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New Method for the Preparation and Biological Activity of CuO Nanoparticles from a Mixed PVA and 2-Aminobenzothiazole Complex

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Abstract : Copper(II) complex of polyvinyl alcohol (PVA) and 2-aminobenzothiazole (ABZ) was synthesized, characterized and used as a precursor for copper oxide nanoparticles (CuO NPs) by calcinations method. CuO NPs characterized by *UV-vis* spectroscopy, X-ray powder diffraction analysis (XRD) and scanning electron microscopy (SEM). The resultant particles are nearly rods and particle size is in the range of 21-43 nm. The obtained complex have been assigned based on elemental analysis, Fourier transform infrared spectroscopy (FTIR), electronic spectral and thermal analysis. The kinetic parameters have been calculated making use of the Coats-Redfern equation. The antibacterial activity of CuO nanoparticles was tested against gram positive bacteria represented by *Bacillus cereus, Staphylococcus aureus* and gram negative bacteria represented by *Escherichia coli, Pseudomonas aeruginosa, Serratia marcescens*.

Keywords : *PVA, CuO-NPs, XRD, Thermal Studies and Biological Activity*.

Introduction

Nanotechnology have led to the great development in various fields including nanoparticles, nanorods, nanotubes and nanowire synthesis[1]. They also display unique physical and chemical properties [2].CuO nanoparticles show the important applications as antimicrobials [3-6], against infectious organisms such as *Escherichia coli, Bacillus subtilis, Vibrio cholerae, Pseudomonas aeruginosa, Syphilis typhus,* and *Staphylococcus aureus*[7,8]. The CuO nanoparticle also finds its application in gas sensors, superconductors, solar energy conversion tools [9-12]. The coordination compounds of ligands containing nitrogen, oxygen and sulphur as the donor atoms exhibit a wide spectrum of biological activities. Poly (vinyl alcohol) which can be represented as PVA is a versatile synthetic polymer with many industrial applications. PVA is the most readily biodegradable of vinyl polymers [13]. PVA exhibits excellent water retention properties [14], also PVA is of great interest due to its nontoxic, flexible, biocompatible and biodegradable properties [15]. Some uses of PVA include adhesive and thickener material in latex paints, paper coatings, hair sprays, shampoos, glues and Children's play putty. Also, PVA uses in eye drops, hard contact lens solution as a lubricant and in protective chemical-resistant gloves[16,17]. 2-aminobenzothiazole (ABZ) is an important scaffold with a wide array of interesting biological activities. Some reviews have been recently reported in literature, briefly describing the synthetic strategies and biological activities of 2-aminobenzothiazole nucleus [18-20]. Metal complexes with

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these ligands are becoming increasingly important as biochemical, analytical and antimicrobial reagents in the design of molecular models and material chemistry [21,22]. In this research, we reported synthesis a new copper(II) complex of poly(vinyl alcohol) (PVA) and 2-aminobenzothiazole (ABZ) and used as a precursor for copper oxide nanoparticles (CuO NPs) by calcinations method. Further CuO NPs were optical characterization using UV-VIS spectrometer, structural characterization using scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and antimicrobial activities.

Experimental

Materials and Reagents

Polyvinyl alcohol (PVA) and copper(II)sulphatepenthydrates were supplied from Sigma Aldrich. 2-aminobenzothiazole was ana E. Merck grade and were used without further purification. All other chemicals were of AR grade.

Synthesis of [Cu(PVA)(ABZ)(H_2O)]

PVA (1g) was dissolved in 40 Ml distilled water by gently stirring at 50°C for 1 hand after cooling, $CuSO_4.5H_2O$ solution (2.83g in 25 mL distilled water)was added drop wise to the PVA solution under quickly stirring, then ABZ solution(1.7 g in 20 mL ethanol) was added to the mixture. The mixture was refluxed for 2h and then cooled to room temperature. A dark green was produced, the latter was separated by filtration, washed with distilled water and ethanol and dried over anhydrous calcium chloride. Anal. Calc. for $C_{10}H_{12}N_2SCuO_3$: C, 39.54; H, 3.95; N, 9.22; S, 10.55. Found: C, 38.72 ; H, 3.83 ; N, 9.03; S, 9.86. IR data: ν(cm^{-1}) = 3415 (m), 3372(m), 3162 (m), 3142(m), 2930(m), 1623(s),1531(s), 1448(m), 1344(m), 1041(s), 890(m), 842(m), 709(m), 676(s), 598(m), 473(m).

Synthesis of Copper Oxide Nanoparticles

Calcination of the prepared[Cu(PVA)(ABZ)(H_2O)]compound in air at 600 °C with a calcination time of 3 hours afforded CuO nanoparticles.

Physical Measurements

The carbon, hydrogen, nitrogen and sulfur contents of the solid complex which were determined by Elemental Analyser system GmbhVario El analyzer.

FT-IR spectra of the complex and copper(II) oxide were obtained by the KBr disc technique in the wavenumber range of 4000-400 cm^{-1}, using Thermo-Nicolet-6700 FT-IR spectrophoto-meter. The electronic absorption spectral measurements in the ultraviolet and visible regions were carried out in DMSO on a UV-2102 PC Shimadzu spectrophotometer using 1 cm matched quartz cell in the wavelength range 200-900 nm. The magnetic moments of the prepared copper(II) complex was measured at room temperature using a magnetic susceptibility balance of type MSB-Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of the Pascal's constants. The calibrant used was $Hg[Co(SCN)_4]$ at room temperature [23]. Simultaneous TGA and DTA analyses were performed employing a Shimadzu DTG-60 instrument using a heating rate of 10 °C/min in the air atmosphere. The average samples weight was 10 mg α-Al_2O_3 was used as a reference material in the DTA measurements. The X-ray powder diffraction patterns of the CuO NPs was recorded an XRD diffractometer Model PW 1710 control unit the (Philips). The anode material was Cu Kα (λ = 1.54180 Å), 40 K.V 30 M.A Optics: Automatic divergence slit. The scanning electron microscope (SEM) was JEOL JFC-1100E ION SPUTTERING DEVICE, JEOL JSM-5400-LV SEM..

Antibacterial Activity

The well-diffusion method was used to assess the antibacterial activity. The antibacterial activity of the CuO NPs was assessed against different bacterial strain represented by gram positive bacteria (*Bacillus cereus, Staphylococcus aureus)* and negative bacteria *(Escherichia coli, Pseudomonas aeruginosa* and *Serratia marcescens)*. Chloramphenicol was used as an antibacterial standard. The nutrient agar and nutrient broth media were sterilized for 20 min at 121 °C and 15 1b pressure before inoccupation then preparing a suspension of the bacterial strains in nutrient broth medium after cooling in a test tube. 0.3 ml from the suspension of

bacterial strain were taken in Petri dishes then the nutrient agar was poured onto the plate and the petri dish was shacked well and allow it to solidify. The plates were then kept in an incubator at 37 °C. The diameter of inhibition zone around the well was measured after 24 h incubation. To prepare inocula for bioassay, bacterial strains were individually cultured for 48h in 100 mL conical flasks containing 30 mL nutrient broth medium [24].

Results and Discussion

Mixed ligand complex of Cu(II) containing polyvinyl alcohol (PVA) and 2-aminobenzothiazole (ABZ) was prepared and used as a precursor for copper oxide nanoparticles (CuO NPs) by the calcinations method. The data correspond to metal: L1:L2 ratio of the 1:1:1 for the compound. This complex is air stable, insoluble in common organic solvents but partially soluble in DMSO. The synthesis of the Cu(II) polymer may be represented as follows

$$CuSO_4.5H_2O + PVA + ABZ \xrightarrow[H_2O]{EtOH} [Cu(PVA)(ABZ)(H_2O)]_n + H_2SO_4$$

Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR was used to characterize the presence of specific chemical groups in the materials. An important absorption peak was verified at v = 1142 cm^{-1}, this band has been used as an assessment tool of polyvinyl alcohol structure because it is a semicrystalline synthetic polymer able to form some domains depending on several process parameters [25]. The band occurring at 2930 $cm^{-1}$and 1142 cm^{-1}, characteristic of hydrogen bonded O-H stretching [26] and antisymmetric stretching vibrations of both CH_2 and COC respectively. In addition, for polyvinyl alcohol cross-linked by copper(II) the band maximum corresponding to bonded OH group at (3430 cm^{-1}), was shifted to lower frequencies; 3372 cm^{-1}.On the other hand, the stretching vibration of the amino group in free ABZ observed at 3220 cm^{-1} is shifted to a lower wave number and appears at 3126 cm^{-1} in the complex suggesting coordination of the amino nitrogen to the Cu(II) ions [27]. The band at 3415 cm^{-1}in the spectra of this complex is assigned to *v*OH of the water molecule. Metal-oxygen and metal-nitrogen bonding are manifested by the appearance of bands in the 598, 473cm^{-1}regions respectively [28](Fig. 1).

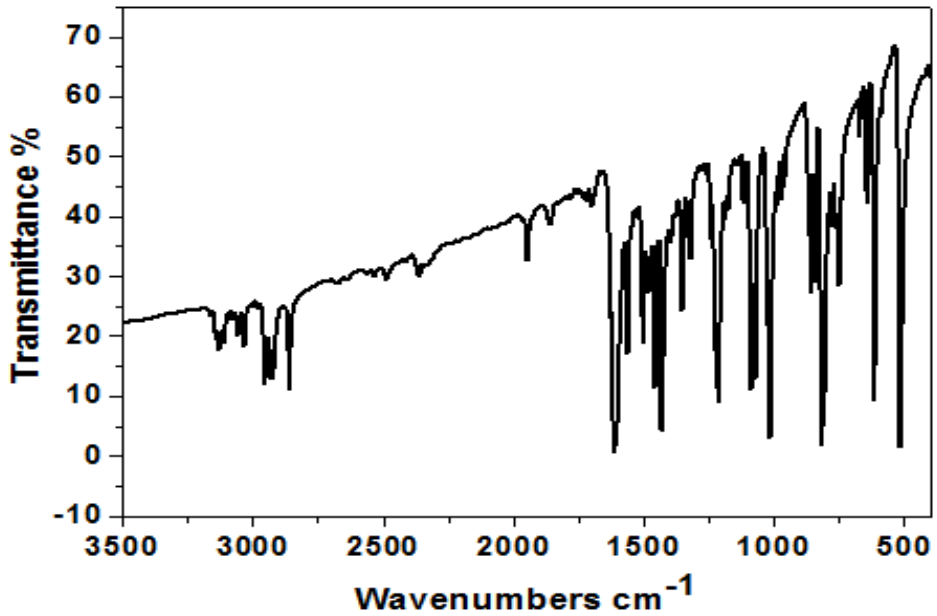

Figure. 1: FT-IR of copper(II) complex.

Electronic Spectra and Magnetic Moments

UV-visible absorption spectra of the prepared CuO NPs are displayed in the Fig. 2.The spectra exhibit maximum absorption at 412 nm. This absorption band at 412 nm specifies the formation of copper(II) oxide

nanoparticles[29].Additionally, the magnetic moment of Cu(II) compound was measured and it has been found that the magnetic moment value of 1.93 B.M is typical of the square planner geometry complex [30,31].The structure of the copper(II) polymer can be postulated in Fig. 3.

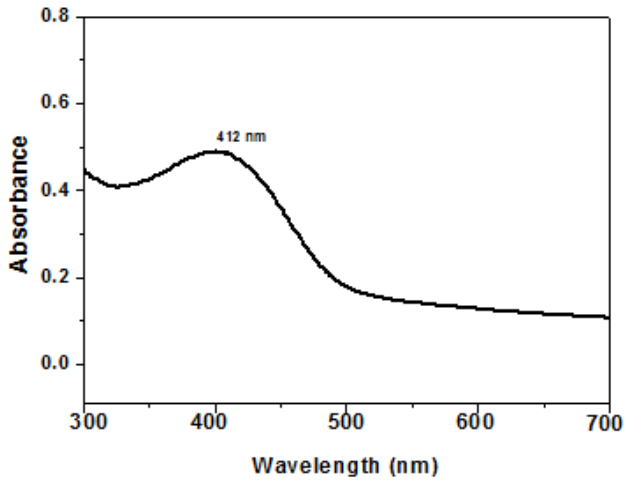

Figure 2: UV-visible absorption spectra of CuO NPs.

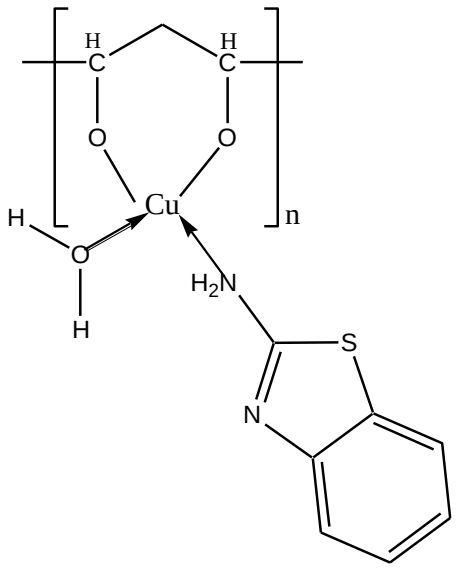

Figure 3:Structure of [Cu(PVA)(ABZ)(H_2O)]$_n$

Thermal Analysis

In dynamic air the TG, DTG and DTA curves of [Cu(PVA)(ABZ)(H_2O)]$_n$complex show that the thermal decomposition processes of the compound involve four stages. These steps occur in the temperature ranges 51-105, 106-208, 209-412 and 413-750 ^oC. The first stage corresponds to the release of the water molecule (calc. 5.92%, found 4.52 %). The DTG curve shows this step at 98 °C and an abroad endothermic peak appears at 101 °C in the DTA trace. The second, third and forth of the ligands decomposition are associated with the DTG peaks at 172, 317 and 520^oC corresponding to exothermic peaks at 174, 319 and 522^oC in the DTA curve. The final product was identified on the basis of mass loss considerations to be CuO as a residual part (calc. 26.18 %, found 24.67 %) (Scheme 1).

$[Cu(PVA)(ABZ)(H_2O)]_n$ 51-105°C $[Cu(PVA)(ABZ)]_n + H_2O$ ↓ 106-750 °C

Decomposition products + CuO

Scheme (1).

The non-isothermal kinetic analysis of the copper compound was carried out applying the Coats-Redfern [32]method. The kinetic parameters of the Cu(II) complex are calculated for the first step and are cited in Table**1**.

Table 1: Kinetic parameters of the thermal decomposition of the [Cu(PVA)(ABZ)(H_2O)] in the dynamic air.

Step	Coats-Redfern equation			
	r	**n**	**E**	**Z x 10^3**
1^{st}	0.9995	0.00	85.5	16.2
	1.0000	0.33	128.3	95.4
	0.9998	0.50	154.4	147.1
	0.9999	0.66	182.9	213.7
	0.9996	1.00	208.8	225.9
	0.9987	2.00	249.1	236.8

E in kJ mol^{-1}.

X-ray Powder Diffraction of CuO Nanoparticles

The X-ray powder diffraction (XRD) was used to characterize of CuO nanoparticles. Fig. 4. displays the XRD pattern of copper(II) oxide NPs. All diffraction peaks are the index with the corresponding planes of CuO. This pattern shows that the most important parts of the particles in this metal oxide is crystalline. The crystallite size has been estimated from the XRD pattern using the Scherrer's equation[33] was applied to estimate the particle size of the compound:

$D = K\lambda / \beta\cos\theta$

where K is the shape factor, λ is the X-ray wavelength typically 1.54 Å, β is the line broadening at half the maximum intensity in radians and θ is Bragg angle, D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The crystallite size corresponding to the highest peak observed in XRD was found to be in the average range of 21-43 nm. The presence of sharp structural peaks in XRD patterns and crystallite size less than100 nm suggested the nanocrystalline nature of CuO NPs.

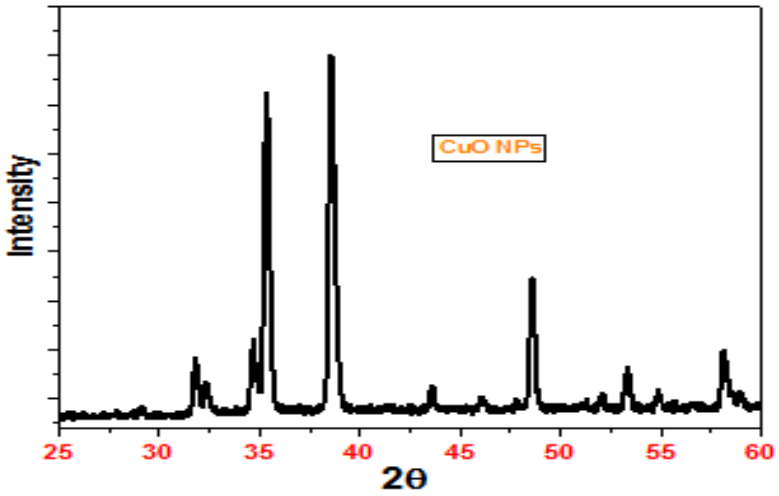

Figure 4: XRD of CuO Nanoparticles prepared by the calcinations method.

Scanning Electron Microscopy (SEM)

The scanning electron microscopy of copper oxide nanoparticles is shown in the Fig.5. From the SEM image, it is observed that the CuO nanoparticles had a well-defined morphology and are nearly rods in shape, which shows the synthesized CuO nanoparticles having the size around 21-43 nm match exactly with the XRD analysis.

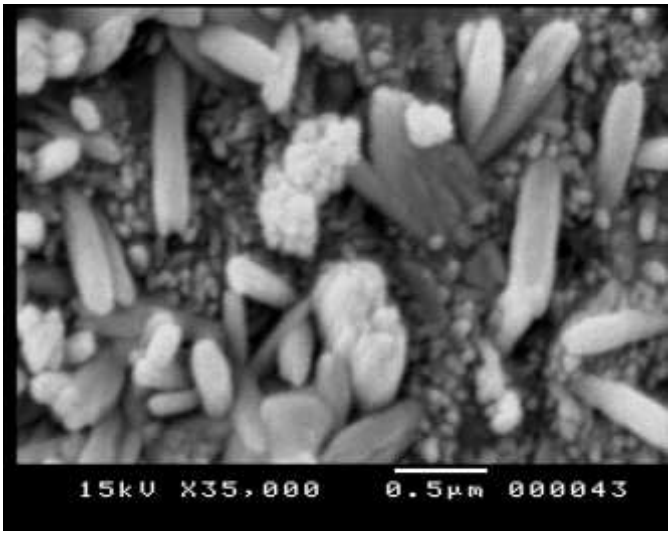

Figure 5:SEM of copper oxide nanorodos.

Antibacterial Activity Screening

The antimicrobial activity of prepared copper oxide nanoparticles was investigated against gram negative and gram positive bacteria. The antibacterial activity of CuO NPs is identified. Hence there are a number of studies in the field of copper oxide nanoparticles by using different type of procedures [34,35]. CuO NPs in this research, show more than one test organism (*P. aeruginosa G-ve)*which was used to increase the chance of detecting the antibiotic principles in the tested materials. Antibacterial activity of the CuO nanoparticles on the microor-ganisms *P. aeruginosa* have been given in Fig. 6. It shows a significant growth inhibition of bacterial culture by CuO nanorods with respect to the control (chloramphenicol). Fig. 7. Show comparison of antibacterial activity.

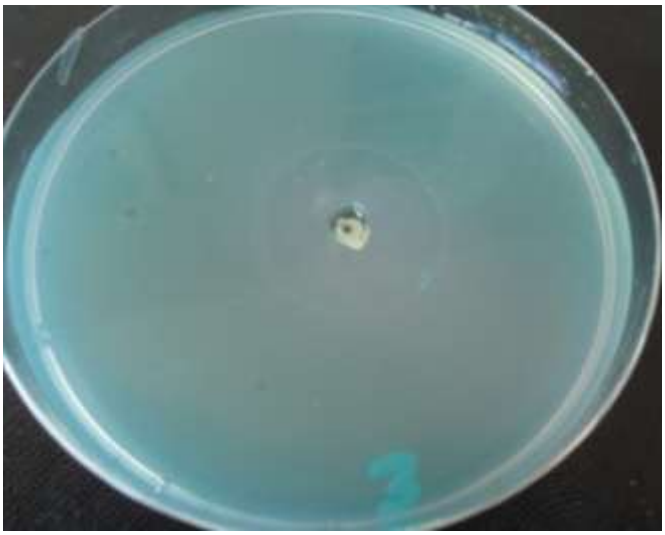

Figure 6: Microbiological screening of the CuO NPs against *Pseudomonas aeruginosa*.

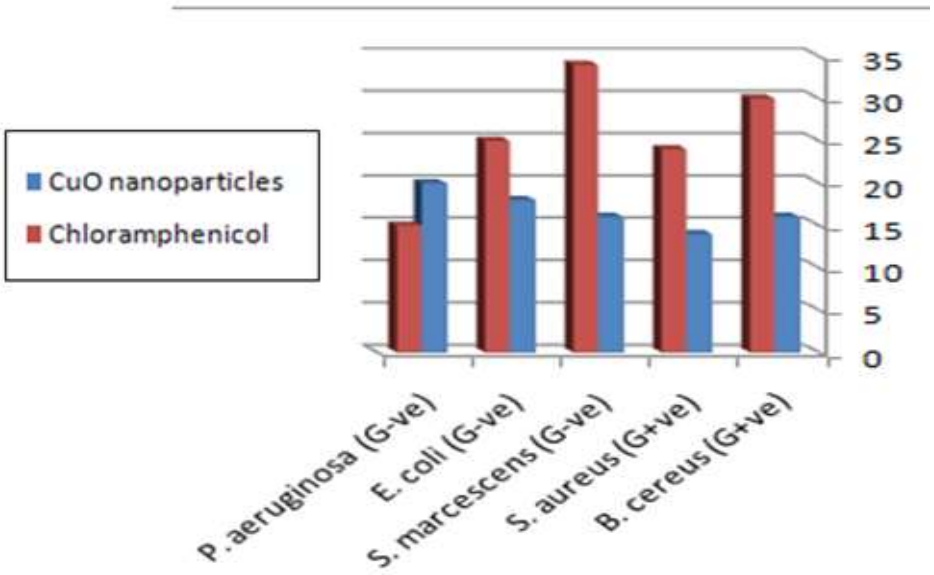

Figure 7: Comparison of the effect of CuO nanoparticles on the growth of different bacteria.

Conclusion

Thus we have successfully synthesized CuO nanoparticles from polyvinyl alcohol and 2-aminobenzothiazole ligands by calcinations. The synthesized CuO nanoparticles with rods nanostructures, the average SEM diameter of CuO NPs size is in the range of 21-43 nm that agreed fairly well with x-ray powder diffraction analysis. CuO nanoparticles showed higher activity antibacterial especially against *P. aeruginosa.*

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