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Microwave-assisted synthesis of copper nanoparticles: influence of copper nanoparticles morphology on the antimicrobial activity

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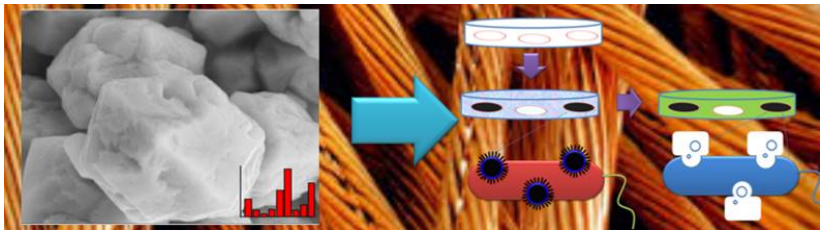
ABSTRACT



Among the several transition metals known to mankind, the synthesis of Cu has remained a major challenge owing to their instinctive oxidative power under ambient conditions. Microwave assisted synthesis of copper nanoparticles (CuNPs) using different types of copper-β-diketonates complexes and glycine as reducing agent. The morphology, size, and structural properties of obtained nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-visible spectroscopy (UV-VIS) techniques. The results of FE-SEM exhibited that the CuNPs of various shapes and size, depended upon the type of copper-β-diketonates complexes used. Furthermore, all the CuNPs exhibited good antimicrobial activity against both, Gram-positive and Gram-negative bacteria. The result shows that, the cubic CuNPs derived from $Cu(acac)_2$ demonstrated a better antibacterial activity against both bacterial strains.

Keywords: Cu nanoparticles, Microwave-irradiation, Antifungal activity

INTRODUCTION

Metal nanoparticles have been received much attention due to their unique optical, electrical, biomedical and catalytic properties.[1] The size, shape and surface morphology of the particles were crucial in tuning these properties of nanosized metal particles. There are many synthesis methods have been developed to prepare metal nanoparticles including, chemical, physical and biological methods.[2] Among these, microwave-assisted synthesis of metal nanoparticles is the simplest and environment friendly method.[3-5]

On the other hand, copper nanoparticles are the most preferred target for microwave-assisted methods due to their diverse applications like, catalysis, electronics, optics, medicine, photonics, and antimicrobial agent.[6] Several synthesis techniques for CuNPs with controlled size and shape have been reported, including vacuum vapor deposition, radiation, microemulsion, laser ablation, super critical techniques and sonochemical.7 One of the main limitations of these approaches, is the use of toxic chemicals and harmful by-products produced during the process. As a consequence, microwave-assisted synthesis have been used by researchers for the synthesis of various metallic nanoparticles. Microwave-assisted synthesis is appealing because it can dramatically reduce reaction time, improve product yield, and enhance material properties when compared to conventional synthesis routes.[7,8] Among the different metallic nanoparticles, CuNPs exhibit good antibacterial activity.[9,10] Very recently, the mechanism of antibacterial activity of CuNPs was reported and

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the CuNPs are known to be very effective against bacteria.[11] CuNPs are preferred to silver nanoparticles because of lower cost of copper than silver, easier mixing with polymers, and relatively more physic-chemical stability.[9,10]

In this work, we reported a facile microwave-assisted method for the synthesis of CuNPs by using different copper metal beta diketonates and reducing agent. The synthesized CuNPs were characterized by UV–visible spectrophotometer, energy dispersive X-ray spectra (EDS), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction crystallography (XRD), and the antimicrobial activity of CuNPs was evaluated.

EXPERIMENTAL

Materials and equipment

All the chemicals used in the present study are of AR grade. Whenever analytical grade chemicals were not available, laboratory grade chemicals were purified and used. We have employed metal β-diketonates as precursor materails,[12,13] which possess low moisture sensitivity and are thus less susceptible to hydrolysis, rendering them superior to metal alkoxides and halides often used in metal/metal oxide synthesis. The metal–oxygen bond present in β-diketonates complexes makes them appropriate precursors for the synthesis of metal/metal oxide nanoparticles. The metal complexes, Cu (II) β-diketonates like, $Cu(acac)_2$, $Cu(maa)_2$, $Cu(eaa)_2$ and $Cu(tbob)_2$, were synthesized and purified in-house.[14-16] ^{1}H- NMR spectra were obtained using a 400 MHz on a Bruker spectrometer (chemical shifts in δ ppm). Mass spectra were recorded using a micro spray Q-TOF MS ES Mass spectrometer.

Synthesis of Cu(β-diketonates)$_2$ Complexes.

To a solution of 6 g copper(II) chloride dihydrate ($CuCl_2.2H_2O$) in 4 mL of distilled water in a 500-mL beaker, add dropwise over a period of 30 minutes a solution of 7.5 mL of β-diketonates in 10 mL of methanol, while maintaining constant stirring. Add to the resulting mixture 10 g of sodium acetate in 30 mL of distilled water over a period of 20 minutes. Heat the reaction mixture with constant stirring for about 30 min on water. After completion of reaction was cooled to room temperature and the obtained precipitate was collected by filtration and cold distilled water and vacuum dry for 30 minutes before drying in an oven at 110^0C. Cu(II)-acetyl acetonate ($Cu(acac)_2$), Cu(II)-methylacetoacetate ($Cu(maa)_2$), Cu(II)-ethyl acetoacetate ($Cu(eaa)_2$), Cu(II)-ter-butyl-acetyl acetonate ($Cu(tbob)_2$), respectively. The formation of Cu(β-diketonates)$_2$ complexes were confirmed by powder XRD technique. The FTIR, ^{1}H- NMR and mass spectra of in house synthesized copper metal complexes are shown in ESI (Scheme 1, S1-S9†).

Synthesis of copper nanoparticles

Copper nanoparticles (CuNPs) were synthesized by reduction of four different Cu(β-diketonates)$_2$ complexes using glycine and potassium hydroxide as reducing agents. In a typical synthesis process, the mixture of $Cu(acac)_2$ (10 mmol) was dissolved in 15 ml of EG (Ethylene Glycol) and 15 mmol of glycine was added with constant stirring. Finally 15 mmol of KOH in 5 ml of EG was added when the solution completely turned blue after 10 minutes of stirring. The resulting mixture was irradiated in a microwave for about 10 minute till a dark red colour appeared. The reaction mixture was cooled and centrifuged for about 10 min at 7000 rpm yield copper nanoparticle. The isolated product was then washed with absolute ethanol and dried under vacuum at 80 °C for 4 h to obtain powdered CuNPs. The Experiment was repeated with $Cu(maa)_2$, $Cu(eaa)_2$ and $Cu(tbob)_2$ respectively, and in every case the end product was CuNPs only.

Characterization of Copper nanoparticles

The crystallinity and phase composition of the copper nanoparticles were investigated using an X-Ray Diffraction (XRD) – analysis was done with Rigaku X-ray difractometer, FT-IR studies were carried out using a Thermofisher Scientific FTIR spectrophotometer (Nicolet 6700 FT-IR). Scanning electron Microscopy (SEM) and X-ray Energy dispersive Spectroscopy (EDS) analysis was done using ULTRA55 FESEM equipped with EDS.

Antimicrobial assay

The antibacterial activities of the synthesized silver nanoparticles were assessed against both gram positive (*S. aureus*) and gram negative pathogen (*P. aeruginosa*) through agar disk diffusion method.[17,18] The pure bacterial and fungal strains were maintained on nutrient agar and potato dextrose agar (PDA), respectively. The dried powder of CuNPs was taken at the concentration of 50 µg/ml for the antibacterial tests. The wells were made in agar plates and 50 µL of CuNPs were added into the wells and subsequently incubated at 37 °C for 24 h. Zone of inhibitions were determined by measuring the diameter of the bacterial growth inhibition around the wells. All assays were carried out in triplicates and results are presented as mean±standard deviation (SD).

RESULTS AND DISCUSSION

Synthesis and characterization

Metal-β-diketonate fragments have attracted widespread attention because of their potential applications as a high quality advanced materials for the synthesis of metal/metal oxide nano materials.[19] Generally, the β-diketone ligands are considered as potential ligands due to their enclosing ability in metal complexes synthesis. Recently, we have reported the synthesis of metal-β-diketonate fragments for the synthesis of different metal/metal oxide nanoparticles.[20,21] We have developed four copper metal-β-diketonate complexes (Scheme 1, ESI†) for the synthesis of copper nanomateraials by MW method. The main stretching modes in the infrared spectra of the complex resulting from β-diketones are υC=O, υM-O, υC-O (ESI, Figure S1†). The coupled vibrations of Cu-O stretching modes appeared below 700-742cm^{-1} in the complex and the 457-489 cm^{-1} band have been assigned as pure υ(Cu-O) vibrations.[22,23] In the H^1- NMR spectrum of Cu (β-ketonate)$_2$ shows, the peak at δ = 4.86-5.47 corresponds to the -CH- proton in between the two carbonyl groups in the acetyl acetone of Cu(β-ketonate) and peak at δ = 1.2-2.22 corresponds to the CH_3-C=O protons (ESI, Figure S2†). The mass spectra (ESI,

Figure S3†) and powder XRD data also (ESI, Figure S4†) supported the formation of Cu(β-diketonates)$_2$.

For the past few years, our research has been focused to develop novel synthetic protocols for the synthesis of metal/metal oxide nanopaerticles maintaining some of the sustainable principles. In this process, we attempted the reaction of Cu(β-diketonates)$_2$ for the synthesis copper nanoparticles by microwave-assisted method in EG. The obtained powder materials was confirmed by the powder XRD spectra (Figure 2).

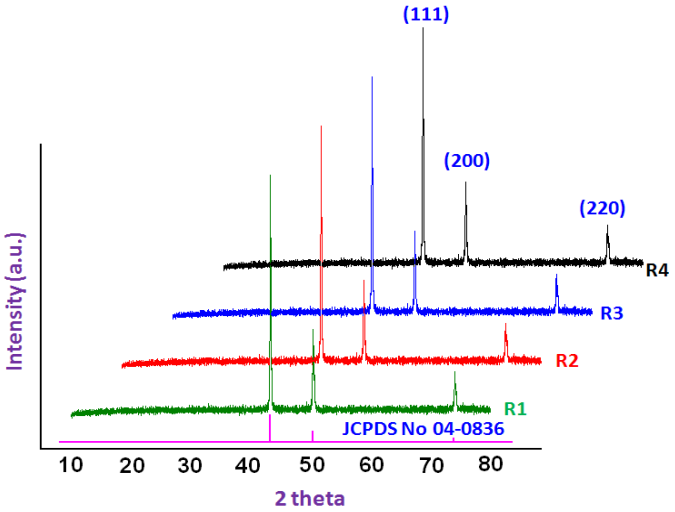

Figure 1: Powder XRD of CuNPs by microwave method.

The powder XRD confirms the formation of pure single crystalline CuNPs is shown in Figure 1. In Figure 1, the 2θ = 43.4, 50.5, and 74.0^0, attributed to the (111), (200), and (220) crystal planes, respectively, belonging to pure copper with face-centered cubic symmetry (FCC) [24,25] and corresponding to the diffraction pattern of metallic copper (JCPDS number 04-0836) [26], as shown at the bottom of this figure.

Microwave technology has been demonstrated to speed up reactions, often achieving good purity and product yield. We decided to investigate the selectivity of the reaction between Cu(acac)$_2$ and glycine and explore the effect of microwave irradiation for the formation of copper nanopartciles. The formation of copper nanopartciles by MW method was studied by powder XRD technique (Figure 1). The each sample was collected 2 min interval of the reaction and centrifuge the samples and characterized by XRD and it clearly shows that, the lower angle peaks (belongs to the organic moieties) was disappeserd with increasing the microwave irradiation time. The peak (111) was appeared at 3 min and peak (200), (220) were apeared at 12 min of microwave irradiation.The pure phase of copper nanoparticle was achieved at 18 min of microwave irradiation.

We have also discussed the effect of different reducing agents for the synthesis of copper naopartilces by microwave method (Table 1). Among the different reducing agents, glycine was produced copper nanoparticles quickly in 18 minutes in good yields compare others.

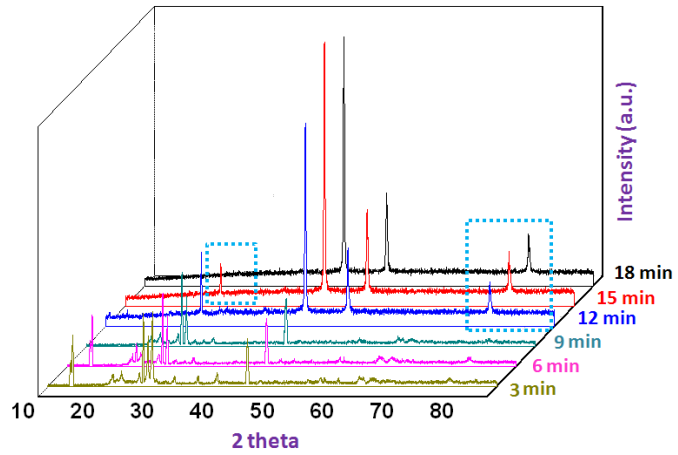

Figure 2: Powder XRD of the CuNPs by microwave method at different time intervals**.**

Table 1. Effect of reducing agents for the synthesis of CuNPs by MW method.

Complex	Reducing agent	Time (min)	Solvent
Cu(acac)$_2$	Glycine (15 mmol)	18	EG
Cu(acac)$_2$	Hydrazine Hydrate (15 mmol)	35	EG
Cu(acac)$_2$	CTAB (15 mmol)	45	EG
Cu(acac)$_2$	$NaBH_4$ (15 mmol)	45	EG

Table 2. Effect of solvents for the synthesis of CuNPs by MW method.

SOLVENT	TIME (MIN)	REDUCING AGENT
Ethanol	40	Glycine (15 mmol)
Propane 1,3 diol	30	Glycine (15 mmol)
Decanol	30	Glycine (15 mmol)
Ethylene Glycol	18	Glycine (15 mmol)

Microwave-assisted reactions is based on the efficiency of the interaction of molecules in a reaction mixture (substrates, catalyst and solvents) with electromagnetic waves generated by a "*microwave dielectric effect*". The reaction medium with a high value of (*tan δ*) at the standard operating frequency (2.45 GHz) of microwave system is required for the good absorption i.e. high heating rate. We different solvents for the synthesis of copper nanoparticles are high-lighted in Table 2.

The powder XRD of the copper nanoparticles in different solvents under microwave irradiation method was shown in Figure 2. The results indicates that, EG has been used because of high boiling point, high dielectric loss constant, because of chelating properties (auto surfactant). There is no extra satellite peaks were absorbed in EG solvent assisted synthesis of copper nanoparticles. The morphology of the copper nanopaticles synthesis form different solvents by microwave method is as shown in Fig 4.

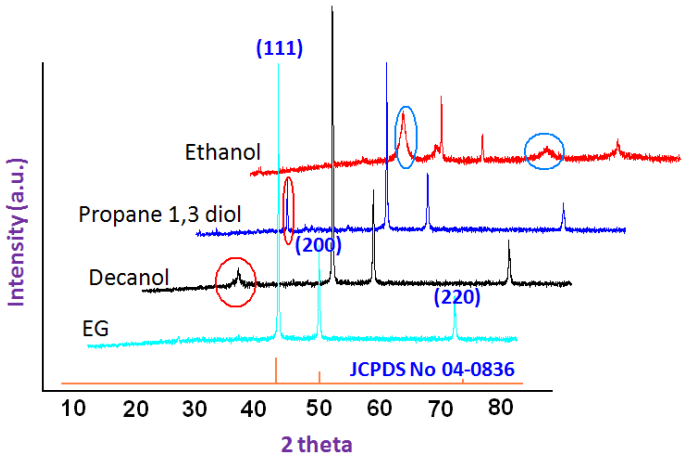

Figure 3: Powder XRD of the CuNPs synthesis by different solvent at microwave method.

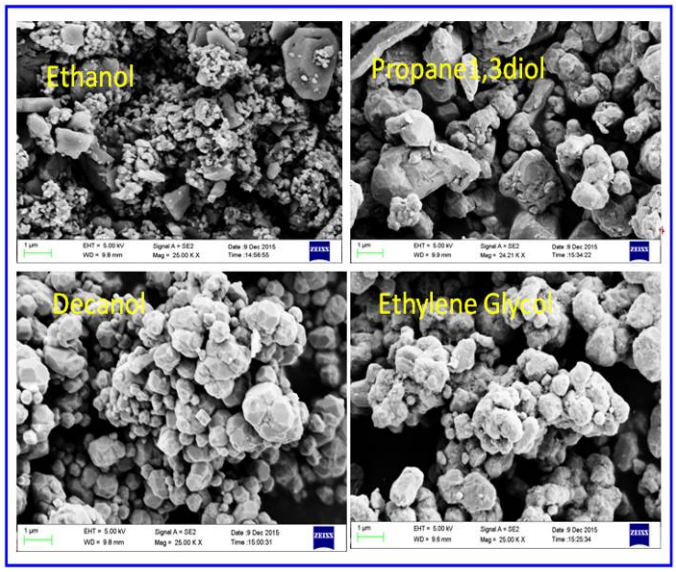

Figure 4: SEM images of the CuNPs synthesis by different solvent at microwave method.

The typical SEM (Figure 5) of CuNPs shows large number of single crystals were formed at 40 min of MW irradiation in EG solvent. Uniform and crystalline CuNPs was obtained because MW provided suitable condition for nucleation and crystal growth (Figure 5). The chemical purity and stoichiometry of the obtained CuNPs were obtained by EDX spectrum (Figure 6).

We studied the effect of different metal β-diketones complexes for the preparation of CuNPs, the presence of β-diketones during the microwave reaction affected the morphology and size of the nanoparticles. From the SEM images and Image J (ESI, Figure S8†) the CuNPs from $Cu(acac)_2$ had an average size of 79.5 nm, and the CuNPs were spherical and uniform as shown in Figure 5(a) (ESI S9†). On the other hand, the CuNPs from $Cu(maa)_2$ had an average size of 36.4 nm with uniform distribution of size and shape as shown in Figure 5(b). The Cu-NPs from $Cu(eaa)_2$ and $Cu(tbob)_2$ had an average size of 85.7 nm and 37.9 nm respectively Figure 5(c,d). The drastic change in the size and

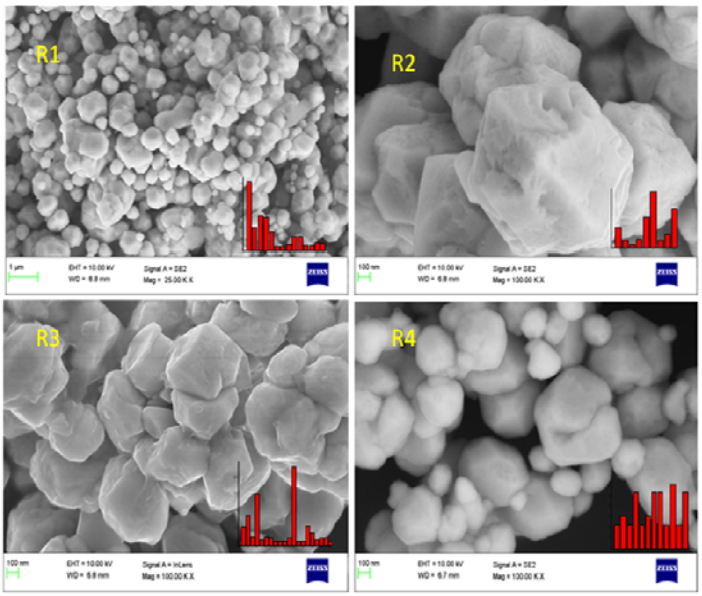

Figure 5. SEM image of single crystalline Cu-NPs: R1= $Cu(acac)_2$, R2= $Cu(maa)_2$, R3 = $Cu(eaa)_2$ and R4 = $Cu(tbob)_2$ respectively.

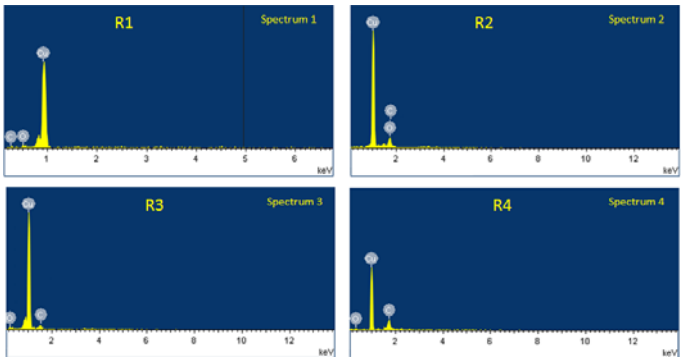

Figure 6. EDX spectrum of R1, R2, R3 and R4 CuNPs respectively.

morphology was thought to be because the presence of glycine enhances the growth of crystalline CuNPs as the temperature is increases. These results clearly showed that the CuNPs were produced from $Cu(maa)_2$, was more crystalline and uniform size distribution compare to other metal complexes.

The formation of copper nanoparticles was also confirmed by FTIR analysis.

X-ray photoelectron spectroscopy (XPS) was employed for copper nanoparticle (R2) resulted from $Cu(maa)_2$. Figure 7 shows the core shell XPS spectra of Cu 2p recorded from powder and supported copper nanostructures. The two strong peaks observed at 932.65 eV and 952.56 eV are in agreement with the binding energies of Cu 2p3/2 and Cu 2p1/2, respectively.[27,28] All the obtained nanoparticles will have different structural morphology with different sizes.

Nanoparticles applications in medicine depend on the size and the composition of the nanoparticles. The ability to target diverse bacterial structures was the important property of nanoparticles. Copper naoparticles have a great bactericidal effect and it possess

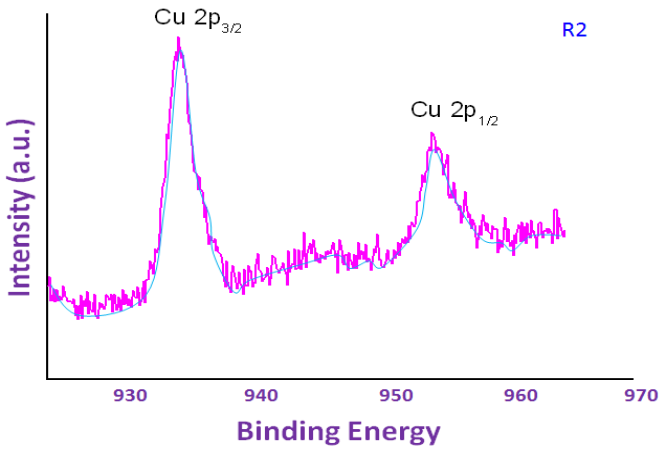

Figure 7. XPS spectra of R2 copper nanoparticles.

Impact of morphology on Antimicrobial activity

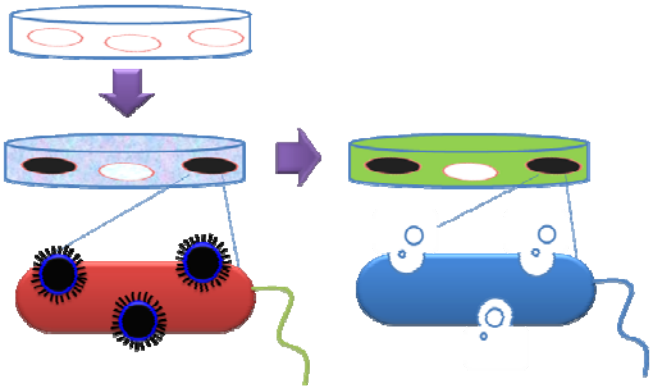

Figure 8 Pictorial demonstration showing the anti-bacterial action of CuNPs respectively.

well-developed surface chemistry, chemical stability and appropriate smaller size which make them easier to interact with the microorganisms. The mechanism of action is as shown in Figure 8. The antibacterial activity of copper naoparticles against gram positive (*S. aureus*) and gram negative pathogen (*P. aeruginosa*) is as shown in Figure 8. Figure 9 shows the enlarged microscopic images of antimicrobial activity. The growth inhibition zones obtained from the antibacterial study of the synthesized copper nanoparticles was shown in Figure 10. The results display that the copper nanoparticles, prepared from all the four copper metal complexes, showed a good antibacterial activity against gram-negative than gram-positive bacteria. The largest inhibition zone was obtained for the Gram-negative bacteria (*P. aeruginosa*) compare to *Staphylococcus aureus*.

The obtained results shows that, the antibacterial activity was dependent on the size of the nanoparticles–the highest activity was observed for CuNPs synthesized from the $Cu(acac)_2$ by microwave-assisted method. In our case, we believe that the CuNPs from microwave-assisted method had the crystalline, smaller size and the largest surface/volume ratio. Small CuNPs are able to be penetrated inside the bacteria and caused further damage, lose their activity and finally cell death. At last, the CuNPs release copper ions, which will have an additional contribution to the antibacterial activity of the CuNPs. This characteristic enhances biological and chemical activity of the nanoparticles with high antibacterial efficacy.

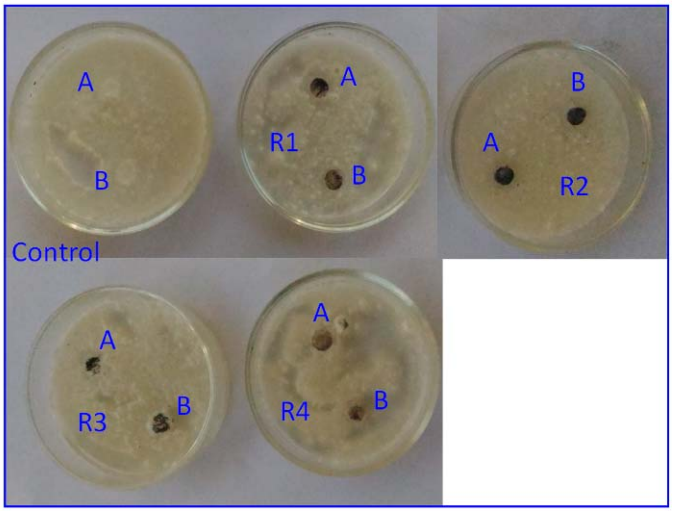

Figure 8. Antimicrobial activity of copper nanoparticles.

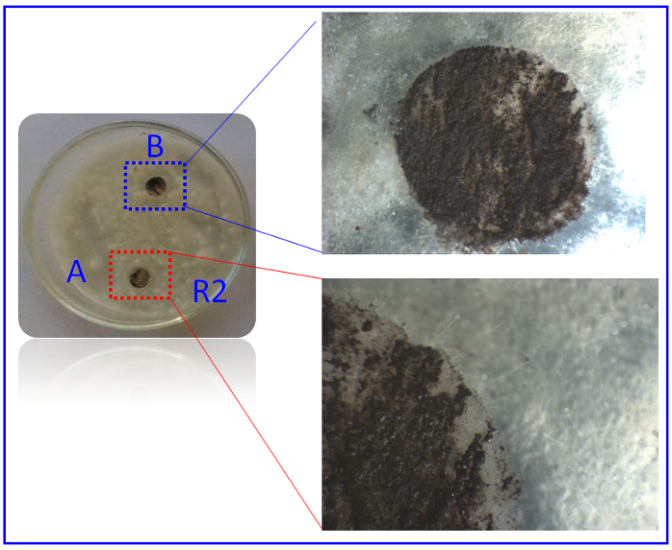

Figure 9. Microscopic images of the antimicrobial activity of copper nanoparticles.

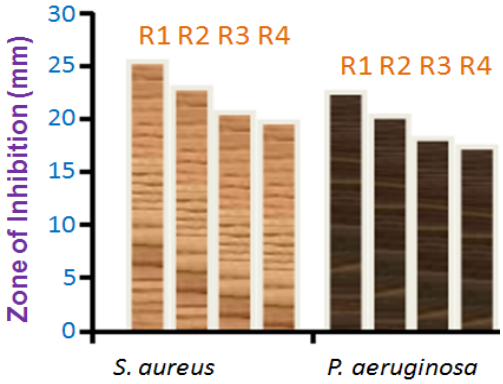

Figure 10. Zone of inhibition of antimicrobial activity CuNPs.

CONCLUSION

Copper nanoparticles were synthesized from different copper metal β-diketones by microwave-assisted method. The crystalline metallic copper nanoparticles were confirmed from XRD results. The morphology of these copper nanoparticles was found to be spherical through SEM micrographs. The SEM analyses revealed that the size of the CuNPs synthesized from different copper metal β-diketones by microwave-assisted method varied in the order: $Cu(acac)_2<Cu(eaa)_2<Cu(tbob)_2<Cu(maa)_2$. Antimicrobial study displayed that the CuNPs synthesized from the $Cu(maa)_2$ showed the highest activity, which can be attributed to the single crystalline and smallest size of the CuNPs. Results obtained from our present work would be helpful in the development of new morphology oriented copper nanoparticles and their potential applications in biological, pharmaceutical and physiological fields in future.

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