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# Synthesis of Copper Precursor, Copper and its oxide Nanoparticles by Green Chemical Reduction Method and its Antimicrobial Activity

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**ABSTRACT**

The present investigation reports, the novel synthesis of Copper and Copper oxide nanoparticles using Chemical reduction method and its physicochemical characterization. The nanoparticles have been prepared using Copper (II) succinate as precursor. Copper nanoparticles are initially formed and subsequently oxidized to copper oxide. As reported the nanoparticles were characterized by UV–visible spectroscopy, Fourier transform infra-red spectroscopy (FTIR), X-ray diffraction measurements (XRD) and scanning electron microscopy (SEM). SEM analysis exhibited nanoparticles with an average diameter of about 45nm. XRD analysis revealed broad pattern of fcc crystal structure of copper metal and cubic cuprites structure for $Cu_2O$. The antimicrobial properties of copper nanoparticles were investigated using *Streptococcus pyogenes, Pseudomonas aeruginosa, Escherichia coli,* and *Staphylococcus aureus.* The bactericidal effects of copper nanoparticles were studied based on diameter of inhibition zone in disk diffusion tests of nanoparticles dispersed in batch cultures. The copper nanoparticles showed excellent activity against *Escherichia coli* and *Staphylococcus aureus*, with excellent inhibition zones of 14 mm and 10 mm, respectively. Bacterial sensitivity to nanoparticles was found to vary depending on the microbial species.

## INTRODUCTION

Due to their size and shape dependent physical and chemical properties, metallic and semiconductor nanoparticles are an interesting material for study. In particular, metallic nanoparticles have found utility in catalytic applications. Since the surface area of a catalyst is a critical factor, metallic nanoparticles, having an immense surface area compared to conventional materials, have been intensely investigated (Lisiecki *et al.,* 1993). Among them, copper and its alloy in nanometric sizes have been applied frequently in catalysis applications (e.g., water gas shift catalysts and gas detoxification catalysts (Barrabés *et al.,* 2006; Mott et al. 2007). Controlling the size, shape, and surface properties of nanoparticles is crucial to understand copper base\d catalysts (Niu *et al.,* 2003; Hoover *et al.,* 2006). Also, copper has been considered as an alternative for gold, silver, and platinum nanoparticles in other areas (e.g., thermal conducting materials and microelec- tronics applications) (Eastman *et al.,* 2001; Lu *et al.,* 2000).

Considering the higher cost associated with these other materials, copper could be a more economical solution (Jeong *et al.,* 2008). Copper nanoparticles have been synthesized using a variety of techniques; typically characterized as either a physical or a chemical process (Feldham *et al.,* 2002; Siegel *et al.,* 1999). Physical methods, such as proton irradiation (Santibanez *et al.,* 2000), laser ablation and vacuum vapor deposition (Liz-Marzan *et al.,* 2004) are capable of producing a wide range of metallic nanoparticles, however the quality of the material is not as high as chemically synthesized materials.

In chemical synthesis techniques, the growth and assembly of metallic nanoparticles is controlled by optimizing reaction parameters (e.g., temperature, varying the reaction chemistry, reagent concentration, etc). (Xie *et al.,* 2004). Examples of the chemical synthesis approaches include microemulsion (Pileni *et al.,* 1997), and sonochemical reduction (Kumar *et al.,* 2001). The antimicrobial properties of silver nanoparticles are well established (Sondi et al. 2004; Siva Kumar *et al.,* 2004; Jain *et al.,* 2005; Cho *et al.,* 2005), and several mechanisms for their bactericidal effects have been proposed.

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Although only a few studies have reported on the antibacterial properties of copper nanoparticles, they have shown copper nanoparticles have a significant promise as bactericidal agent (Cioffi *et al.*, 2005). However, other nanoparticles, such as platinum, gold, iron oxide, silica and its oxides, and nickel have not shown bactericidal effects in studies with *Escherichia coli* (Cho et al. 2005; Ruparelia et al. 2006).

Yoon *et al.*, (2007) reported the antibacterial effects of silver and copper nanoparticles using single representative strains of *Escherichia coli* and *Staphylococcus aureus*. The copper nanoparticles demonstrated superior antibacterial activity compared to the silver nanoparticles. Silver and copper nanoparticles supported on various suitable materials, such as carbon, polyurethane foam, polymers and sepiolite have also been effectively used for bactericidal applications (Li 2006).

## EXPERIMENTAL

### Materials

All the chemicals, reagents used in our experiments were of analytical grade and were used as received without further purification. Succinic acid, Copper sulphate, NaOH, $NaBH_4$, were purchased SD Fine and were used as received, hexane SDF and ethanol from distillery.

### Synthesis of the Copper(II) succinate precursor

The $CuSO_4$ $5H_2O$ (2 mmol) was dissolved in 10 mL of distilled water to form a homogeneous solution. A stoichiometric amount of sodium hydroxide (NaOH) and Succinic acid were dissolved in distilled water the sodium succinate thus formed was drop wise added into the above solution under magnetic stirring. The solution was stirred for about 30 min and a green precipitate was obtained which was centrifuged and washed with ethanol several times. The product was dried. The copper(II) succinate was characterized by FT-IR.

### Synthesis of the Copper nanoparticles

$NaBH_4$ (0.6 mmol) solution in water was added drop wise to the Copper(II) succinate (0.2 mmol) solution kept in ultrasonicater bath. The reaction mixture was kept in the ultrasonicater bath for 60 min. Upon the addition of the $NaBH_4$ solution, the green colored solution instantly turned black, which implied that Copper nanoparticles had been produced (Premkumar et al., 2006). Isolation of the black suspension under ambient conditions resulted in very high yields of a black powder (Fig 1).

### Characterization

XRD patterns were recorded on a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained on a Philips XL- 30ESEM equipped with an energy dispersive X-ray spectroscope. The compositional analysis was done by energy dispersive X-ray. Fourier transform infrared (FT-IR) spectra were recorded on a Shima dzu spectrophotometer using KBr pellets.

## RESULTS AND DISCUSSION

### IR measurement

FT-IR spectroscopy is a useful tool to understand the functional group of any organic molecule Fig. 2a is IR spectrum of Copper(II) succinate precursor. Fig. 2b is IR spectrum of nanoparticles. A peak at 619 $cm^{-1}$ indicated the Cu-O Stretching vibration.

The metal salt (Cu-O-C) Peak appeared at 1255 $cm^{-1}$.A Peak at 3570 $cm^{-1}$ indicate OH stretching of the water in the precursor which disappeared in the nanoparticles. In Fig.1a peak at 1620 $cm^{-1}$ and 1429$cm^{-1}$ indicating metal carbonyl ( C=O) group disappeared in Fig. 1b of nanoparticles.

### UV Visible Spectra

Copper nanoparticles typically exhibit around 450 nm (Masoud Salavati-Niasari et al. 2009) however the Copper nanoparticles synthesized here show an absorption peak around 411 nm (Fig. 3). This peak can be assigned to the absorption of nanoparticles of copper.

### XRD measurement

Powder diffraction analysis indicated that the product was copper and its oxides (Fig. 4) (Cullity et al. 1978). Particle size was predicted by using Debye Scherrer formulae,

Average Crystalline Size

$$D=0.9\lambda/\beta \cos\theta$$

$$\lambda=1.5406\times10^{-10}m$$

β = Full width at half maximum (radian) The Size of the nano is about 45.07 nm.

### SEM

The morphology of the product was examined by SEM. Fig. 5a and 5b depicts the SEM images of nanoparticles. It shows that the Copper and copper oxide nanoparticles are flower shaped. The size of particle observed in SEM image is in the range of 1µm.

### Antibacterial activity

All bacterial isolates were obtained from clinical samples (*Streptococcus pyogenes*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Staphylococcus aureus*). The antimicrobial test was carried out primarily by the agar well diffusion method (Li *et al.*, 2006).

Bacterial pathogenic inoculums were prepared from 18 h grown cultures (~$10^4$–$10^6$cells/mL). Petridishes containing the bacterial inoculums on nutrient agar was used for the study. Using a cork borer (6 mm diameter), wells were made in the culture plates and 70 µ L of the freshly synthesized nanoparticles (both C-NPs and M-NPs) was loaded.

The plates were then incubated at 37° C for 24 h, after incubation, the zone of inhibition (ZOI) was measured (Table 1; Fig 6 A-D). Nanoparticles without any organic molecules exhibit lower zone of inhibition compared to the precursor as shown in the table.

**Table. 1:** In vitro antimicrobial activity of some human pathogenic bacteria on nanoparticles by disc diffusion assay.

| S.No. | Test organisms | Zone of inhibition (mm) | | | |
|---|---|---|---|---|---|
| | | **Nature of Bacteria** | **Ofloxacin (15 μg)** | **Copper(II) Succinate Precursor** | **Copper nanoparticles (NaBH4)** |
| 1. | Streptococcus pyogenes | Gram (-) | 10mm | 25mm | 15mm |
| 2. | Pseudomonas aeruginosa | Gram (-) | 27mm | 20mm | 8mm |
| 3. | Escherichia coli | Gram (-) | 20mm | 30mm | 14mm |
| 4. | Staphylococcus aureus | Gram (+) | 23mm | 34mm | 10mm |

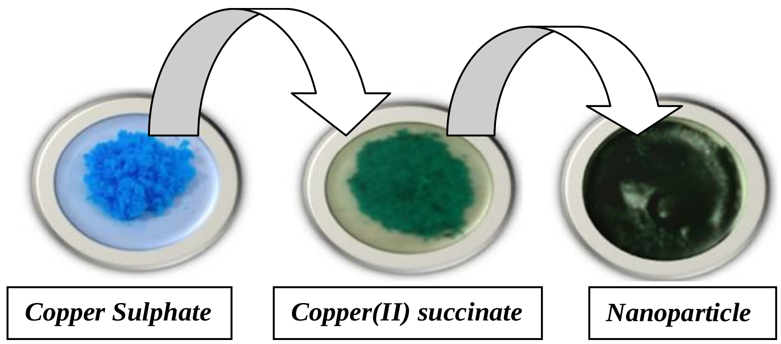


**Fig. 1:** Photographic views for complete preparation of nanoparticles.

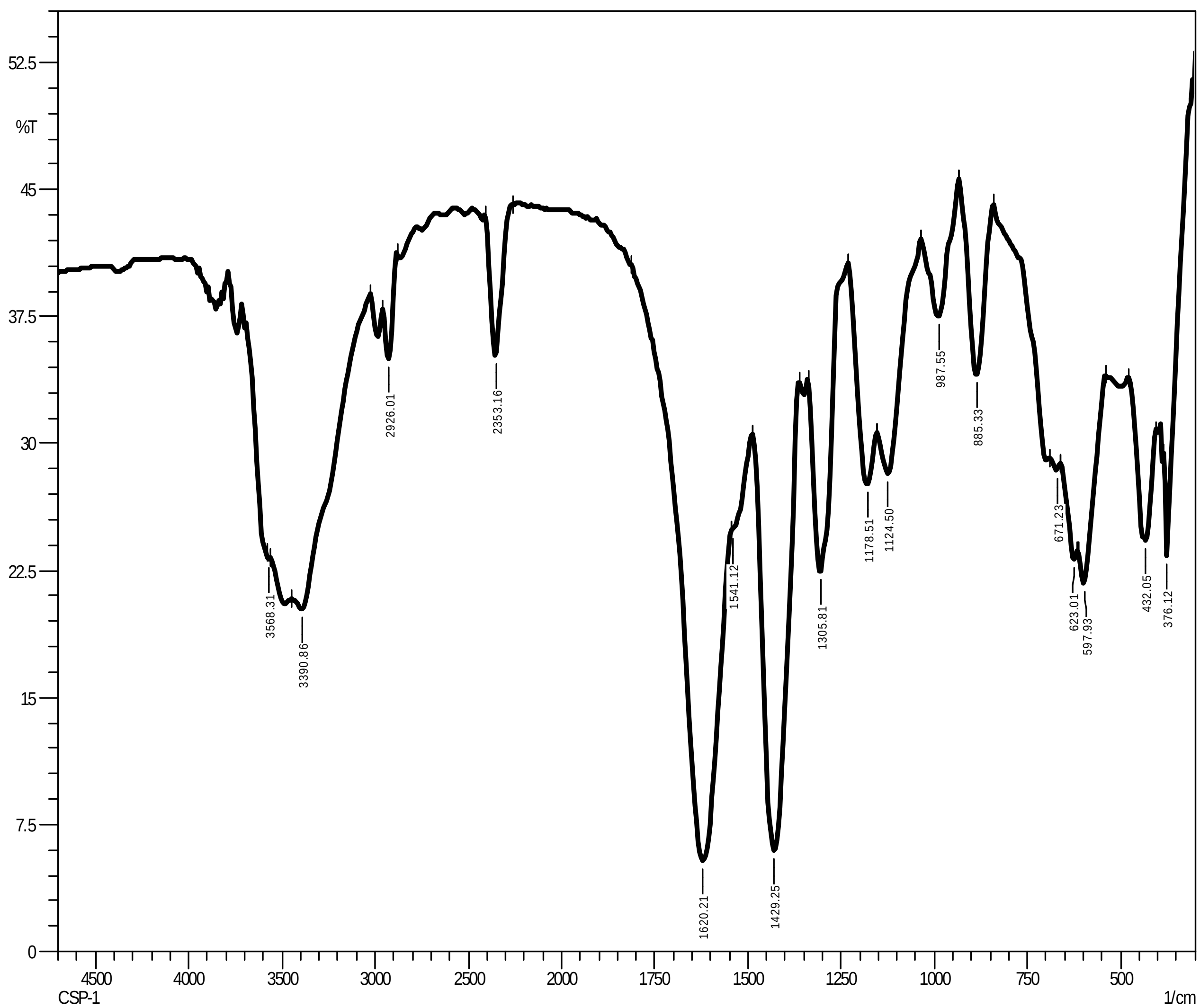


**Fig. 2(a):** FT-IR spectra of Copper(II) succinate precursor.

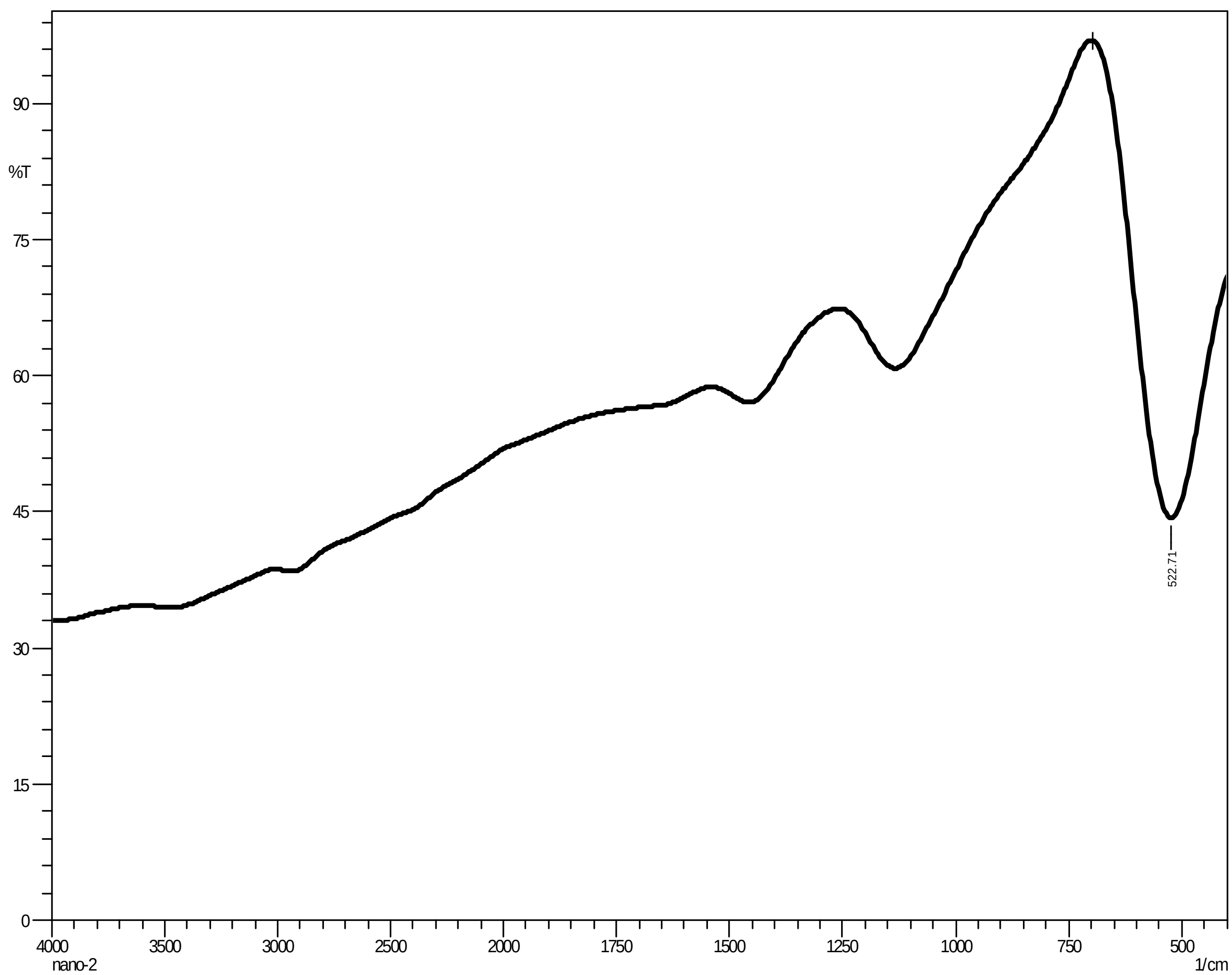


**Fig . (2b):** FT-IR spectra of Copper nanoparticles.

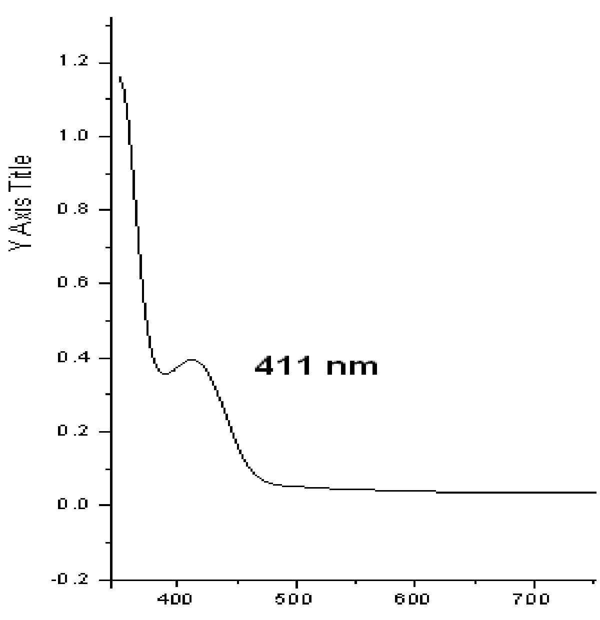


**Fig. 3:** UV-Vis spectrum of Copper nanoparticles.

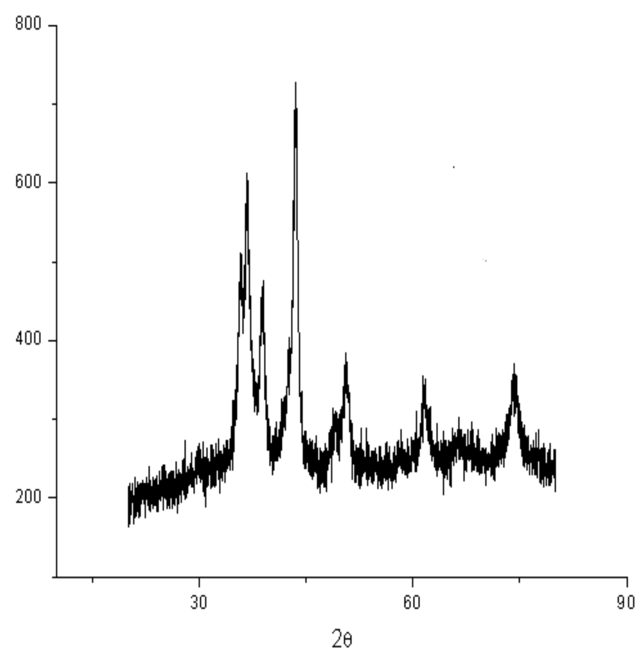


**Fig.4:** XRD pattern of the Cu, $Cu_2O$ and CuO nanoparticles.

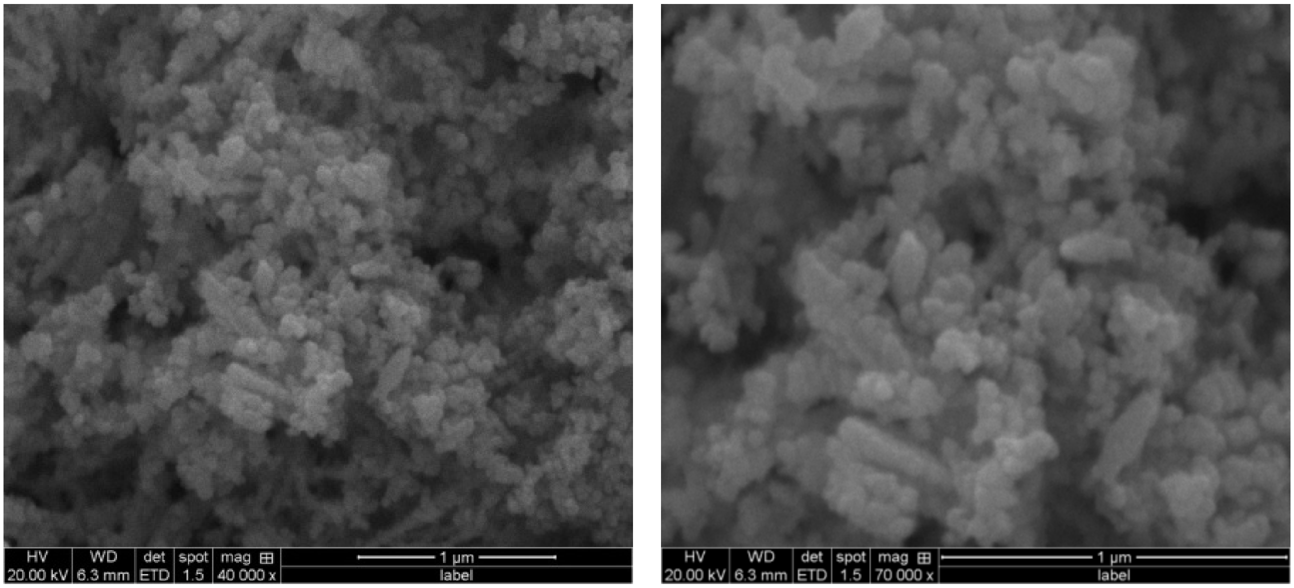


**Fig. 5a and 5b:** SEM images of the nanoparticles.

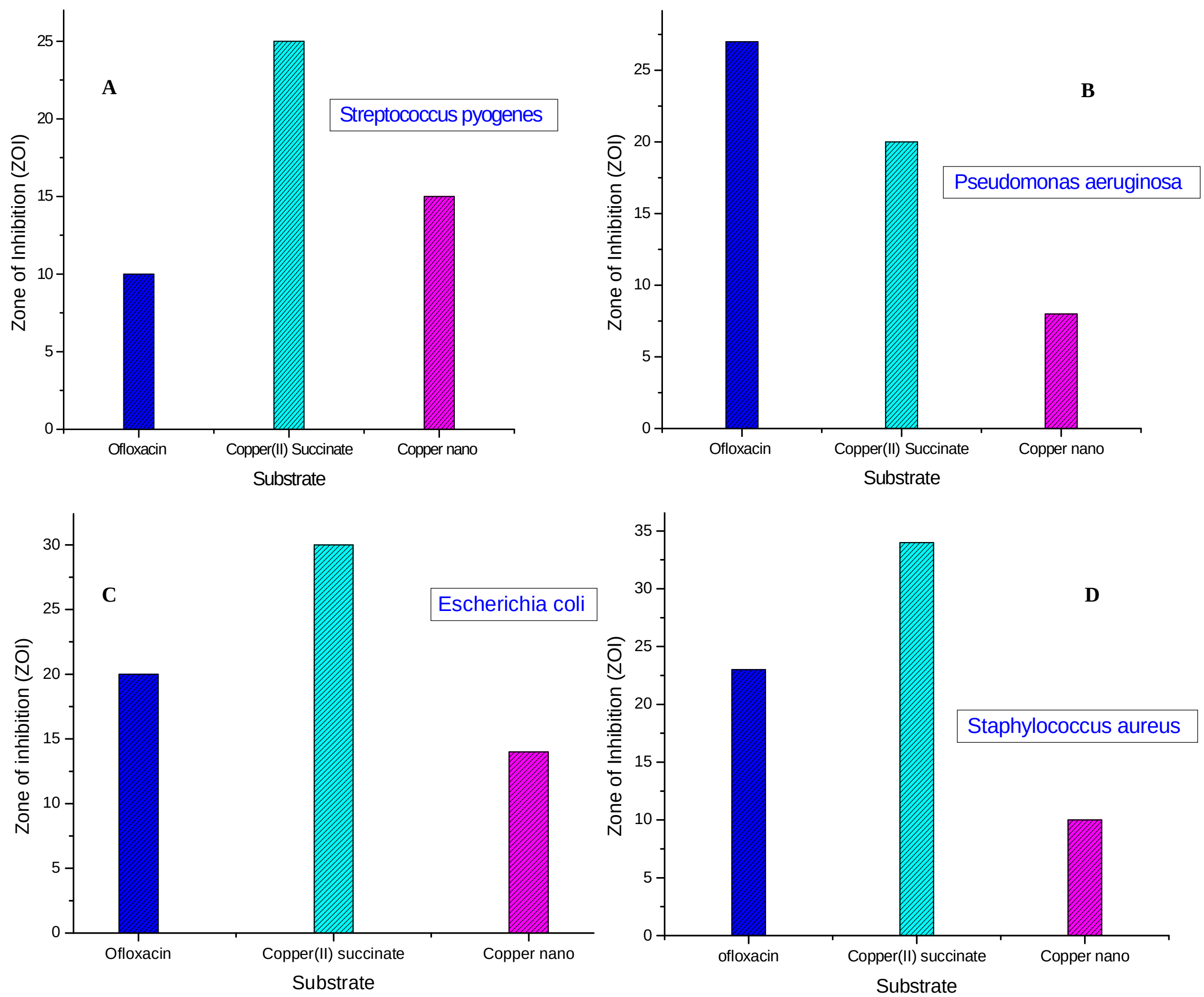


**Fig. 6(A-D):** The diameter zone of inhibition (ZOI) of Drug, Copper(II) succinate and copper nanoparticle impregnated disks in presence of *Streptococcus pyogenes*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Staphylococcus aureus* microorganisms.

## CONCLUSIONS

The green chemistry approach used in the present work for the synthesis of nanoparticles is simple, cost effective and the resultant nanoparticles are highly stable and reproducible. In summary, a novel method was developed to synthesize nanoparticles by reducing Copper(II) succinate with $NaBH_4$ in reduction method. The result showed that $NaBH_4$ used as the reducing agent decreased the particle size of the powder. The overall antimicrobial activity effect of Copper(II) succinate that are consistent showed excellent activity and application against *Streptococcus pyogenes*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Staphylococcus aureus*, with strong zone of inhibition. Nanoparicles without any organic molecules exibit lower Zone of inhibition than the precursor. In the future, copper and copper oxide nanoparticles could replace some antibiotic medicines used to combat human pathogenic microorganisms (bacteria), safe and cost effective in the Pharmaceutical industry.

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