

PREPARATION, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF BIONANOCOMPOSITES OF COPPER OXIDE NANOPARTICLES BASED CARBOXYMETHYL CELLULOSE DERIVED FROM ASPARAGUS STALK END

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Abstract

Green, sustainable bionanocomposites have the potential to be useful in diagnostic and biomedical applications. In the present study, a series of copper oxide nanoparticles-based carboxymethyl cellulose (CuCMC) bionanocomposites with different weight ratios of carboxymethyl cellulose (CMC) derived from asparagus stalk end to copper oxide nanoparticles (CuO NPs) were prepared. The prepared bionanocomposite of copper oxide nanoparticles based carboxymethyl cellulose (CuCMC) material was characterized by using XRD, FT IR, UV-Visible, SEM and TG-DTA techniques. SEM, and XRD studies indicated the in situ generation of CuO NP in the carboxymethyl cellulose matrix. FT IR analysis confirmed the presence of both CuO NPs and CMC. TG-DTA results indicated that the CMC content of CuCMC was between 61.9 and 73.6 % by weight. Finally, the synthesized CuO, CMC, and CuCMC were tested for their antimicrobial activity. The results obtained from those different studies revealed that carboxymethyl cellulose and copper oxide bionanocomposite can be used effectively for biomedical applications.

Keywords: Copper oxide nanoparticles, carboxymethyl cellulose, antimicrobial activity, bionanocomposite

Introduction

Nanocomposites are materials which consist of two components, with one of them having dimensions in the nanometer range (10^{-9} m). As environmental problems worsen, more and more emphasis has been placed on green chemistry. Asparagus (*Asparagus officinalis* L.) is a nutritious and perennial vegetable continuously used as an antifungal, anticancer, and anti-inflammatory herbal medicine in Asia. In the processing of asparagus, the spears, which are 2-3% of the total weight of the asparagus, are typically processed into three types of products: canned, fresh, and frozen. The processing residues were used for animal feed and produced low-value products due to their high cellulose content. As a result, tons of asparagus stalk ends are produced as an agricultural by-product, which can pollute the environment. It is a rich source of celluloses which can be isolated from the asparagus stalk end (Klunklin *et al.*, 2021). Carboxymethyl cellulose (CMC), one of the most important cellulose derivatives, is obtained by chemical modification of natural cellulose. It is a linear, long-chain, water-soluble ionic polysaccharide derived from cellulose. In addition, the purified cellulose is white to cream-coloured as well as tasteless and odourless, and it is a free-flowing powder. Furthermore, carboxymethyl cellulose has an acid fusion, meaning that CMC is an anionic polyelectrolyte, CMC has many interesting properties when dissolved in an aqueous solution, but this depends on the CMC grade and the solution condition.

Due to its water-soluble heteropolysaccharides with high molecular weight properties, CMC is often blended with starch to provide a desirable mixture, enhance product quality and stability, control moisture, and also improve water mobility (Hong, 2013).

Copper oxide nanoparticles are technically interesting because of their physical and chemical properties, such as high temperature superconductors, batteries, gas sensors, solar energy

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conversion, and low-cost and low-toxicity antibacterial properties. It can also be used as an antibacterial agent (Paternela *et al.*, 2018). Recently, much interest has been focused on the preparation of antimicrobial bionanocomposite materials due to their excellent biomedical relevance. These antibacterial agents have great potential to inhibit the growth of microorganisms and to save the environment.

In this respect, copper-based materials are attractive alternatives because they are known to have important antibacterial activity in addition to being low cost and easy to release from the human body. The advantage of copper nanoparticles is that they oxidize to form copper oxide nanoparticles. It mixes easily with polymers and macromolecules and is relatively stable in terms of both chemical and physical properties. Therefore, copper-based nanocomposites are very important (Yadollahi *et al.*, 2015).

Materials and Methods

Asparagus stalk ends were purchased from the local market. Copper (II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), sodium silicate (Na_2SiO_3), isopropanol ($\text{C}_3\text{H}_8\text{O}$), monochloroacetic acid (MCA), methanol (CH_3OH), acetic acid (CH_3COOH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), hydrochloric acid (HCl), and sulphuric acid (H_2SO_4) were supplied by the Department of Chemistry, University of Yangon, Myanmar. Where necessary, distilled water was used with all the chemicals in this study.

Preparation of Copper Oxide (CuO) Powder

The copper (II) sulphate pentahydrate was used to prepare copper oxide nanoparticles according to the well-known co-precipitation method with some modifications. In brief, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.48 g) was dissolved in 250 mL of distilled water and stirred continuously. And then, 5M sodium hydroxide (NaOH) solution was added dropwise into the copper(II) sulphate pentahydrate solution until the pH 12 solution was reached. The colour of the solution changed from green to bluish green and finally to black as the reaction proceeded. For 6 h, the solution was continuously stirred at 85 °C. Then, the solution was centrifuged at 8000 rpm for 10 min. The synthesized CuO NPs were washed free of alkali metals several times with distilled water until they reached a neutral state (pH 7). This was washed again with ethanol and dried in the oven at 60 °C for 8 h. After that, the dried CuO NPs were calcined in a muffle furnace at 500 °C for 4 h to achieve stable CuO NPs. This was crushed with a mortar and pestle and sieved with a 90 µm size screen. Finally, the samples were stored in a sealed bottle and placed in a desiccator for further use.

Preparation of Carboxymethyl Cellulose Derived from Asparagus Stalk End

Cellulose from dried asparagus stalk end powder was extracted according to the method of Klunklin *et al.*, 2021. Briefly, the dried powder sample of asparagus stalk end was treated at 100 °C for 3 h with a ratio of cellulose to 10 % (w/v) NaOH solution at 1:20 (w/v). The black slurry was filtered and rinsed with cold distilled water until neutral (pH 7) rinsed water was obtained. To obtain the cellulose fiber, the washed fibre residue was dried in an oven at 55 °C for 24 h. The dried fibre residue was bleached with 6 % sodium silicate and 50 % hydrogen peroxide on magnetic stirrer for 3 h. The white cellulose was obtained and dried in an oven at 55 °C for 24 h. The bleached cellulose was then ground using a mortar and pestle and sieved through a 90 µm size mesh. The bleached cellulose powder was stored in a sealed bottle.

The cellulose powder was then modified to carboxy methyl cellulose by alkalization and esterification processes. In briefly, 100 mL of concentrations of NaOH at 40 % (w/v) and 500 mL of isopropanol were blended with 10 g of cellulose powder extracted from asparagus stalk

ends, and this was stirred for 1.5 h. Subsequently, the carboxymethylation reaction was carried out. 15g of monochloroacetic acid was added while stirring and stirred further for 1.5 h. This obtained solution was covered with aluminium foil and placed in an oven at 55 °C for 3 h. And then, two phases appeared. The solid phase was suspended in 66.67 mL of absolute methanol and neutralized with 90 % acetic acid. This neutral solution was filtered through the Buchner funnel. The product was soaked in 200 mL of 70 % v/v ethanol for 10 min and washed 5 times with distilled water. And then the product was washed again with 200 mL of absolute methanol. CMC was obtained and dried in an oven at 55 °C for 12 h.

Preparation of Copper Oxide Nanoparticles Based Carboxymethyl Cellulose Bionanocomposite (CuCMC)

A 1 g of copper oxide powder was dissolved in 2.5 mL of epichlorohydrin and 30 mL of 25% (v/v) acetic acid solution and stirred continuously at room temperature for 12 hours to form a green-coloured CuO NPs mixture solution. The five different amounts of CMC (0.1, 0.2, 0.3, 0.4, and 0.5 g) were added to the prior CuO NPs mixture solution, and then the mixed polymer composite solution was stirred at room temperature for 30 min. This was allowed to stand for 24 h to obtain CuCMC bionanocomposite. Finally, the obtained CuCMC was dried in an oven at a temperature of 60 °C for 12 h and powdered by using a mortar and pestle. A series of CuCMC bionanocomposites are coded as CuCMC(0.1)(0.1 g of CMC), CuCMC(0.2) (0.2 g of CMC), CuCMC(0.3) (0.3 g of CMC), CuCMC(0.4) (0.4 g of CuCMC) and CuCMC(0.5) (0.5 g of CMC), respectively.

Characterization

The surface morphology of bionanocomposite materials was studied using SEM (EVO-18, Germany) at 7 kV. The dried sample film was cut, sputter-coated with EVO-18 using platinum, and viewed through the microscope. Fourier transform infrared spectrophotometer (Shimadzu, Japan) was used. The resolution was 1 cm^{-1} and the scanning was performed in the range of 400–4000 cm^{-1} . The X-ray diffraction (XRD) measurements of CuO NPs, CMC, and CuCMC bionanocomposites were recorded using a Rigaku D/Max 220 X-ray diffractometer (Rigaku, Japan) with a detector operating under a voltage of 40.0 kV and a current of 30.0 mA using Cu K_{α} radiation ($\lambda = 0.15418$ nm). The recorded range of 2θ was 10–80 ° and the scanning speed was 6 °/min. The thermal stability of CuO, CMC, and CuCMC bionanocomposites was evaluated by a simultaneous TG-DTA (DTG-60 H) operated under a nitrogen atmosphere.

Results and Discussion

Characterization of CuCMC Bionanocomposites

X-ray diffraction analysis

Figure 1 shows the XRD patterns of CuO NPs, CMC, and CuCMC bionanocomposites. As seen in Figure 1(a), the diffractive region of CuO NPs is observed at 2θ values of 35.69°, 38.75°, 48.48°, 61.69°, 66.01° and 68.23°, respectively, and the corresponding Miller indices are (110), (111), (112), (202), (311), and (113) planes. The higher intensity values of 2θ for CuO indicate that the mixed phase has a major proportion of CuO with a highly oriented crystalline structure. Using Scherrer's equation, the average crystallite size of CuO NPs was found to be 18.46 nm. In Figure 1(b), pure CMC shows characteristic peaks at around 2θ values of 19.71°, 31.75°, and 45.83°, which indicate the amorphous and crystalline structures. The strength of hydrogen bonding and crystallinity contribute to the microstructure of CMC material. Figure 1(c) shows that the main diffractive region of all CuCMC is found with a weak broad peak at 2θ value of 34.10°, 37.14°, 46.58°, 50.32°, 55.99°, 59.52°, 64.98°, 66.66°, 70.81° and 73.25° which are

assigned to the crystal planes of (110), (111), (112), (200), (020), (202), (220), (311), (113) and (400). These values confirmed the presence of two crystalline phases of CuO and Cu₂O. When incorporation of CuO into the CMC chemical structure of the CMC hydrogels changes due to overlap of biopolymer diffraction, it indicates that there was mainly physical interaction but scarcely a chemical reaction between CMC and CuO NPs (Alothman *et al.*, 2020). The calculated mean crystallite sizes of the CuCMC(0.1), CuCMC(0.2), CuCMC(0.3), CuCMC(0.4), and CuCMC(0.5) were found to be 50.88 nm, 55.28 nm, 57.06 nm, 59.43 nm, and 64.33 nm, respectively. The higher the amount of CMC, the larger the crystallite size of CuCMC nanoparticles produced.

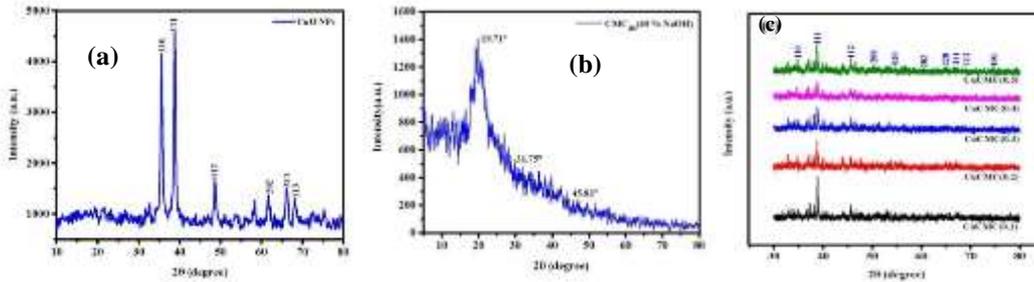


Figure 1. XRD patterns of pure (a) CuO NPs, (b) CMC, and (c) CuCMC bionanocomposites

FT IR spectroscopy

FT IR experiments were carried out to investigate the interaction between CuO and CMC. As shown in Figure 2(a), in the spectrum of CuO, the peaks at 3414, 1632, and 608 cm⁻¹ correspond to O-H stretching vibration, C=O stretching, and Cu-O vibration, respectively (Luna *et al.*, 2015). In the spectrum of CMC in Figure 2(b), there is one characteristic absorption band at 1588 cm⁻¹, which corresponds to the carboxyl group (COO⁻), where the hydroxyl group was replaced with the carboxyl group after etherification (Pormsila *et al.*, 2019). As seen in Figure 2(c), the CuCMC spectra show peaks at 3469, 3472 cm⁻¹ (O-H stretching), and 1595 cm⁻¹, as well as a superposition band assigned to the C=O stretching vibration. 1423 cm⁻¹ is due to the CH₂ scissors, and 1052 cm⁻¹ assigned to the C-O-C of aliphatic ether (Basta *et al.*, 2021). Moreover, the band corresponding to the Cu-O stretching vibration shifts to a lower wavenumber, 626 cm⁻¹.

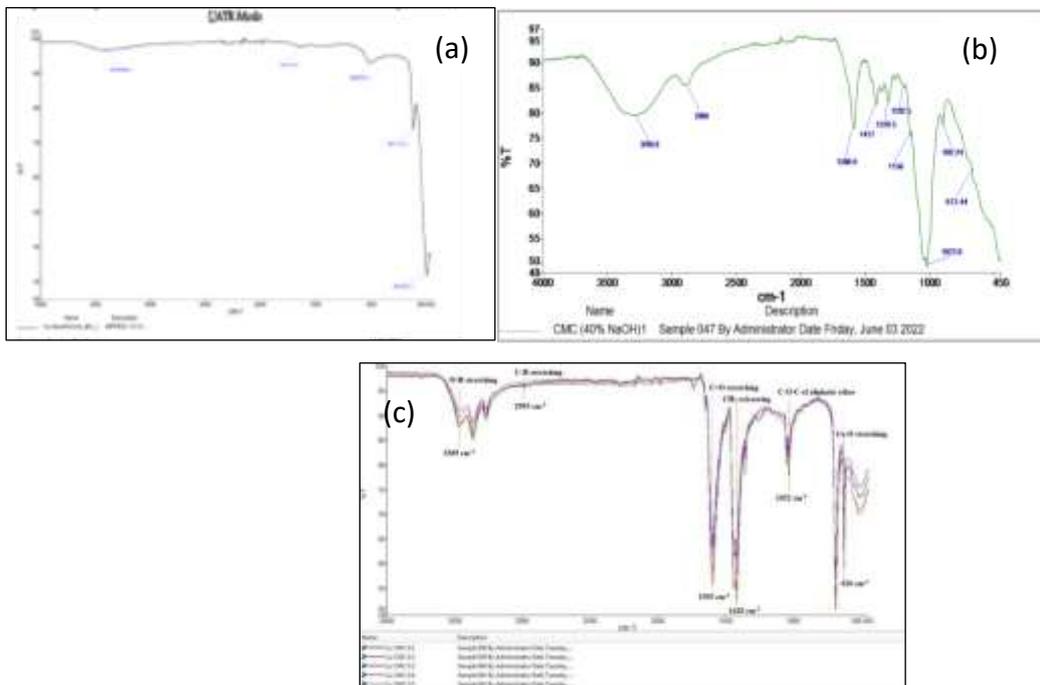


Figure 2. FT IR spectra of (a) CuO NPs, (b) CMC and (c) CuCMC bionanocomposites

UV-vis absorption spectra

The UV-Vis spectrum (Figure 3(a)) of pure CuO NPs shows absorption peaks at 272 nm. The CuCMC bionanocomposite shows 228 nm, 247 nm, and 260 nm. It was found that the intensity of the CuCMC bionanocomposite was lower than that of CuO. After attachment with CMC, the peaks of CuO have shown a bathochromic shift. This shift in absorption maxima might be attributed to the formation of nanoscale particles. Optical absorption is an important tool to obtain the optical energy band gap of crystalline and amorphous materials. The fundamental absorption corresponds to the electron excitation from the valence band to the conduction band and can be used to determine the nature and value of the optical band gap. The absorption spectrum reveals that the increase in concentration of CuCMC NPs produces a shift in the absorption peak and results in a high band gap. The absorption peak in the UV region was used to study the shifting in the optical energy band gap for CuCMC NPs at 25 °C. The optical energy band gap, E_g , is calculated from the relation:

$$(\alpha h\nu) = B(h\nu - E_g)^n$$

where $h\nu$ is the photon energy, B is the constant, and n is the power factor and that takes 1/2, 2, 3/2, and 3 for direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions, respectively.

Figure 3(b) shows that the optical band gap for CuO NPs is 3.18 eV, 3.31 eV for CuCMC(0.1), 3.38 eV for CuCMC(0.2), 3.43 eV for CuCMC(0.3), 3.49 eV for CuCMC(0.4), and 3.54 eV for CuCMC(0.5). CMC addition, as shown in the figure, raises the optical band gap from 3.31 eV to 3.54 eV. This may be attributed to salt complexation with the polymer matrix in addition to the expected nanoparticle aggregation. The absorption decreases and the optical band gap increases due to charge transfer transitions. The prepared CuCMC NPs in the present study are expected to be more useful in photonic and electronic device applications.

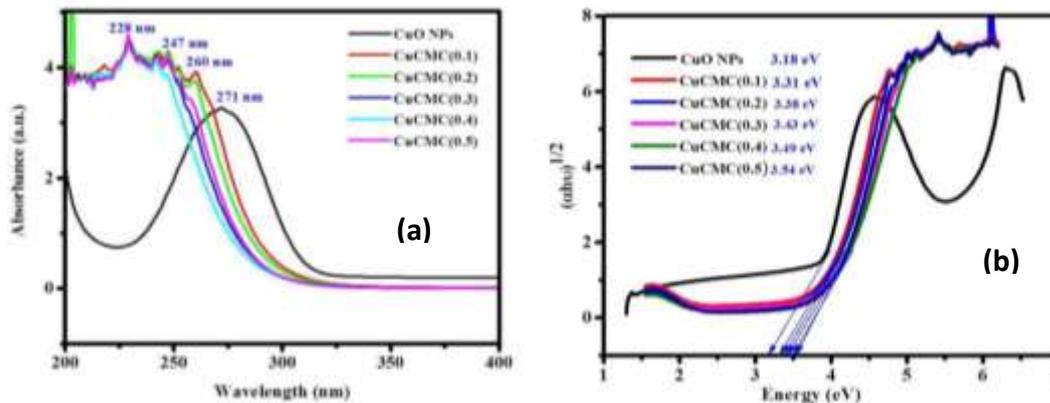


Figure 3. (a) UV spectra (b) plots of $h\nu$ vs $(\alpha h\nu)^{1/2}$ of CuO NPs and CuCMC bionanocomposites

SEM Analysis

The morphology of the prepared CuO, CMC, and CuCMC was investigated by the scanning electron microscopy technique. The surfaces of the CuO, CMC and CuCMC display a generally smooth morphology, as shown in Figures 4 (a) to (g), indicating that the CuO nanoparticles are uniformly aggregated and clustered. CMC was found to be rod-like or ribbon-shaped and CuCMC bionanocomposites were found to be cube-like structures. In the case of using a surface with some pores, its chelation with CMC appears as a surface coated with a white fibrillar layer of CMC (Basta *et al.*, 2020).

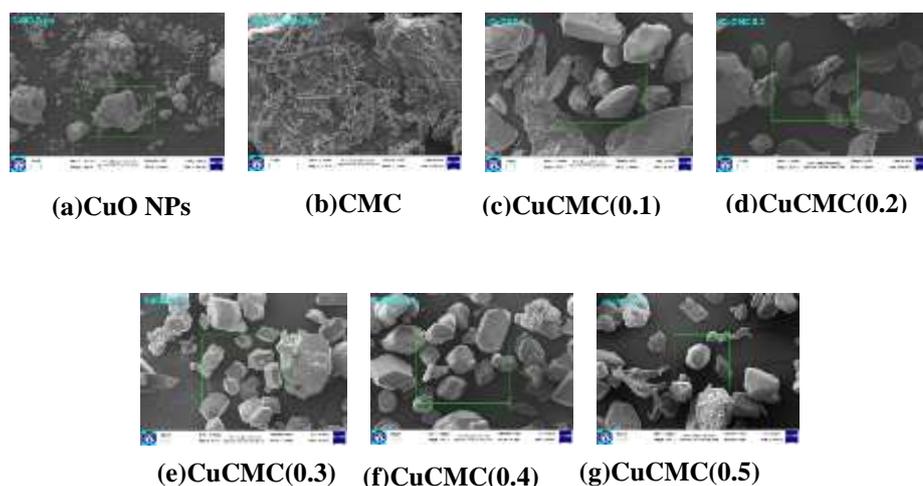


Figure 4. SEM images of (a) CuO NPs, (b) CMC, and (c,d,e,f,g) CuCMC bionanocomposites

TG-DTA Analysis

The thermogravimetric analysis was used to investigate the thermal stability of pure CuONPs, CMC, and five different ratios of CuCMC composite powder (CuCMC0.1, CuCMC0.2, CuCMC0.3, CuCMC0.4, and CuCMC0.5). The thermal stability of CuO NPs was observed due to a weight loss of 0.938% within the temperature range of 38 °C to 340 °C, as shown in Figure 5(a). This is attributed to the thermal decomposition of unstable groups containing oxygen and the evolution of CO₂ gas. Figure 5(b) depicts CMC's thermogram, which shows weight loss in four stages. The first stage occurs in the temperature range of 37 °C to 59 °C with 2.88 % weight loss. This is a result of moisture evaporation. In the second stage, the temperature range between 59 °C to 76 °C was observed to have an 8.65 % weight loss. This is attributed to the volatile organic compounds with low molecular weight. In the third stage, a loss of weight of 17.31 % was observed to take place within the temperature range of 76 °C to 158 °C. At this stage, weight loss may be due to the volatile organic compounds with low molecular weight. The fourth stage occurred at temperatures ranging from 158 °C to 238 °C, with a weight loss of 46.15 %. This is due to the decarboxymethylation of CMC with the elimination of CO₂ and the temperature range between 300 °C to 600 °C is due to the residual organic fractions. The total weight loss of the CMC is 74.99 %.

The thermograms of all CuCMC composites are shown in Figures 5(c) to 5(g), with weight loss in three stages. The temperature ranges from 38 °C to 157 °C in the first stage, with weight loss of 0.98 % in CuCMC(0.1), 6.50 % in CuCMC(0.2), 7.84 % in CuCMC(0.3), 6.71 % in CuCMC(0.4), and 7.06 % in CuCMC(0.5). There is an evaporation of water. The second stage was observed to lose 15.69 % in CuCMC(0.1), 12.99 % in CuCMC(0.2), 15.69 % in CuCMC(0.3), 20.14 % in CuCMC(0.4), and 20.14 % in CuCMC(0.5) at temperatures ranging from 157 °C to 238 °C. This is due to the decomposition of the substituted sites in the methylated derivatives. In the third stage, the temperature ranges from 238 °C to 600 °C, with a weight loss of 45.19 % in CuCMC (0.1). The broad exothermic peaks at 229 °C, 240 °C, 229 °C, 229 °C, and 272 °C correspond to 45.47% in CuCMC(0.2), 47.06 % in CuCMC(0.3), 47.00 % in CuCMC(0.4), and 35.58 % in CuCMC(0.5). At this stage, weight loss is due to the depolymerization and pyrolytic processes of the main polymer chains. The total weight loss percents of CuCMC bionanocomposites were in the range of 61.9-73.6%. The results show that the maximum weight loss percent of CuO NPs is lower than that of CuCMC bionanocomposites.

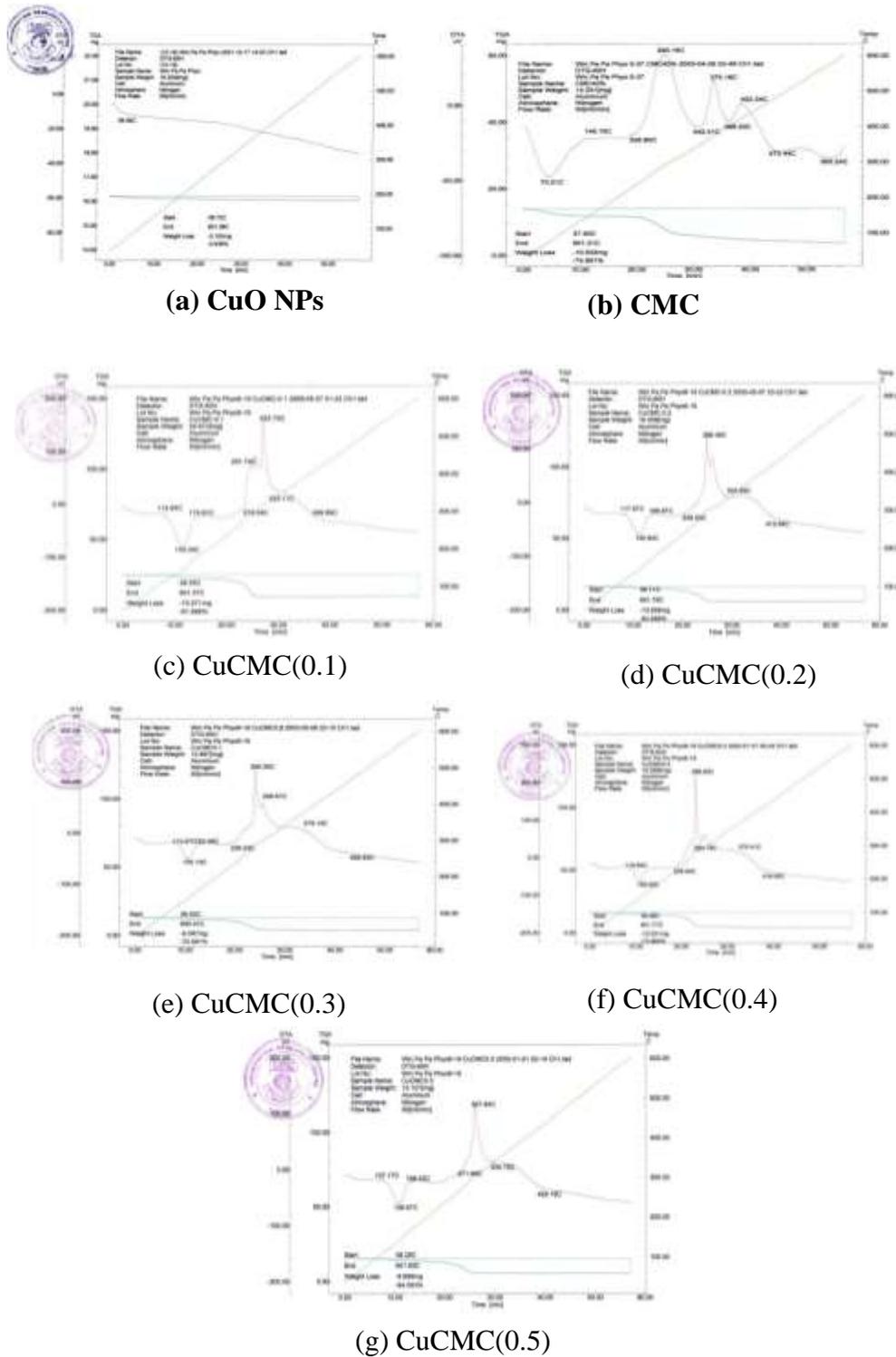


Figure 5. (a) TG curves (b) DTA curves for CuO NPs and CuCMC Bionanocomposites

Antimicrobial Activity

Screening the antimicrobial activity of three samples of nanoparticles was done by the agar well diffusion method. In this investigation, the nanoparticles were tested against eight microorganisms, namely *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas fluorescens*, *Bacillus pumilus*, *Candida albicans*, *Escherichia coli*, *Agrobacterium tumefaciens*, and *Micrococcus luteus*. The inhibition zone diameter, including the filter paper, showed the degree of antimicrobial activity. The larger the inhibition zone diameter, the higher the antimicrobial activity. The inhibition zones of nanoparticles against the eight microorganisms tested are shown in Figure 6, and the observed data are summarized in Table 1.

From the results, CuO NPs and CuCMC(0.5) NPs had antimicrobial activity, but CMC did not show any antimicrobial activity. It was found that CuO NPs possessed an 11~14 mm inhibition zone against *C. albicans*, *P. fluorescens*, and *S. aureus*, respectively, whereas CuCMC(0.5) exhibited an inhibition zone diameter range of 30-36 mm against all tested microorganisms. The antimicrobial activity of CMC did not show activity. It can be concluded that, according to the antimicrobial activity, the CuCMC(0.5) NPs may be intended to be used as an antibiotic agent.

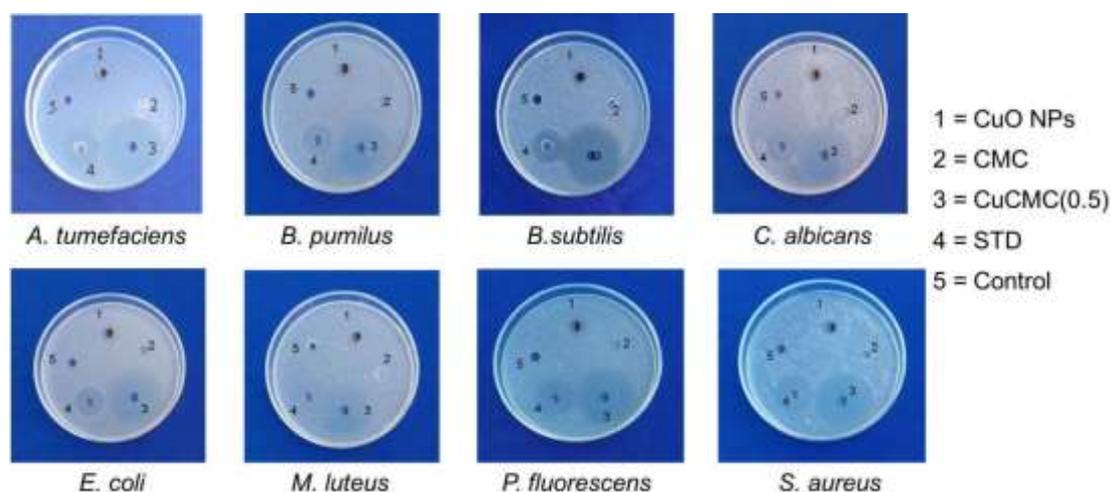


Figure 6. Antimicrobial activity of CuO NPs, CMC and CuCMC on eight microorganisms by agar well diffusion method

Table 1. Inhibition Zone Diameters of CuO, CMC, and CuCMC NPs Against Microorganisms by Agar Well Diffusion Method

Tested microorganisms	Inhibition zone diameters (mm)			
	CuO NPs	CMC	CuCMC(0.5)	*STD
<i>A. tumefaciens</i>	-	-	32	23
<i>B. pumilus</i>	-	-	30	21
<i>B. subtilis</i>	-	-	34	21
<i>C. albicans</i>	14	-	34	22
<i>E. coli</i>	-	-	36	20
<i>M. luteus</i>	-	-	36	18
<i>P. fluorescens</i>	11	-	35	22
<i>S. aureus</i>	11	-	35	23

*STD, for bacterial = choramphenicol, for fungus = Nystatin; (-) = not detected

Agar well diameter ~8 mm

10 mm ~14 mm = weak activity; 15 mm~19 mm = moderate activity; 20 mm and above = potent

Conclusion

The bionanocomposites of copper oxide nanoparticles based on carboxymethyl cellulose were successfully prepared by the co-precipitation method. It is observed that CuO NPs are dispersed on a molecular scale in the CMC matrix, and some interactions occur between the CMC and CuO NPs. In CuCMC bionanocomposites, FT IR showed the strong absorption band of the Cu-O bond at 626.96 cm^{-1} . The XRD patterns confirmed the formation of CuO NPs with a size range of 50.88–64.33 nm within the CMC matrix. SEM images confirmed the linking and grafting of CuCMC. SEM measurements revealed that the higher the CMC content, the larger the average diameter. All the results demonstrated that copper oxide was well-dispersed in the CMC matrix. TG-DTA measurements indicated the homogeneous dispersion of CuO within the CMC polymer matrix. The synthesized bionanocomposite was found to have greater thermal stability. The presence of both components of the bionanocomposite was confirmed by UV-Vis and FT-IR spectral studies. These studies also indicate a strong interaction between CuO and CMC in the bionanocomposites. The antimicrobial activity was measured by the agar well diffusion method. The CuCMC0.5 has more potent antimicrobial activity than the other two samples of CuO NPs and CMC. The main contribution of the present research is that the synthesis of copper-based carboxymethyl cellulose bionanocomposite may be used in the biomedical field.

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