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RESEARCH PAPER

# Effect of water-methanol binary solvent system in the green synthesis of copper nanoparticles with derived from tobacco leaf extract

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**Abstract:** The increasing demand for environmentally friendly nanoparticle synthesis, as a viable strategy for pollution control, has prompted an exploration of green chemistry methods. This study meticulously investigates the synthesis of copper nanoparticles utilizing tobacco leaf extract obtained through both cold and hot extraction techniques. The primary focus lies in scrutinizing the impact of various solvents employed for plant extracts and metal ion solutions on reduction dynamics and particle size. The study employs UV-Vis and phytochemical analyses to discern differences in chemical composition and efficacy, particularly between the water and methanol-water systems, despite their resemblance in UV-Vis spectra. Intriguingly, the results unveiled the choice of solvent significantly influenced the particle size distribution and colloidal stability of nanoparticles. The methanol-water system, in particular, yields smaller and more uniform particles compared to other solvent systems. This research sheds light on the pivotal role of solvent selection in nanoparticle synthesis, emphasizing its profound impact on both the reduction process and the resulting particle size distribution. The findings underscore the relationship between solvent choice and the characteristics of the synthesized nanoparticles, providing valuable insights for optimizing environmentally friendly synthesis methods. Ultimately, this study contributes to the growing body of knowledge on green chemistry approaches for nanoparticle synthesis with implications for pollution control and sustainable materials production.

**Keywords:** Copper Nanoparticles, Tobacco extract, Methanol-water system

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## INTRODUCTION

The synthesis of nanoparticles (NPs) with environmentally friendly methods is currently a demand as an effort to control pollution, especially those caused by chemicals. The investigation of the structural characteristics encompassing both the bulk and atomic levels of metal oxide nanoparticles is a focal point of interest. Large surface area, pore size, shape, and considerable reactivity are just a few of the distinctive physicochemical properties of NPs [1]. The unique physicochemical properties of nanoparticles, such as their large surface area, pore size, shape, and significant reactivity, may present challenges in terms of inflammatory and immune responses upon their introduction [2]. Food technology, energy technology, medical products (including various medications and drug delivery systems, diagnostics, and medical technology), information and communication (such as electrical and optoelectronic sectors) are the industries that have adopted nanotechnology at the fastest rate.

New issues could arise as a result of nanomaterial toxicity.

Plants are utilized to as a bio-based feedstock in "green synthesis" of metal nanoparticles due to its benefits in environmental and economic perspectives. [3]. The synthesis processes in this study adhere to the principles of green chemistry, specifically emphasizing the efficient and environmentally benign production of materials in accordance with the principles of waste prevention and atom economy. Plants, algae, bacteria, yeast, and fungi have been considered as sources for nanoparticle synthesis. Plant extracts such as *Catha edulis, Eucalyptus Globulus, Celastrus paniculatus,* and *Justicia schimperiana* leaves extracts were used as capping and reducing agents during the synthesis of copper oxide (CuO) NPs [4,5,6, 7]. The synthesis of CuO NPs from plant extracts has been demonstrated to be quick, easy, cost effective, and environmentally benign [8]. Copper nanoparticles can be made from plant extracts with inexpensive, biocompatible, and environmentally friendly reducing agents [9]. Ascorbic acid in *Morinda citrifolia* leaf extract enhances the formation of copper oxide nanoparticles [10]. Saponins, flavonoids, alkaloids, terpenoids, phenols, and tannins are among the secondary metabolites found in *Parthenium hysterophorus*. These metabolites have the ability to convert $Cu^{2+}$ into $Cu^{0}$ species [11, 12]. However, most of the research on green synthesis of nanoparticles took place in aqueous systems, so the effects of other competing ion has not been widely studied.

In this research, copper nanoparticles were synthesized from aqueous $CuSO_4$ solution reduced with tobacco leaf extract. Tobacco leaf extract was provided in two systems, namely the water system and the methanol system. The water system tobacco leaf extract consisted of only an aqueous $Cu^{2+}$ solution, while methanol system tobacco extract presented a water-methanol binary solvent system with aqeous $Cu^{2+}$ solution. An interesting point has been observed when contrasting differences seen in the particle size distribution in the two systems.

This study seeks to synthesize CuO nanoparticles utilizing a bio-based reducing agent, such as tobacco leaf extract, in contrast to conventional reducing agents like NaBH4, aiming to minimize environmental impact and promote sustainable nanoparticle synthesis practices. The novelty of this study lies in the comparative analysis of the particle size distribution obtained from two different systems, namely the aqueous and methanol systems of tobacco leaf extract. This investigation addresses a research gap in the existing literature, as most studies on green nanoparticle synthesis focus on aqueous systems, with limited exploration of the effects of other solvents on particle characteristics.

## MATERIALS AND METHODS

Dried tobacco leaves were obtained from a farm located in Central Lombok, West Nusa Tenggara Indonesia. Copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) and methanol (98%) were obtained from Merck Millipore. This research also involved instruments such as Fourier Transform-Infra Red (FTIR) (Parkin Elmer) to analyze the vibrations of functional groups present in tobacco leaf extract, UV-Vis Spectrophotometer (Thermo-Scientific) to analyse the color change of Cu-Nicotine complex. The particle size distribution of copper nanoparticles formed was monitored by Particle Size Analyser (Microtrac) and Electron Dispersive X-Ray.

*Extraction Process*

Extraction of tobacco leaves was carried out in two ways, namely cold and hot methods. Hot extraction was conducted by soaking 50 g of tobacco leaves into 300 mL of distilled water at 90 °C. This extraction was carried out until the volume of distilled water was reduced by half. After cooling, the mixture was filtered and then stored at room temperature. Cold extraction was carried out by macerating 50 g of dried tobacco leaf powder with 150 mL of methanol (98%) for 24 hours. The mixture was then filtered to obtain tobacco leaf extract in methanol. Both extracts were monitored by thin-layer chromatography and phytochemical tests.

Copper Nanoparticles Synthesis

Synthesis of copper nanoparticles was carried out by mixing 50 mL of 0.4 M $CuSO_4$ solution with 100 mL each of tobacco leaf extract water system and methanol system. The mixture was then incubated at $42^oC$ for 24 hours. Colour changes were observed every 2 hours using a UV-Vis Spectrophotometer. To obtain copper particles, the mixture was centrifuged and the precipitate was dried and calcined at $700^oC$

## RESULTS AND DISCUSSION

Phytochemical screening was performed as the initial confirmation of tobacco leaf extract with water and methanol solvents, with the findings detailed in Table 1. As anticipated, both extracts were tested for alkaloids using Mayer reagents; however, the results were negative for flavonoid and tannin tests. Conversely, tobacco leaf extracts with methanol solvents yielded positive results for flavonoids and tannins. This can be attributed to the methanol solvents' tendency to degrade plant cell walls, enabling better extraction of additional secondary metabolites compared to highly polar water solvents.

Table 1. Phytochemical screening test results (alkaloids, flavonoids and tannins) of tobacco leaf extract in water and methanol solvents.

| Tobacco leaf extract in | Phytochemical Screening | | |
|---|---|---|---|
| | Alkaloid | Flavonoid | Tannin |
| Water | + | - | - |
| Methanol | + | + | + |

Tobacco leaves contain a significant secondary metabolite in the form of nicotine, an alkaloid molecule with a specific molecular weight. Tobacco grown in Indonesia, particularly in Lombok, reportedly contains nicotine levels ranging from 3-4% (w/w) [13]. The presence of nicotine in tobacco leaf extract can be determined using phytochemical assays and an FT-IR analysis. Strong and broad absorption in the wavenumber ranged from 3100 to 3500 $cm^{-1}$ was correlated to the interaction between O-H and water molecules, whereas a sharp and narrow absorption at wavenumber 1641 $cm^{-1}$ is attributed to the vibration of the aromatic C=N bond from the pyridine ring in nicotine.

UV-Vis absorption spectroscopy was employed to investigate chemical dynamics and colour changes (Figure 1). The spectra of tobacco leaf extract in both water and methanol-water systems exhibit strong UV absorption (300-450 nm) but no significant absorption in the visible region (450-900 nm), indicating the absence of secondary metabolite compounds with strong conjugated systems, such as certain derivatives of flavonoids, anthocyanins, and chlorophyll. However, the primary constituents, nicotine and tannins, are expected to show maximum absorption in the UV region. The observed UV-Vis absorption band pattern reveals a racemic mixture of (*R*)-nicotine and (*S*)-nicotine in the tobacco leaf extract [14]. Upon combining $Cu^{2+}$ solution with the extract, a notable change occured. The absorption peak of $Cu^{2+}$ ions at 810 nm in aqueous media was abolished in both systems, suggesting reduction by nicotine molecules, which caused the precipitation of $Cu^{2+}$ ions [15].

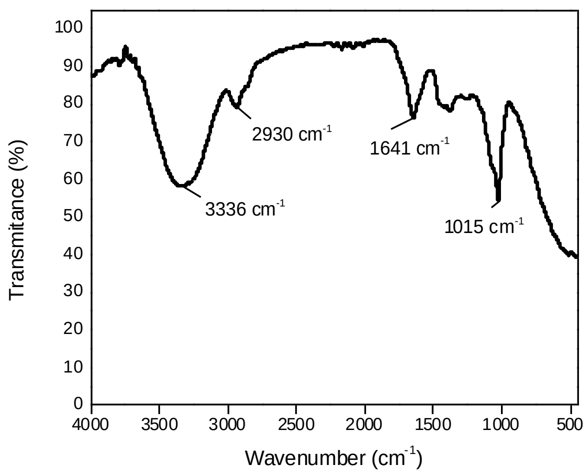


Figure 1. FT-IR Spectra of Tobacco extracts

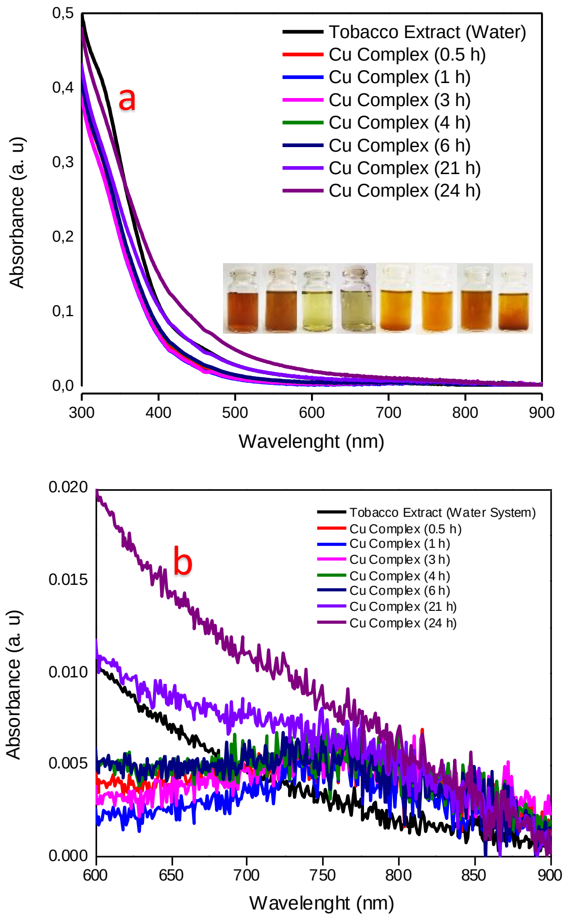


Figure 2. UV-Vis Spectra of Tobacco leaf extract and Copper Complex in the water system with a range of (a) 300-900 nm and (b) 600-900 nm

In the methanol system, a notable change is observed in the UV-Vis spectrum within the visible absorption region (600-900 nm), showing a gradual increase in absorption starting at reaction's initiation and stabilizing until the 24-hour mark, reaching a peak

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around 775 nm (Figure 3). This aligned with the visual observation of a consistent bright green color throughout the mixing process and the 24-hour incubation period. A distinctive finding emerges when $Cu^{2+}$ solution is introduced to tobacco leaf extract in a water system. Initially, a maximum absorption peak at 765 nm is detected, but after an incubation time of 6 hours to 24 hours, the absorption band in this visible area returns to its original following the absorption band of tobacco leaf extract before mixing and even begins to form deposits that can be observed (Figure 2). The emergence of an absorption peak around 700 nm suggests the formation of a Cu-Nicotine complex [16].

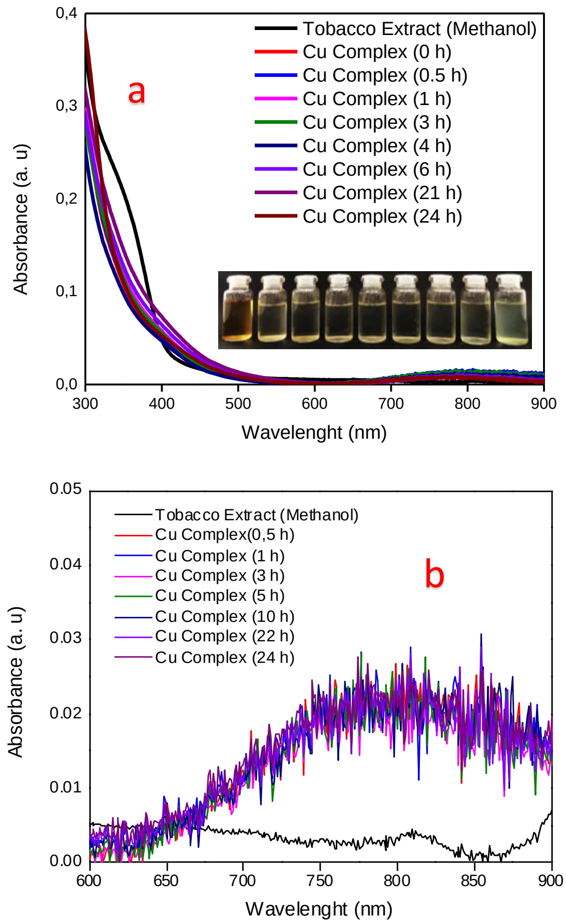


Figure 3. UV-Vis Spectra of Tobacco leaf extract and Copper Complex in the methanol-water system with a range of (a) 300-900 nm and (b) 600-900 nm

Several phenomena are observed in both solvent systems through UV-Vis spectroscopy absorption studies and color changes. Variations in the solvent systems, particularly the presence of $Cu^{2+}$ solution and tobacco leaf extract in both water and methanol-water system, play a significant role. The chemical composition differences in tobacco extracts between the two systems may occur based on phytochemical test results, but the UV-Vis spectra absorption indicates similar efficacy. Therefore, it can be assumed that nicotine is the dominant active species in the tobacco leaf extract.

In the water system, nicotine facilitates the reduction of hydrated $Cu^{2+}$ ions, leading to chelation with the resultant $Cu^{0}$ for an extended period, evident from the consistent light green color (lasting up to six hours). However, the presence of sulphate ions in this aqueous system promotes $Cu^{0}$ aggregation by disrupting the $Cu^{0}$-nicotine, chelate system, causing precipitation. The saline and acidic conditions protonate nicotine on one or both nitrogen atoms, impacting its metal complexing ability [17]. The scenario changes when species like methanol molecules are adequately present [18], stabilizing the $Cu^{0}$-nicotine chelate system, thereby preventing aggregation and sedimentation.

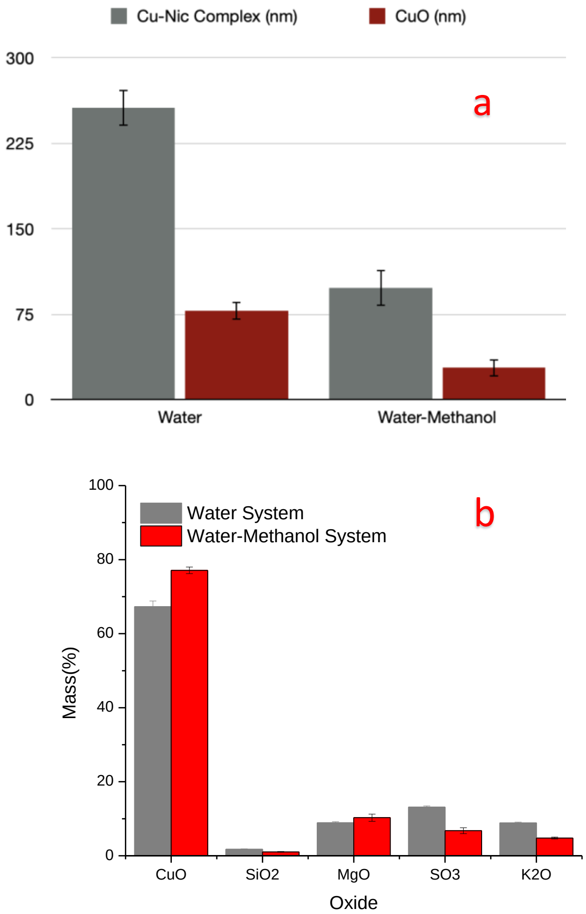


Figure 4. (a) Particle size distribution obtained using a Particle Size Analyzer (PSA) and (b) oxide composition analysis via Energy-Dispersive X-ray (EDX)

Particle size measurements were conducted on the CuO deposits and the colloidal system (Figure 4). The

CuO particle size chelated with nicotine in the methanol-water system was smaller, ranging from 88-102 nm, compared to that in the water system, where it ranged from 235-265 nm. In the methanol-water system, the generated CuO nanoparticles were 22-35 nm, while in the water system, they measured 75-89 nm. Elemental analysis using EDX confirmed these findings, revealing a CuO mass composition of 66.78% for the water system and 78.91% for the methanol-water system. Interestingly, Notably, the presence of $SO_3$ composite in the water system exceeded that in the water-methanol system, suggesting an unstable $Cu^0$-nicotine chelation system in the water system generated by sulphate ions.

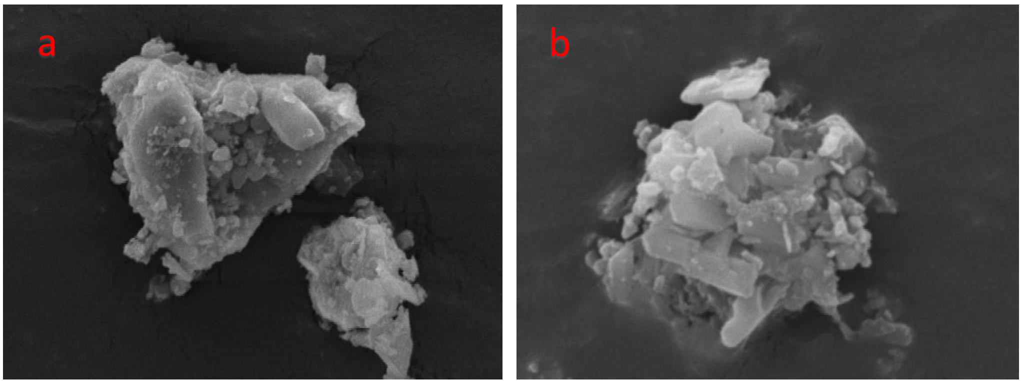


Figure 5. Morphology of copper particle nanoparticles at 10,000× (a) and 15,000× (b) magnification

Scanning Electron Microscopy (SEM) was utilized to characterize the morphology of copper nanoparticles. Image magnification was conducted at scales of 10,000× and 15,000× (Figure 5). The examination revealed a diverse range of shapes and sizes among the nanoparticles [19]. This variability in size is attributed to nanoparticle aggregation effects, leading to the presence of non-uniform particles [20].

## CONCLUSION

The use of different solvents between metal ion solutions and solvents for plant extracts found to affect the dynamics of the reduction process and the particle size. The use of methanol to extract tobacco leaves has an effect on the stability of colloidal nanoparticles formed by suppressing the ionic strength in the bulk phase thus prevented NPs aggregation. It was also found to yield on smaller and uniform NPs compared to the single solvent system using water.

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