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Preparation and characterization of polysaccharide mediated copper nanoparticle: The effect of time-varying exposure

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Abstract. This paper reported the synthesis of copper nanoparticles (Cu-NPs) via the chemical method in the presence of $CuSO_4.5H_20$ as precursor, polysaccharide as a stabilizer and ascorbic acid was acted as a reducing agent. In this study, the irradiation time was varied to evaluate the effect of time exposure with the Cu-NPs production. The analysis of samples without and with polysaccharide was characterized using ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD) and Fourier-transform infrared coupled with attenuated total reflection instrument (ATR-FTIR). Based on the observation, reddish-brown colour solution demonstrated the formation of Cu-NPs and UV-Vis proved the plasmon resonance (SPR) spectra at the peak of 580 nm. The sharp peak of XRD at angle 2Θ gives the value of 43.69°, 50.81°, and 74.42° was attributed to Cu-NPs and the presence of polysaccharides maintained the crystallinity of Cu-NPs. FTIR results shows that the interaction peaks were occurred based on shifting of the peak to higher wavenumber. In conclusion, Cu-NPs were successfully produced by using the microwave method and be a function of time.

1. Introduction

Copper is one of the metallic nanoparticles that has the antifungal and antimicrobial activity which is proven against the bacteria such as *E. coli* and *Staphylococcus sp*. [1,2] Its availability is a better choice due to it having similar properties as other nobles' nanoparticles. Besides that, copper is highly reactive and can be easily oxidize at the atmospheric condition to form copper oxide (CuO) and copper (II) oxide (Cu_2O). The structural and thermal properties of the nanoparticle would be change if it is got oxidize. Therefore, to stabilize the nanoparticle it needs to be encapsulated by varies organic and inorganic agent. Thus, there are two basic techniques for preparation of Cu-NPs either with or without stabilizer which are physical and chemical methods [3]. Physical methods commonly used are pulsed laser ablation, vacuum vapor deposition, pulsed wire discharge and mechanical milling. As for chemical method, commonly used techniques were chemical reduction, microemulsion technique, sonochemical reduction, electrochemical, microwave assisted and hydrothermal [3].

Biopolymers such as polysaccharides that composed of multiple monosaccharide units that joined together by glycosidic linkages. Commonly cellulose, starch, heparin, chitosan, dextran, glucose etc. which are natural polysaccharides have been used as stabilizing agent. Nanoparticles that used polysaccharide as capping agent offers in energy efficient and a completely green process due to the absence of toxic solvent. The steric stabilization of the metal nanoparticle is to be happened due to the presence of a number of hydroxyl groups' complexes, the metal ion; via ion-dipole interaction. The separation of the nanoparticles from the reaction becomes easier due to weak chemical interaction between polysaccharide and nanoparticles thus making the process with energy efficient [4].

Pullulan is chosen to form copper nanoparticle as it is non-toxic, renewable and biocompatible. Polysaccharides such as pullulan gives several advantages for the replacement of synthetic polymers in plastic industries due to its low cost, non-toxic and its availability [5]. The conventional and common method to synthesis this nanoparticle is by chemical reduction techniques. This technique gives drawbacks due to its toxicity of reducing agent, unstable stabilizers within the strict and complex reaction conditions. Therefore, this research is to study and investigate the synthesis of polysaccharide mediated copper nanoparticles via microwave irradiation as a green synthesis method and the effect of time-varying exposure for polysaccharide mediated Cu-NPs as well as to analyse the characteristic of Cu-NPs produced by using UV-VIS, FTIR-ATR and XRD analysers.

2. **Method**

2.1. Materials

The copper sulphate pentahydrate salt ($CuSO_4.5H_20$), polysaccharide (pullulan) powder, sodium hydroxide (NaOH) and ascorbic acid were purchased from R&M Chemicals, Malaysia. All the materials used were dissolved and diluted using double distilled water. The material and chemicals used in this research were analytical grade and used directly without further purification.

2.2. Preparation of Copper Nanoparticles

The preparation of copper nanoparticles was performed by using previous methodology reported by Ismail and co-researcher with some modification [6]. For preparation of copper sulphate solution, 0.4g $CuSO_4.5H_20$ was dissolved in 10 ml of water (4 wt%) and stir homogenously for 10 minutes. The polysaccharide solution was prepared by dissolve 10 g of polysaccharide powder in 100 ml of water (10wt%) by heating at 90°C with stirring using 800 rpm. The prepared solution ($CuSO_4$) was mixed and stirred homogenously with polysaccharide in about 10 minutes copper sulphate solution without polysaccharide was used as control. After that, 10ml of sodium hydroxide (0.6 M) was added into the solution to make it basic at the pH:10 and stir for 10 minutes. Then, 10 ml of ascorbic acid (1 M) was added and make it homogenous for 10minutes.

2.3. The Effect of Polysaccharide Concentration

Five set of experiments were performed by varying the volume of polysaccharide added into the copper sulphate solution. Copper sulphate solution without polysaccharide was used as a control. In order to study the effect of polysaccharide, the volume of polysaccharide used was varied in the range of (0.05ml, 0.1ml, 0.2ml, 0.4ml, and 0.8ml). For this step, 0.05 ml of polysaccharide was mixed homogenously with copper sulphate solution and sodium hydroxide and ascorbic acid was added using mentioned methodology.

2.4. The Effect of Microwave Time Exposure
All of the six samples with different volume of polysaccharide solution were performed by varying the microwave time exposure. The time varying-exposure was performed within 2, 4, 6, 8 and 10 minutes with one bar of microwave power (167kV).

2.5. Characterization of Copper Nanoparticles
All the samples were characterized using UV-VIS using Shimadzu UV-2600 to confirm the formation of copper nanoparticles. The red brown solution produced was dropped into clean quartz cell (10 drop) at suitable concentration and was scanned in the wavelength range of 220 nm to 800 nm. The double distilled water was used as a blank sample. The crystallinity of copper nanoparticles was evaluated using X-ray diffraction (XRD) instrument (Empyrean, Malvern PANAlytical X'pert Pro, UK). Data were obtained in the 2Θ (°) range at the scan rate of 0.01 per min with long scan technique. All the points produced were plotted using Microsoft Office (Excel) software. The interaction and functional group of all samples were analysed using ATR-FTIR (IR-Tracer 100, Shimadzu, Japan). All the dried samples were scanned in ATR mode with a 16 scan, resolution 16 cm^{-1} and wavenumber ranging from 650 to 4000 cm^{-1}.

3. Result

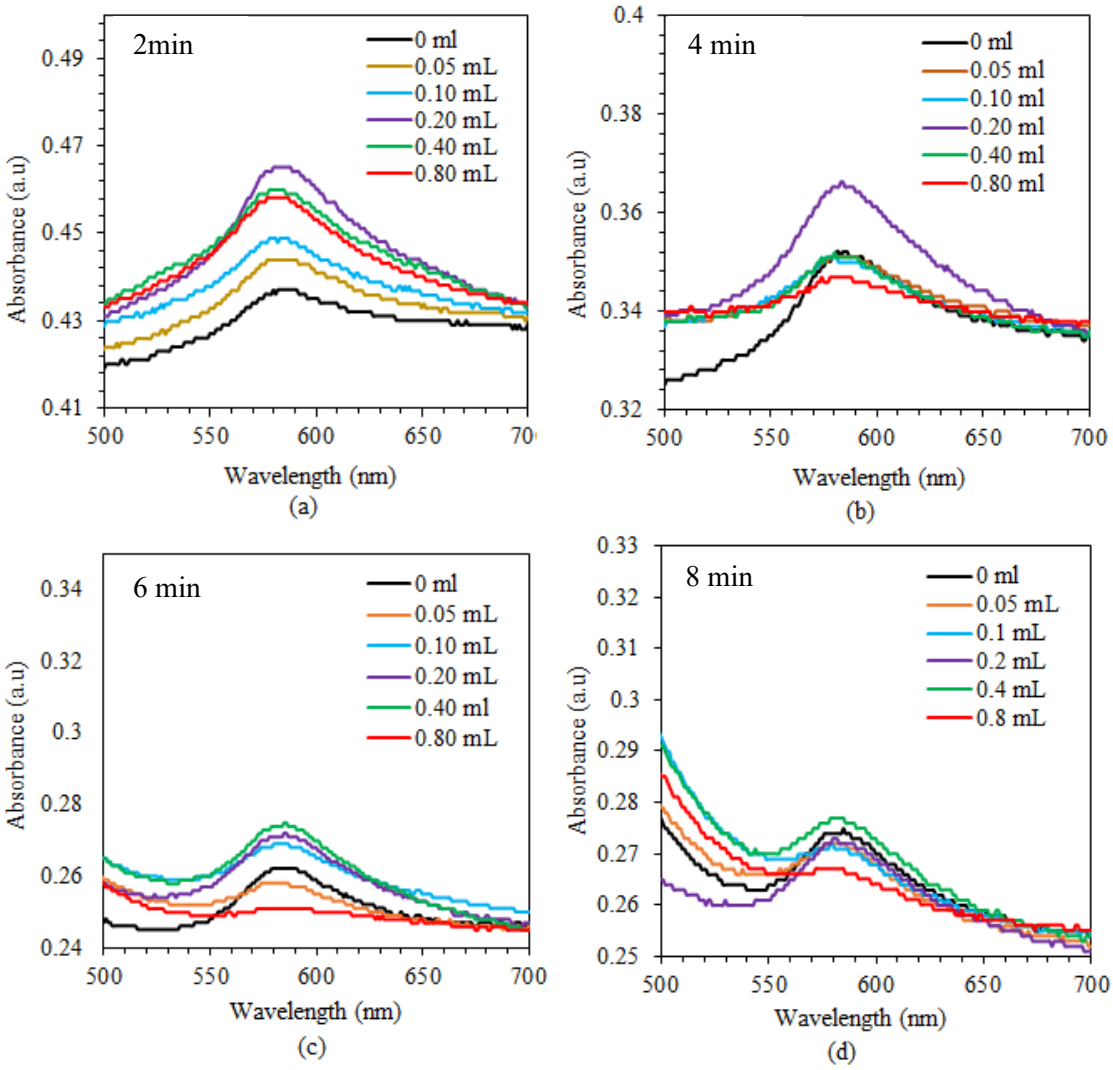
3.1. Characterization of Copper Nanoparticles

3.1.1. UV-VIS Analysis Cu-NPs. UV-VIS spectrum was used to confirm the formation of Copper nanoparticles by observing the peak at wavelength 580 nm [7]. In order to study the effect of time with amount of polysaccharide, different solution with polysaccharide (0.05ml, 0.1 ml, 0.2 ml, 0.4ml and 0.8 ml) were prepared. Figure 1(a-e) shows the absorbance peak for Cu-NPs with polysaccharide at different microwave irradiation dose started from 2, 4, 6, 8, and 10 minutes, respectively.

Based on the UV-Vis spectrum at 2 minutes of microwave time, the production of Cu-NPs increased from 0 ml until 0.2 ml of polysaccharide amount. After that, the lower number of Cu-NPs was produced at 0.4 ml and 0.8 ml of polysaccharide. It means that 0.2 ml was the optimum volume of Cu-NPs synthesized at 2 minutes of irradiation time exposure. At 4 minutes of irradiation time, the same trend was observed, and 0.2 ml of polysaccharide became the optimum value for Cu-NPs synthesis. By increasing the time exposure to 6 and 8 minutes, the new trend was observed where 0.4 ml volume of pullulan became the optimum condition suitable for Cu-NPs production. 0.8 ml volume of pullulan is not suitable for all condition which shows the broad and lowest peak of spectrum except at 2minutes irradiation time. At 10 minutes of microwave irradiation, sample with no pullulan and lowest volume of pullulan was produced highest absorbance peak. However, 10 minutes of microwave times was reduced the volume of total solution. Thus, it was concluded that 10 minutes of microwave time is not suitable for this experiment. As the conclusion, sample with 0.2 ml and 0.4 ml volume of pullulan was suggested suitable to be used for further step including for involvement with polymer for antibacterial plastic packaging.

3.1.2. XRD Analysis Cu-NPs. The crystalline nature of the stabilized copper nanoparticle can be expected from the XRD analysis graph pattern. Figure 4.2 shows the XRD patterns of non-stabilized Cu nanoparticles attributed to the sample prepared with and without using any stabilizing agent. Three reflection peaks can be seen at 2θ values of 43.69°, 50.81° and 74.42° represented (111), (200) and (220) crystallographic planes, respectively [8]. Sharp peak obtained due to the high nano-crystalline nature obtained from the copper. The analysis of XRD pattern confirms that synthesized copper nanoparticles have face cantered cubic (FCC) [9]. Based on XRD graph, the crystallinity intensity of Cu-NPs with polysaccharide were lower compared to Cu-NPs without polysaccharide. This is due to the existence of polysaccharide which is an amorphous compound. Thus, the presence of polysaccharide decreased the

crystallinity of the nanoparticle. However, the crystallinity of Cu-NPs still exists although with the presence of this polymer.



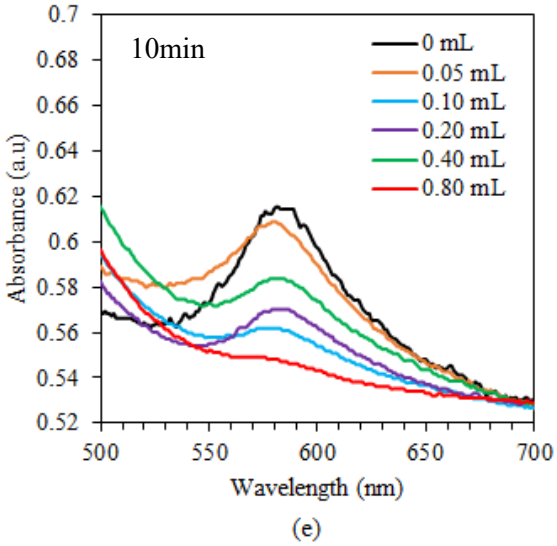


Figure 1. The UV-Vis Spectrum of Cu-NPs with different volume of polysaccharide (0.05, 0.1, 0.2, 0.4, 0.8 ml) at different irradiation time. a) 2 minutes, b) 4 minutes, c) 6minutes, d) 8 minutes, e) 10 minutes

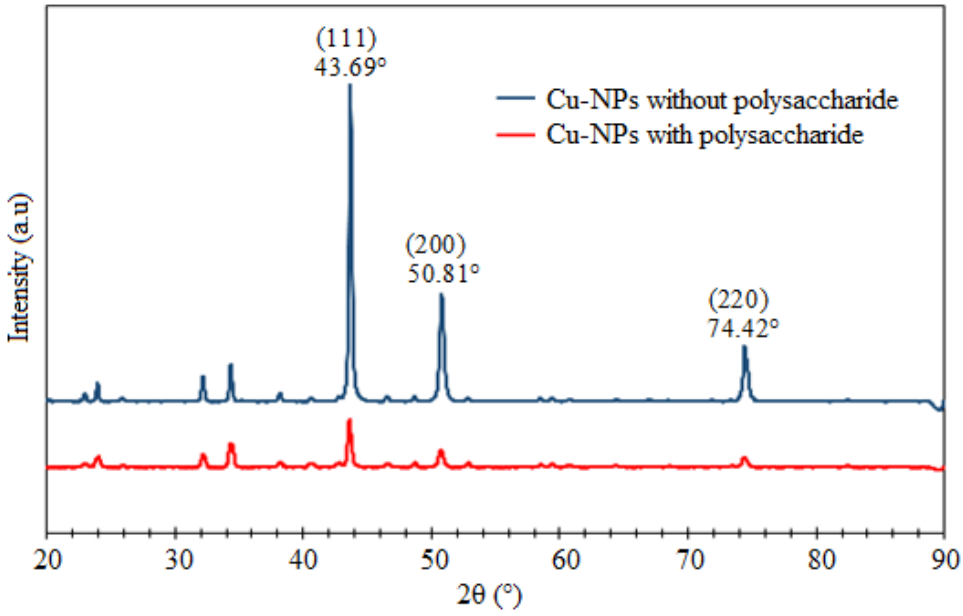


Figure 2. The X-ray diffraction pattern of Cu-NPs with and without polysaccharide

3.1.3. FTIR Analysis of Cu-NPs. Figure 3 shows the ATR-FTIR spectrum of pure polysaccharide as control, and Cu-NPs with and without polysaccharide. The characteristic peak of pure polysaccharide sample which not exposed to humidity exhibited a hydrogen bonding of O-H stretching at 3325 cm^{-1} and second peak at 2914 cm^{-1} is due to the sp^3 hybridization of C-H bond. One single peak of pullulan was appeared at 1637 cm^{-1} is supposed to be attributed to the vibration stretching of O-C-O functional group [10]. The sharp peak at 993 cm^{-1} was corresponding to glycosidic linkages in the pullulan. This founding was supported with previous literature where Mitic Zarco and co-researcher found that appearance band at 935 cm^{-1} refer to α-(1,4) glycosidic bond [11]. After irradiation process, polysaccharide mediated copper nanoparticles show the absorbance band was shifting to higher wavenumber. The same trend was observed in the previous paper reported by Afini and co-author where they produced Cu-NPs with honey as stabilizer [12]. The absorbance peaks at 1637 cm^{-1} (O-C-O) was

shifting to 1737 cm^{-1} was refer to Cu-NPs interaction with polymer bonding [10]. That peak without polysaccharide at around 1722 cm^{-1} is less intense compared to Cu-NPs with polysaccharide. As conclusion, an interaction was occurred between Cu-NPs and polysaccharide, thus indicated that polysaccharide polymer was successful in giving it function as stabilizer.

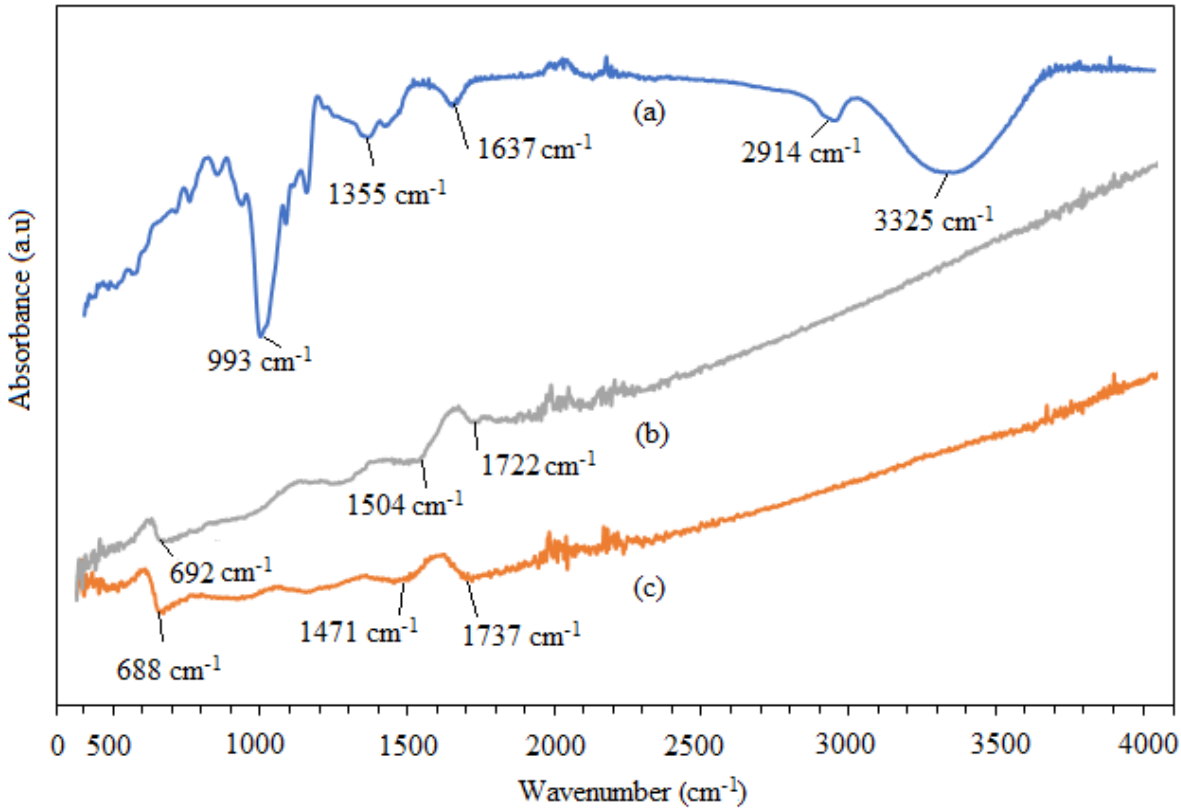


Figure 3. ATR-FTIR spectrum of (a) pure polysaccharide as control (b) Cu-NPs without polysaccharide (c) Cu-NPs with polysaccharide.

4. Conclusion

In conclusion, Cu-NPs was successfully produced via microwave irradiation method with polysaccharide was used as a stabilizer. The wavelength peak at 580 nm SPR band centred of UV-Vis shows the appearance of Cu-NPs and crystallographic planes of XRD at (111), (200) and (220), indicates that the presence of polysaccharide was maintained the crystallinity of Cu-NPs. FTIR provides evidence that Cu-NPs with and without pullulan was successfully produced using this methodology.

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Declaration of conflicting interest
All authors are declared there is no conflict of interest in this publication.

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