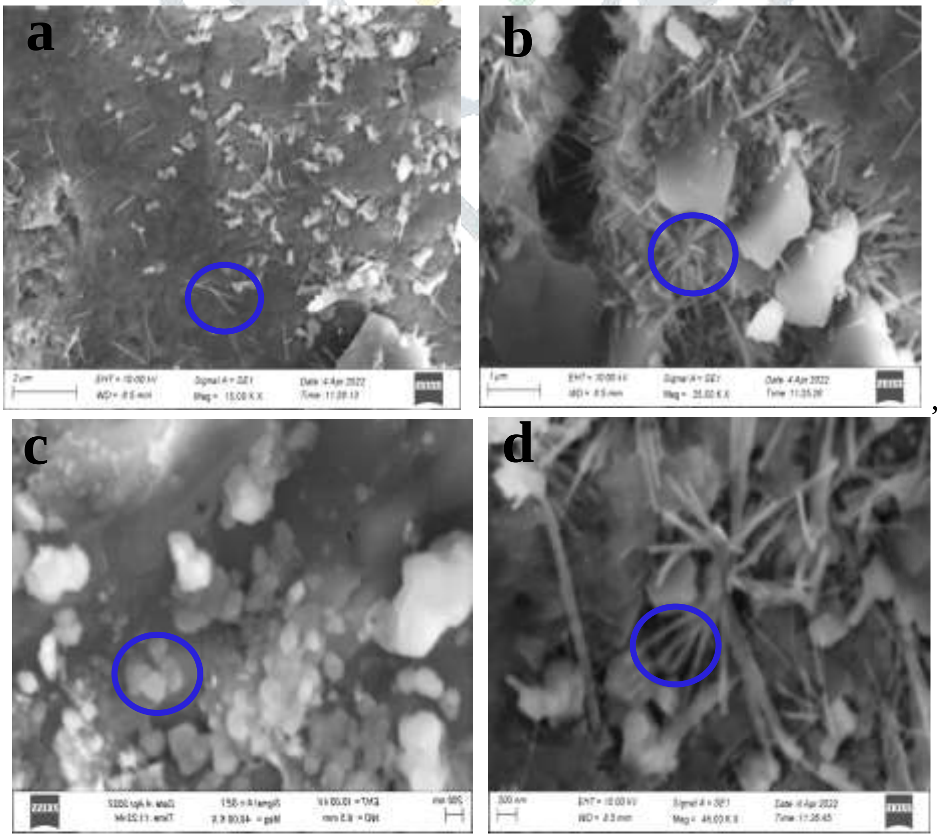


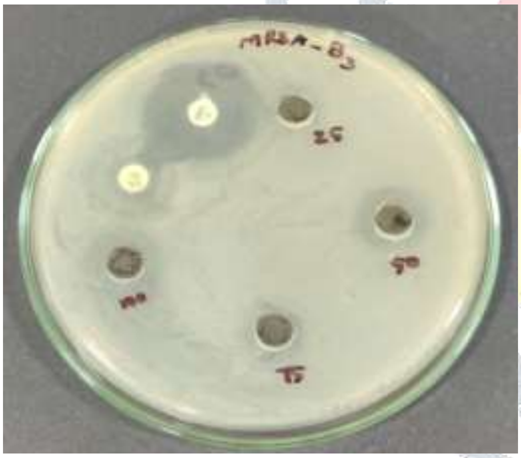
Fig.3.4. (a-d) SEM images of CuO-ZnO nanocomposite

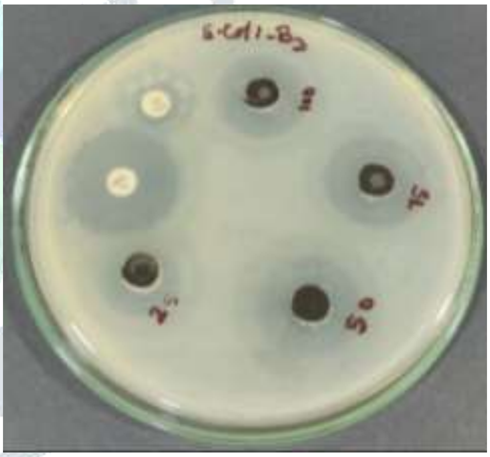
4. Antibacterial activity of CuO-ZnO nanocomposite:

The antibacterial activity of CuO-ZnO NC was evaluated against human pathogenic bacteria such as *Escherichia coli* (ATCC10536) and *Staphylococcus aureus* (ATCC33591) by using well diffusion method and the obtained experimental photographs were shown in fig. 4 (a), (b), (c) and (d). The CuO-ZnO nano composite gives the most potent antibacterial action because of the release of highly active Cu^{2+} and Zn^{2+} cations [17]. The smaller crystallite size leads to more antibacterial effects because it was well- known that Cu^{2+} (1.4Å) ions have a lower radius that that of Zn^{2+} (1.39 Å) ions [18]. The prepared CuO-ZnO shows more susceptible to the Gram negative bacterial E.coli than the Gram positive bacteria S. aureus. The Gram negative bacteria's cell wall has a significant negative charge comparatively than Gram positive bacteria's cell wall so that the metal cations are strongly attached on the surface of E. coli and cause serious damage to bacterial cell [31]. When the two or more oxides of antibacterial material era combined to make nanocomposite that can produce a larger amount of ROS, which leads to enhancing the antibacterial property of composite material [32].

4. a. Inhibition zone of *Staphylococcus aureus* 4. b. Inhibition zone of *Escherichia Coli*

Control- chloramphenicol





4. c. Inhibition zone of *Staphylococcus aureus* 4. d. Inhibition zone of *Escherichia coli*

Control- Gentamicin, Cefalexin

Table: 4.2. Antibacterial activity of CuO-ZnO NC against *Staphylococcus aureus*

S.No	**SAMPLE**	**ZONE OF INHIBITION (mm) *Staphylococcus aureus* (ATCC33591)**					
		CONTROL		**25µl**	**50µl**	**75µl**	**100µl**
1.	**CuO-ZnO**	**C**	29	10	13	15	18
		GEN	27	12	15	16	17
		CN	20	12	15	16	17

Table: 4.3. Antibacterial activity of CuO-ZnO NC against *Escherichia coli*

S.No	SAMPLE	ZONE OF INHIBITION (mm) *Escherichia coli* (ATCC10536)					
		CONTROL		25µl	50µl	75µl	100µl
1.	CuO-ZnO	C	28	2	3	3	4
		GEN	26	19	22	23	24
		CN	13	19	22	23	24

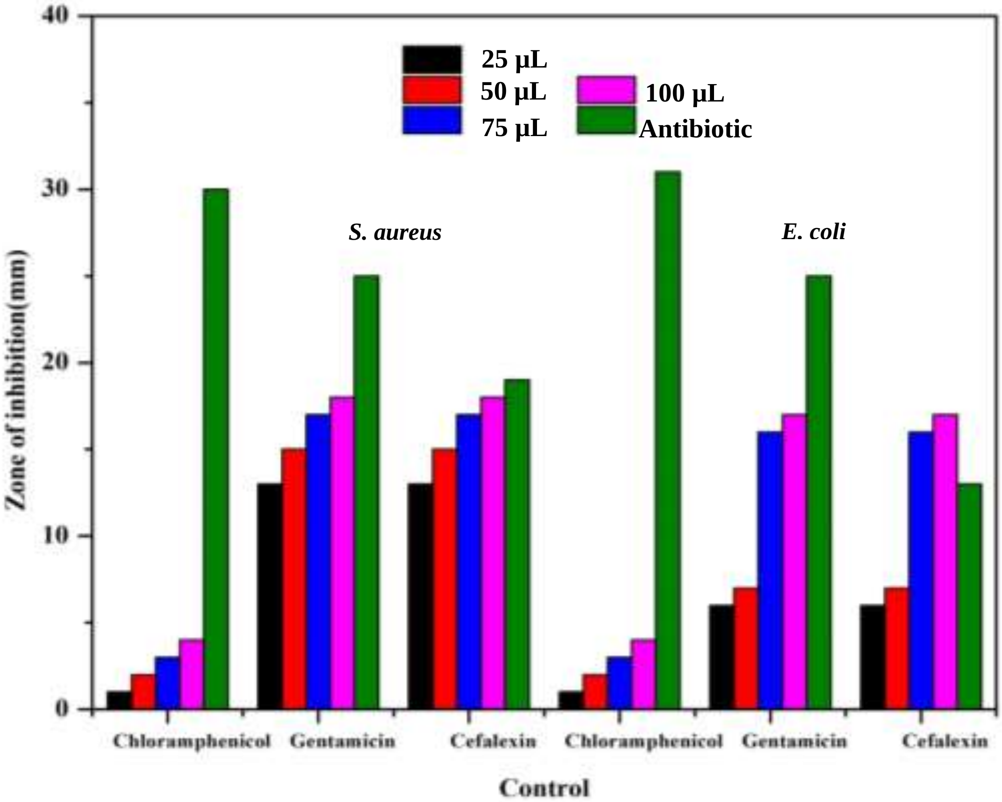


Fig.4.4. Bar graph representing antibacterial activity of CuO-ZnO nanocomposite

5. Conclusion:

The progress of science and technology has created the pressing need of advancement nanotechnology in biomedical research. The optical studies of the chemical mediated nanocomposite showed two strong absorption peaks around 261nm and 365 nm for CuO-ZnO NC and indicating a red shift with relative to the ZnO NPs and CuO NPs respectively. Based on the optical absorption spectral data, band gap energy was calculated with the help of Tauc plot. From the FTIR Spectral analysis, characteristic absorption bands of Cu–O and Zn–O were noticed at 433 and 517 cm^{-1}, respectively. In XRD analysis, the crystallite size of the CuO-ZnO NC was found to be 30.42 nm and cubic in structure of CuO and ZnO. The prepared nanocomposite was highly crystalline in nature without occurrence of any impurity peaks. From SEM images, CuO –ZnO heterostructure was observed such as needle and cubic shape with slight agglomeration. The antibacterial activity of CuO-ZnO nanocomposite shows good inhibition zone against human pathogenic bacteria such as S. aureus and E. coli. G -ve bacterial strain was more sensitive than G +ve bacterial strain. From the results we conclude that CuO-ZnO nanocomposite has great antibacterial potential due to the synergistic action both CuO and ZnO.

ACKNOWLEDGEMENT:

The authors are duly acknowledged the PG and Research Department of Chemistry, NMSSVN College for providing the lab facilities for carrying out research.

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