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A NOVEL SYNTHESIS PATHWAY FOR SILVER NANOPARTICLES USING *ANTHURIUM BIPINNATIFIDUM*

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Abstract

The field of nanomaterial synthesis has grown substantially in recent years. However, many existing synthesis methods have significant drawbacks, such as the use of organic solvents that are harmful to the environment and the high cost of inorganic reducing agents. To address these issues, we developed a simple and cost-effective method for synthesizing silver nanoparticles (AgNPs) using Anthurium bipinnatifidum extract as a reducing agent and water as a green solvent. This green chemistry approach offers a quick and straightforward synthesis process, with the optimum incubation time and volume were 1 hour and 0.5 mL, respectively. The results of this new method show promising characteristics, as demonstrated by SEM, UV-Vis spectrophotometry, and FTIR analyses. Additionally, the surface plasmon resonance (SPR) of the synthesized AgNPs was observed at 431 nm, which aligns with the typical SPR for AgNPs. The particles formed were spherical, with sizes ranging from approximately 40 to 80 nm. This research establishes an efficient new procedure for AgNPs synthesis with excellent outcomes.

Keywords: *Anthurium bipinnatifidum; silver nanoparticle; green synthesis; AgNPs; SPR.*

Introduction

Particles with sizes from 1 to 100 nm are well known as nanoparticles, with nanoscales in all dimensions, including its length and diameter. Their small size presents unique properties; for instance, different shapes could resulted in different color, for example gold could exhibit red color at ~ 500 nm with a sphere shape and when the structure is rod shape the size is ~700 nm with purple color. (Gao et al., 2022; Ratri et al., 2023)The desired size and shape could be achieved with specific synthesis steps. The synthesis of nanoparticles is divided into two big groups: bottom-up and top-down. Bottom-up is an approach that builds nanoparticles from the atom into nano size. On the other hand, the top-down approach is by reducing the object's size from a big size to a nano size. (Abid et al., 2022)The bottom-up method has recently become preferable since it is convenient to modify and utilize. However, the bottom-up method has several limitations; for instance, the complex chemistry routes, (Escudero et al., 2021) require an inorganic reducing agent, (Szczyglewska et al., 2023) and an organic solvent. (Ganguly et al., 2019) Therefore, a safer and simpler method for nanomaterial synthesis is vital.

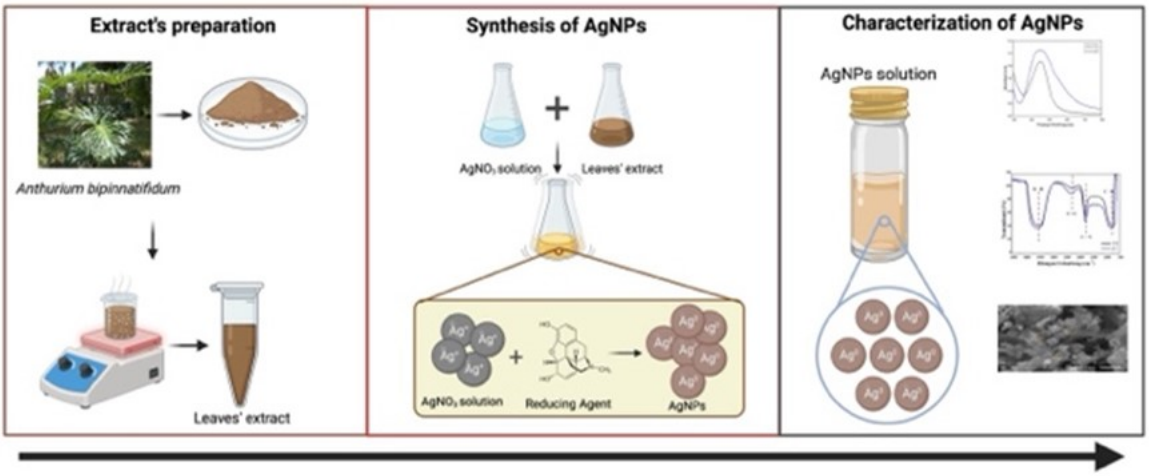

Figure 1. The process of silver nanoparticle synthesis (a) extract preparation, (b) synthesis of AgNPs, and (c) characterization of synthesized AgNPs.

In addition, nanoparticles have been exploited for many fields due to their unique properties, such as their tiny size, shape, and composition. In recent years, nanoparticles, for instance metal nanoparticles such as silver nanoparticles (AgNPs), have been developed in medical applications due to their excellent properties including antibacterial, anti-inflammation, cancer therapy, and cosmetic materials. (Dawadi et al., 2021; Yaqoob et al., 2020)Moreover, the ease of modifying their shape and size has exploited these materials in industries such as food and electronics. (Burlec et al., 2023).

To overcome the shortcomings of the common bottom-up method, a simple and safer synthesis route with essential reducing agents from natural products and a green chemistry approach has the potential to be developed. Green chemistry is a concept that leads to achieving environmental sustainability. (Mukherjee, 2021) This concept is related to reducing the use of organic solvents and producing a safer material for the environment. In terms of nanomaterial synthesis that needs a material as a reducing agent, a bio-reducing agent is a choice for the safer chemical for nanoparticle synthesis. (D Meer et al., 2022).

As a tropical country, Indonesia has various natural products such as flowers, plants, herbs, oil, and leaves that are significantly applied in various industries. (Putra et al., 2023) Furthermore, some plants and flowers have fantastic prices in the market when it's become trendy. However, as time passed, the popularity of some flowers and plants dropped and needed to be addressed. For example, *anthurium* were expensive, up to 50 million USD at that time, but in recent years, they are barely noticeable. (da Silva et al., 2015) *Anthurium bipinnatifidum* is one of the *anthurium* species that is easy to get in Indonesia and has phenolic compounds, such as flavonoid, tannin, steroid, saponin, alkaloid, and terpenoid. (Sariwati et al., 2019) Those phenolic compound is a bioactive compound that can be used as a reducing agent, antioxidant, anticancer, and antiviral. (Mutha et al., 2021).

In this work, we developed a novel synthesis method for AgNPs based on green chemistry, using water instead of organic solvents and *Anthurium bipinnatifidum* extract as a reducing agent. This synthesis pathway offers a safer method for AgNP production. Moreover, the simplicity of the pathway helps reduce synthesis time. This method was simple and effective. Based on FTIR, UV-Vis spectrophotometry, and SEM analysis, it produced high-quality AgNPs. The particle sizes ranged from approximately 40 to 80 nm, with a uniform spherical structure according to the SEM data. Thus, this approach can be a potential alternate to overcome the limitations of common bottom-up method.

Method

Materials

All chemical reagents were used without further purification. *Anthurium bipinnatifidum* was harvested from Sanata Dharma University's garden, Indonesia and $AgNO_3$ purchased from Merck (Germany). All other chemical and organic solvent used were reagent grade or better.

Procedures

The $AgNO_3$ synthesis method shown in the Figure 1.

Preparation of *Anthurium bipinnatifidum* extract.

Two grams of *Anthurium bipinnatifidum* powder were added into 40 mL of distilled water. Then, the solution was heated to 50 – 60 ^oC for 15 minutes on the magnetic stirrer hotplate. (Jain & Mehata, 2017) Whatman No. 1 paper was used to filter the solution and the filtrate were obtained. The extract was then stored at room temperature or in the refrigerator at 4 ^oC before used.

Characterization of *Anthurium bipinnatifidum* extract.

To evaluate its phenolic compound, the extract was characterized by using a UV-Vis spectrophotometer (Shimadzu UV-1800) with the range of scanning spectra set to 300 to 700 nm. The functional group in the extract was observed with Fourier transform infrared spectroscopy (FTIR) (Shimadzu IR-Spirit), with scanning spectra starting from 500 to 4000 cm^{-1}. The expected functional group are related to the phenolic compound.

Method optimization.

(a) The optimization of incubation time:

The volume of 0.002 M $AgNO_3$ used for obtaining the incubation time was 5 mL of $AgNO_3$ and reacted with 1 mL of *Anthurium bipinnatifidum* extract. The incubation time variations were 0, 1, 2, 3, 4 and 5 hours.

(b) The optimum volume of extract for AgNPs synthesis:

The volume of *Anthurium bipinnatifidum* extract were set to 0.25, 0.50, 0.75, and 1 mL. The volume of 0.002 M $AgNO_3$ that has been used for the synthesis was 5 mL, and the incubation time used was 1 hour. The color change was observed to confirm the formation of AgNPs, at the beginning the color of the solution was clear (no color) and change into dark brown. The analysis then followed by the UV-Vis spectrophotometer analysis (Shimadzu UV-1800) to confirm the formed AgNPs from the observed SPR.

Synthesis of AgNPs.

An *Anthurium bipinnatifidum* extract was added into 5 mL of 0.002 M $AgNO_3$ and shake until it mixed completely. Leave the solution for 1 hour. The formation of AgNPs was confirmed by the solution's color change, followed by serial characterization such as UV-Vis spectrophotometer analysis, FTIR and SEM analysis.

Nanoparticle characterization.

The AgNPs were then characterized using a spectrophotometer UV-Vis (Shimadzu UV-1800) to confirm the maximum wavelength that presents the SPR of AgNPs. The scanning area was ranged from 300 to 700 nm. The functional group of the AgNPs was obtained using FTIR (Shimadzu IR-Spirit), with a scanning area between 500 and 4000 cm^{-1}. The morphology of synthesized AgNPs was examined using a Scanning Electron Microscope (JSM—7100F, Jeol). The sample for SEM analysis was prepared on top of a silicon wafer by dropping 0.4 μl onto it and allowing it to dry before further use.

Results and Discussion

Preparation of and characterization of *Anthurium bipinnatifidum* extract

Initially, *Anthurium bipinnatifidum*s were dried using an oven at 60 ^oC for 24 hours, then ground into powder. The boiling method was used to obtain the extract of *Anthurium bipinnatifidum*. The temperature was set at 60°C for 15 minutes, with a ratio of 2:40 (w/v) for *Anthurium bipinnatifidum* to DI water.(Jain & Mehata, 2017) This extraction

Figure 2. The extraction process of Anthurium bipinnatifidum (a) Anthurium bipinnatifidum (b) The Anthurium bipinnatifidum before drying process (c) The Anthurium bipinnatifidum after drying process (d) The grinded Anthurium bipinnatifidum (e) Anthurium bipinna

method was chosen because it yielded more extract than the others. In particular, the extraction process used medium temperature and short boiling time to avoid the damage of the extract. (Wijaya et al., 2018) The entire preparation before the extraction processes is shown in Figures 2a-d. Meanwhile, Figure 2e shows the *Anthurium bipinnatifidum* after it was extracted. Here, the extract has a pale-yellow color. Thus, the *Anthurium bipinnatifidum* extract was ready being used for further experiments.

Table 1. Comparison of the Functional Groups of Flavonoid Compounds with the Functional Groups in Anthurium bipinnatifidum Extract (Coates, 2006)

Functional group	Frequency (cm^{-1})	Result (cm^{-1})
O-H	3600-3200	3.354-3.327
C=C	2500-2100	2300-2100
C=O	1680-1630	1630-1680
C-H	1420-1410	1420
C-C	1350-1000	1300
C-O	1200-1050	1080

The extract of *Anthurium bipinnatifidum* was characterized using FTIR. This analysis aimed to identify the functional groups in the specimen. Spectral data shown in Figure 3 presents the functional groups which are listed in Table 1. The alcohol, phenol, alkane, aromatic compounds, and other functional groups were found in the extract sample.

Table 1 provides information about the functional groups in the *Anthurium bipinnatifidum's* extract. The O-H group was detected in the range of 3354-3327 cm^{-1}, indicating the presence of alcohol and phenol bonds. Additionally, in the 2300-2100 cm^{-1} range, a C=C group was observed, suggesting the existence of an alkyne bond. Furthermore, an aromatic C=O bond was identified in the absorption range of 1630-1680 cm^{-1}. Moreover, C-H, C-C, and C-O groups were detected in each of the absorption areas at 1420 cm^{-1}, 1300 cm^{-1}, and 1080 cm^{-1}. These results indicated that the *Anthurium bipinnatifidum* extract contains flavonoids and other phenolic compounds, which could be used as reducing agents in AgNPs synthesis.

Method optimization

Incubation time

In this synthesis, two kinds of materials were used; the first one was 5 mL of $AgNO_3$ 0.0002 M which was used as a precursor, and 1 mL of *Anthurium bipinnatifidum* extract which was used as the reducing

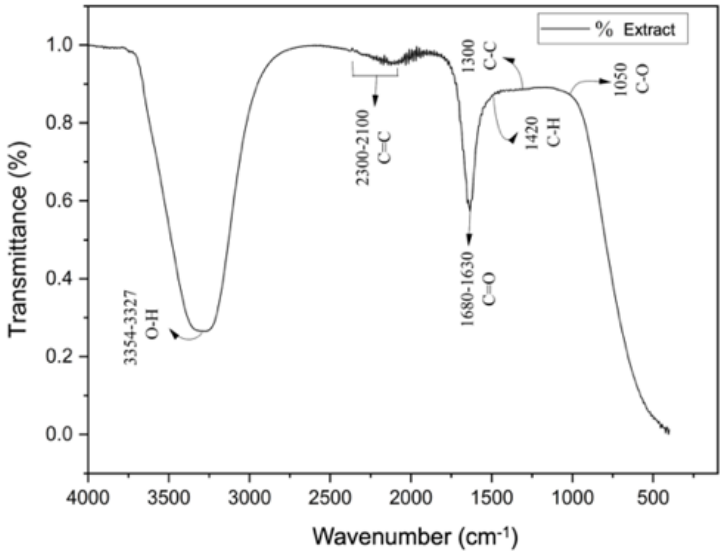

Figure 3. FTIR spectra of Anthurium bipinnatifidum extract

agent. The incubation time was varied from 0 to 5 hours to obtain the optimum synthesis condition. After adding the *Anthurium bipinnatifidum* extract to $AgNO_3$, a change in solution was observed. Initially, the color of the mixed solution was clear yellow; then, after stirring for 1 hour, the color changed and became darker. The color continuously became darker and finally it became darker brown after 5 hours (Figure 4a). This change in color was caused by the silver ion reduction process and led to AgNPs formation.(Xiong et al., 2021)

The optimum condition for incubation was 1 hour based on the UV-Vis spectrophotometer data (Figure 4b). Figure 4b presents the maximum wavelength of synthesized AgNPs (431 nm) which was the SPR wavelength of AgNPs. These data confirmed that AgNPs were produced. The reduction pathway in the synthesis reaction for AgNPs is illustrated in Figure 4c describes the presence of phenolic group, Ag^+ and it was reduced to Ag^0.

***Anthurium bipinnatifidum* extract's volume**

The optimum volume of *Anthurium bipinnatifidum* extract as the reducing agent was determined to obtain the best synthesis condition. The synthesis optimization was conducted by varying the volumes of extract, i.e. 0.25, 0.50, 0.75, and 1 mL, along with 5 mL of 0.002 M $AgNO_3$ and an incubation time was set to 1 hour. The synthesis results are shown in Figure 4d. Initially, the solution was yellow clear in color; however, after 1 hour, it turned dark brown. The volume of extract affected the AgNPs synthesis, as evidenced by the color change and the UV-Vis spectrophotometer data based on its SPR wavelength. Increasing the extract volume resulted in a darker color of the AgNPs solution. Figure 4e shows that 0.5 mL of extracted sample yielded into a sharper spectra; that means better size variation. Furthermore, 431 nm was the SPR wavelength of AgNPs**.** Therefore, for the AgNPs synthesis, the volume required of *Anthurium bipinnatifidum* extract is 0.5 mL.

Synthesis of AgNPs.

After optimization, the optimum condition of the AgNPs synthesis were achieved with an incubation time of 1 hour and extract volume of 0.5 mL. Once the dark color of the AgNPs solution had formed, it was tested using a UV-Vis spectrophotometer to ensure the maximum wavelength. This was followed by FTIR analysis to check for shifts in functional groups. Finally, SEM analysis was performed to examine the particle shape and size.

Based on Figure 5a, the maximum wavelength is 431 nm which indicates the wavelength of AgNPs.(Fahmi et al., 2024) FTIR data which shows in Figure 5b

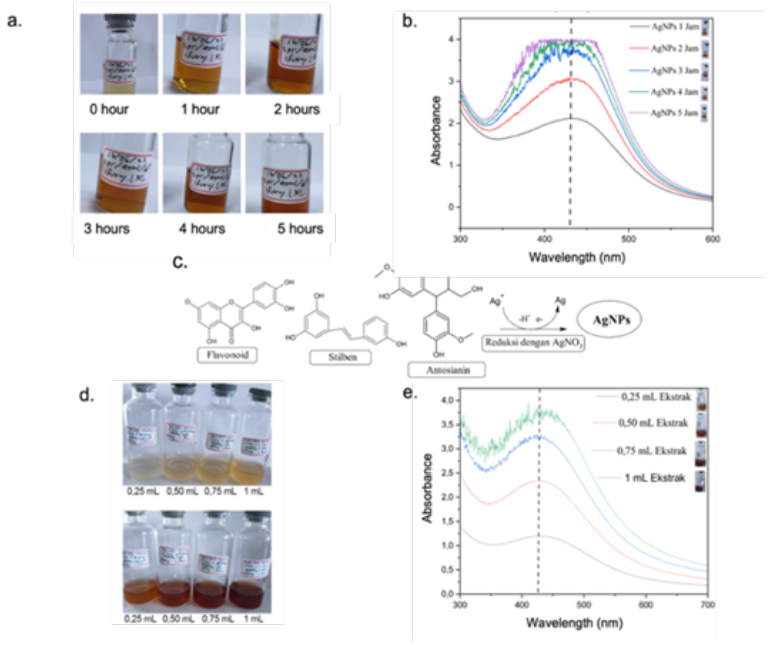

Figure 4. The optimization results for time and extract volume are as follows: (a) The AgNPs solution after time optimization (b) The UV-Vis spectrophotometer data for time optimization. (c) Reduction reaction in the synthesis of AgNPs. (d) The AgNPs solution wi

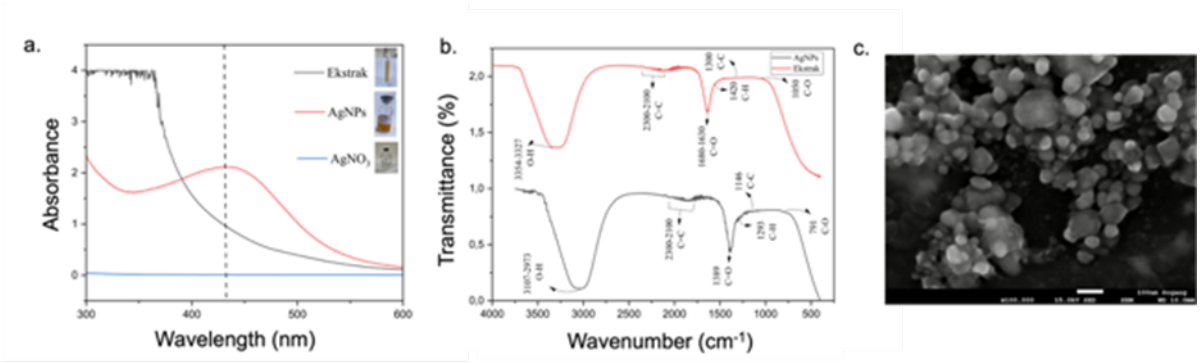

Figure 5. The AgNPs characterization. (a) UV-Vis spectrophotometer data for a comparison between extract, AgNO3 and AgNPs. (b) FTIR spectrum for both extract and AgNPs. (c) SEM analysis of AgNPs.

represent the shifting of wavenumber of several functional group, the O-H group was detected in the 3354-3327 cm^{-1} region, characteristic of flavonoids, tannins, saponins, and polyphenols. Meanwhile, in AgNPs, there was a shift in the 3107-2973 cm^{-1} region. Additionally, the C=C functional group in the extract was observed at 2300-2100 cm^{-1}, however, in AgNPs, it shifted to 2051-1782 cm^{-1}. The C=O functional group, also characteristic of phenolic compounds, was located in the absorption region of 1680-1630 cm^{-1}. The C-H, C-C, and C-O functional groups also exhibited significant shifts in their absorption regions. In the extract, these functional groups had absorption peaks at 1420, 1300, and 1080 cm^{-1}, while in AgNPs, the absorption peaks were observed at 1293, 1146, and 791 cm^{-1}. (Taba et al., 2019) The morphology data from SEM analysis shows that the size exhibits a somewhat broad variation, ranging from approximately 40 to approximately 80 nm (Figure 5c). The shape and size demonstrate the characteristics of nanoparticles, with sizes ranging between 1 and 100 nm.

Conclusion

In conclusion, *Anthurium bipinnatifidum* is an effective compound as

reducing agent in the synthesis of AgNPs. Color changes occur when $AgNO_3$ reacts with extract, indicated by a maximum wavelength of 431 nm. In addition, 1 hour of aging process of AgNPs resulted in best condition of the AgNPs characteristics, with a extract volume was 0.5 mL. As a result, we expect those condition could be a candidate to resolve current synthesis method with easy steps based on green chemistry approach. According to the results, this synthesis pathway can be used for the synthesis of AgNPs with safer materials and a faster synthesis time.

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