International Journal of Scientific Research in Science and Technology
Available online at : www.ijsrst.com
Print ISSN: 2395-6011 | Online ISSN: 2395-602X doi : https://doi.org/10.32628/IJSRST5231044

Effect of Heating Time Variation in Green Synthesis of Copper Nanoparticles with Sweet Orange Juice (*Citrus Sinensis*) Bioreductor using Microwave Assisted Method

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ARTICLEINFO

Article History:

Accepted: 20June 2023
Published: 10 July 2023

Publication Issue
Volume 10, Issue 4
July-August-2023

Page Number
44-50

ABSTRACT

Inexpensive and environmentally friendly synthesis of copper oxide nanoparticles (CuO NPs) was produced using microwave-assisted green synthesis method. In this method, microwave (ME731K Solo with Ceramic enamel, 20 L) was used. the effect of time was examined to produce CuO NPs. Nanoparticles were produced when micro waves (800 watts) irradiated a solution of CuSO4.5H2O mixed with sweet orange extract (Citrus Sinensis). The fabricated CuO nanoparticles of C. Sinensis were further characterized by UV-Visible spectroscopy (UV-Vis). Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Time variation has been used in the preparation of CuO NPs. UV-Vis test showed the formation of CuO NPs at the absorbance peak around 270-300 nm. Time variation affects the wavelength shift and the absorbance level is an indication of the concentration of the amount of nanoparticles produced. FTIR spectra identified functional biomolecules from the nanoparticles at a wavelength of 618 nm. X-ray diffraction (XRD) analysis revealed the crystalline structure of the copper nanoparticles at 36°.

Keywords : Copper Oxide Nanoparticles, Microwave-Assisted, Green Synthesis, Bioreductor Citrus Sinensis Extract

I. INTRODUCTION

According to the Encyclopedia of pharmaceutical Technology, nanoparticles are solid colloidal particles with sizes varying from 1 to 1000 nm (1 micron) [1]. Metal nanoparticles are receiving much attention due to their potential in biomedical and pharmaceutical fields [2]. Nanoparticles made from metal oxides are considered to have an increasing appeal as they possess unique optical and chemical properties due to their superior properties and ability to be applied in various fields, such as biomedicine, catalysts, and sensors, Fe, Ni, Cu, Ti, and Mg nanoparticles have attracted much attention in recent years [3]. Cuprum, often known as copper, is a yellow metal similar to gold that is abundant and inexpensive. Copper nanoparticles have potential as antibacterials due to their toxicity to microorganisms but low toxicity to humans [4].

Nanoparticle synthesis using natural strains and plant extracts contain phytochemicals that act as reducing agents. Green nanoparticle synthesis using plant extracts is believed to act as a reductant as well as a stabilizing agent and is environmentally friendly because it does not cause hazardous waste [5]. Several previous studies using green synthesis using citrus bioreductors have been carried out including research on microwave irradiation mechanisms that offer solutions to accelerate the synthesis process [6].
Microwave is a method that can help to achieve energy efficiency, contiguity, and economic value with a fast, efficient, energy-efficient, and relatively small cost synthesis process. microwave methods not only offer solutions in the industrial field but also solutions for materials research, especially metastable materials and understanding the interaction of solids with electromagnetic fields. [7].

Previous research synthesizing copper nanoparticles using the microwave assisted method has been carried out by Jahan, et al., 2020. but not only one sample with 5 minutes heating with 700 W power. so the aim of this study is the development of copper nanoparticles using orange peel bioreductors with variations in micro-wave heating time to determine its effect on the most optimum nanoparticle productivity.

The bioreductor mechanism of citrus extracts contains chemical compounds that are secondary metabolites such as essential oils, flavonoids, saponins, citronella and steroids. In citrus extracts with different types of varieties have the same chemical compound content but there are some different chemical compounds [8]. Flavonoids are secondary metabolite substances in citrus that have the highest concentration of [9] orange extract contains flavonoid compounds that have hydroxyl groups (-OH) can play a role in the ion reduction process Cu^{2+} into Cu nanoparticles. The nature of this compound that easily undergoes oxidation, namely the release or donor of electrons to inhibit antioxidant molecules into free radicals [10].

Mechanism of nanoparticle formation with microwaves. The difference between conventional heating and using a microwave is that conventional heating is done through conduction heating, so it takes time in heat propagation including passing through the container as a medium. Therefore, the heat coming from the source is reduced when it reaches the reacting material or the solvent. Microwave heating has the advantage of avoiding molecular decomposition, especially those close to the container, besides that heating is done quickly and also more specifically. This rapid heating makes the reaction homogeneous but also specific through dipolar molecular oscillations. Microwave irradiation is a fast and efficient method in the synthesis of a variety of compounds due to the selectivity of absorption of microwave energy on polar molecules [10].

There are two main principles in microwave, namely the dipolar mechanism and the electric conductor mechanism. The dipolar mechanism arises when at high frequencies in an electric field, polar molecules attempt to follow an aligned field. When this happens, the molecules release heat to drive the reaction. In the second mechanism, the irradiated sample is an electrical conductor and charge carriers (electrons, ions) move through the material under the influence of the electric field, resulting in polarization. The induction causes heat in the sample due to electrical rejection [11].

II. METHODS AND MATERIAL

2.1 Reagent Preparation

Figure 2.1 Precusor Copper (II) Sulfate Pentahydrate (CuSo45H$_2$O))

Once the materials were ready for use, equipment including beakers, measuring cups and knives were sterilized. Materials used included copper purchased from Sigma Aldrich in St. Louis, Missouri, USA. The materials were dissolved with 50 ml of ultra-pure deionized water from a water purification system (Purelab flex, Veolia Water Solutions and Technologies, Tienen, Belgium).

2.2 Citrus Extract Preparation

(a) (b)

Gambar. 2.2. Ekstrak jeruk yang (a) sebelum dan (b) setelah disentrifuge

Fresh fruits were cleaned with distilled water before slicing. Water was squeezed out and the supernatant was separated from the extract by centrifugation (using a Sigma 2-16 PK centrifuge) for 10 minutes at 5000 rpm. The light yellow-colored filtrate was collected and stored in a clean, dry container maintained at 4°C.

2.3 Synthesis of Copper Oxide Nanoparticles

Synthesis of copper nanoparticles A stock solution for copper nanoparticle biogenesis, 10 mM copper(II) sulfate pentahydrate (CuSO45H2O), was prepared using ultra-pure deionized water, and 50 mL of this saline solution was mixed with 100 mL of citrus extract (in a ratio of 1:2). This combination was then exposed to the bejana tertutup gelombang mikro kelas laboratory at 700 W with time variations of 5 minutes, 7 minutes, 9 minutes, 11 minutes, and 15 minutes. The colloid is blackish brown in color which indicates the formation of copper nanoparticles. The solution was alkalized to obtain powder.

Figure 2.3 comparison before (right) and after microwave (left)

2.4 Purification and Characterization of Copper Oxide Nanoparticles

After the synthesis was completed, the colloidal solution containing NPs was filtered to remove large waste particles using a centrifuge for 15 minutes at 5000 rpm. The remaining orange juice extract was then removed by discarding the supernatant and collecting the precipitate. This process was repeated several times using distilled water. To collect the NP powders and store them properly in dark vials for further analysis, the final CuNPs were placed into a laboratory grade dryer operating under vacuum. A Shimadzu UV-1700 UV-vis spectrophotometer was initially used to track the bioreduction of copper nanoparticles. Deionized ultra-pure H2O served as a blank for the spectra, which were acquired in the wavelength range of 200-800 nm. An FT/IR-6300 spectrometer (JASCO, Tokyo, Japan) was used to perform IR spectroscopic measurements in the 4000-500 cm-1 region. Spectra were obtained using the FTIR grade potassium bromide (KBr) pellet technique. The crystallinity of the phytosynthesized CuNPs was assessed using X-ray diffraction method. The XRD patterns were estimated at room temperature with a step size of 0.02 over the diffraction angle range (2) 10 to 90. The XRD graphs were regenerated using the Origin 8.5 program (Origin Lab Corporation, Northampton, MA, USA).

III. RESULTS AND DISCUSSION

3.1 Effect of microwave heating time variation on Color change of Sample

Cu has been successfully produced in various liquid media. Figure 2.4 displays the results of nanoparticle synthesis on microwave in order

(a) (b) (c) (d) (e)

Figure 2.4 Synthesis results for time variations (a) 5 minutes, (b) 7 minutes, (c) 9 minutes, (d) 11 minutes, and (e) 15 minutes.

Based on the difference in the wakna sampe synthesized with time variations, it shows that the longer the heating time the wakna is getting thicker from light green to brownish green. This indicates that the success of nanoparticle production increases with the length of heating. [12].

3.2 effect of microwave heating time variation on UV-visible light absorption

The formation of copper nanoparticles via the bioreduction reaction process was initially monitored using orange juice extract and UV-Vis spectroscopy. Indicating the synthesis of CuNPs from Copper(II) sulfate pentahydrate, a strong peak for biosynthesized CuNPs was seen at 560 nm (Fig. 2.5). The absorbance peak between 200 nm and 300 nm is noteworthy due to Surface Plasmon Resonance (SPR), and is used as a sign to confirm the preparation of metallic copper nanoparticles from copper oxide [13]

UV-Vis results on the variation of time produced that almost all variations have absorption peaks respectively at a time of 15 minutes produced a wavelength of 324 nm, at a time of 11 minutes a wavelength of 245 nm, a time of 9 minutes a wavelength of 326 nm, a time of 7 minutes a wavelength of 248 nm while at a time of 5 minutes no absorption peak was formed. So it can be said that the shorter the microwave time, the higher the wavelength peak is [14]

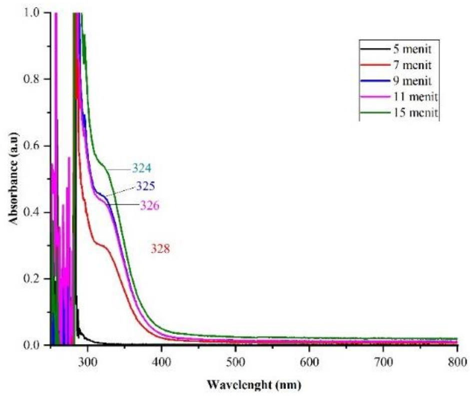


Figure 2.5 UV-vis absorbance spectrum of time-varying copper oxide nanoparticles

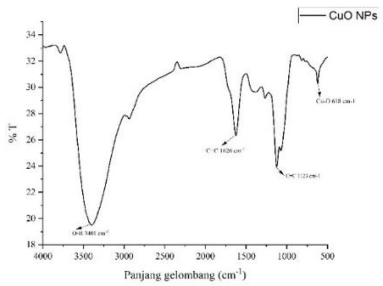
Table. 1 Data table of the effect of microwave heating time variation on wavelength

Minute	Wavelength (nm)
15	324
11	325

9	326
7	328
5	-

3.3 Effect of irradiation time variation on fourier transform infrared spectroscopy (FTIR) readings

FTIR analysis is used to identify biomolecules and their functional groups (Fig. 2.6). The FTIR spectrum of copper nanoparticles showed bands at 3401 cm-1; 1626 cm-1; 1123 cm-1; and 618 cm-1. The presence of O-H stretching is indicated by the absorption peak at 3401 cm-1. However, the band at 1626 cm-1 matches the significant C-C stretching in monosaturated alkyl chemistry. C=C stretching peaks at 1123 cm-1 absorption [6]. And the presence of Cu-o stretching at the absorption at 618 cm-1 [15]



Gbr. 2.6. Representasi grafis dari nanopartikel tembaga yang dibiosintesis dari Analisis spektrum inframerah

3.4 Analysis using X-ray diffraction (XRD)

Using extracts of several plants, X-ray diffraction investigations were conducted to reveal the presence of crystallinity in phytosynthesized copper nanoparticles. XRD of copper nanoparticles (Fig. 2.7).

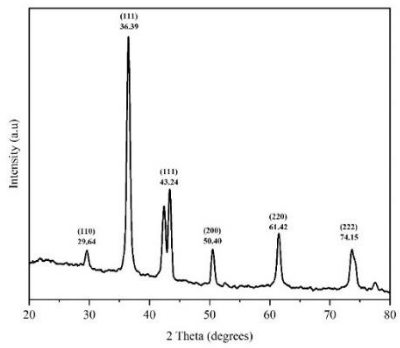


Figure 2.7 XRD pattern of phytosynthesized copper nanoparticles

Six important reflections were found at 29.64, 36.39, 43.24, 50.40, 61.42, 74.15 which are generally consistent with the standard spectra of Cu metal consistent with the (110), (111), (111), (200), (220), and (222) planes. JCPDS (Joint Committee on Powder Diffraction Standards) standard database file no: 04-0784 [16]. supports or coordinates these planes, which is a typical Bragg diffraction plan for copper with a surface-centered cubic crystal structure. The faint and broad reflection at 36 in the XRD profile, indicates the presence of cuprous oxide (Cu2O) = 29.6. This may be due to the very high sensitivity of metallic copper nanoparticles to oxygen and the tendency to oxidize easily.

IV. CONCLUSION

In this study, a fast, simple, inexpensive and environmentally friendly protocol has been established for the first time for the production of copper nanoparticles by using citrus extract (Citrus sinensis) as a reducing, stabilizing and capping agent. A microwave-mediated system with two optimized parameters (time and temperature) was used for easy and rapid phytosynthesis of copper NPs. Microwave heating provided high reaction kinetics in the reaction medium during the synthesis process which confirmed higher yields in less time. Moreover, the phytosynthesized monodisperse CuNPs showed excellent stability without any aggregation when monitored over a specific period of 9 months. The variation of microwave heating time also affects the color of the sample where the longer the time, the more intense it is due to the increase in nanoparticle production concentration, from the UV-Vis characteristics, it shows that it has the highest concentration of nanoparticles. SPR CuO band, then the best one sample was taken to be tested for FTIR and XRD. The results of FTIR readings formed biomolecules and functional groups at the Cu-O stretching peak at 618 cm-1 absorption peak.

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Cite this article as :

Inayah Mumpuni Budiati, Ali Khumaeni, Iis Nurhasanah, "Effect of Heating Time Variation in Green Synthesis of Copper Nanoparticles with Sweet Orange Juice (Citrus Sinensis) Bioreductor using Microwave Assisted Method", International Journal of Scientific Research in Science and Technology (IJSRST), Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 10 Issue 4, pp. 44-50, July-August 2023. Available at doi : https://doi.org/10.32628/IJSRST5231044
Journal URL : https://ijsrst.com/IJSRST5231044