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Biosynthesis of silver nanoparticles using *Melicope Ptelefolia* leaf extract and its catalytic activity for 4-nitrophenol reduction

Norfazreen Saffee and Mustaffa Shamsuddin

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
Corresponding Author: mustaffa@kimia.fs.utm.my

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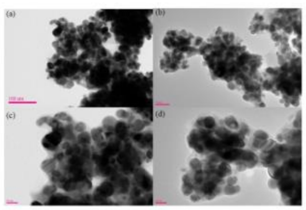
GRAPHICAL ABSTRACT



TEM images of silver nanoparticles low magnification (a and b) and high magnification (c and d)

ABSTRACT

Biosynthetic approach for the preparation of silver nanoparticles (AgNPs) using the aqueous leaf extract of *Meliocope ptelefolia* (tenggek burung). The reduction of Ag^{+} ions into elemental Ag nanoparticles was monitored using ultraviolet-visible (UV-Vis) spectroscopy. Characterization of Ag nanoparticles was using FTIR to detect biomolecules present, XRD to detect its crystalline nature, FESEM to determine its shape and TEM will determine its size. Furthermore, the biosynthesized AgNPs show good catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol in presence of excess hydrazine.

Keywords :*Melicope ptelefolia, UV-Vis spectroscopy, FTIR, XRD, FESEM.*

1. INTRODUCTION

Plant extract is the most effective method for biosynthesis of silver nanoparticles compared to physical and chemical synthesis. This is due to it abundant availability and easy to handle without culturing and maintenance process. Thus, plant extracts are getting much more attention as bio-reducing agent due to its simple procedure in the preparation of extract.

This study involved the synthesis of silver nanoparticles using aqueous leaf extract of *Melicope ptelefolia*. The formation of the silver nanoparticles will be monitored by UV-Vis spectroscopy at wavelength 400-450 nm according to Mata *et al*. (2015). The green synthesised silver nanoparticles will be characterized by SEM-EDAX, TEM, XRD and FTIR spectroscopy. SEM will analyze the surface morphology of *Melicope ptelefolia* silver nanoparticles and EDAX data will provide its elemental composition. TEM will analyze the surface structure and dimension of the silver nanoparticles. XRD analysis will evaluate the crystalline nature of the AgNPs meanwhile FTIR spectroscopy will provide information on the presence of bioactive or functional groups on the surface of the AgNPs. The catalytic activity of silver nanoparticles will be determined in the reduction of 4-nitrophenol to 4-aminophenol and will be monitored by using UV-Vis spectroscopy.

2. EXPERIMENTAL

Fresh *Melicope ptelefolia* leaf extract were collected, washed thoroughly with deionised water and dried at room temperature. The dried were powdered using a mixer grinder. 2 g of *Melicope ptelefolia* was mixed with 200 mL of deionised water in a round bottom flask and followed by Soxhlet extraction for 8 hours. Then, the leaf extract was heated, boiling and dried. The powdered solid obtained was kept in a vacuum dessicator for further use. In order to prepare 10 percent of leaf extract solution, 10 mg of the leaf extract powder was dissolved in 100 mL deionised water in a volumetric flask. 6 mL of the *Melicope ptelefolia* leaf extract solution was added to a 10 mL of silver nitrate ($AgNO_3$) (1 mM) solution. The mixture was allowed to stand at room temperature for 1 hour after which the color of the solution had changed from pale yellow to yellowish brown indicating the formation of silver nanoparticles.

The catalytic activity of *Melicope ptelefolia* silver nanoparticles was analyzed by using 4-nitrophenol (4-NP) in the presence of N_2H_4. 2 mL of 4-NP (0.01 x 10^{-3} M) was mixed with a freshly prepared aqueous solution of 2 mL of hydrazine hydrate (0.03 x 10^{-3} M) under continuous stirring at room temperature. Then, 0.7 mg of the silver nanoparticles powder was added into the above reaction mixture. The UV-Vis absorption spectrum of the reaction mixture was recorded with time to monitor the change in absorption intensity of the reaction mixture in the scanning range of 200-500 nm.

3. RESULTS AND DISCUSSION

In this research, silver nanoparticles have been successfully synthesized via green synthesis approach utilising aqueous leaf extract of *Melicope ptelefolia*. The formation of the AgNPs via the bioreduction of Ag^+ ions into Ag was easily monitored by UV-vis spectroscopy. The formation of the nanoparticles was visually confirmed by the colour changes from pale yellow to yellowish brown. In the UV-visible spectrum, the surface plasmon resonance (SPR) band for AgNPs appeared at 445 nm as shown in figure 1. Then, the complete reduction of $AgNO_3$ to AgNPs was being monitored in 24 hours of time as shown in Figure 2. FESEM micrographs in figure 3 showed that Ag nanoparticles exhibit spherical shape with high degree of agglomeration. EDAX analyses confirm the presence of Ag metals by the appearance of strong signal of this metal at 2 keV as shown in Figure 4.

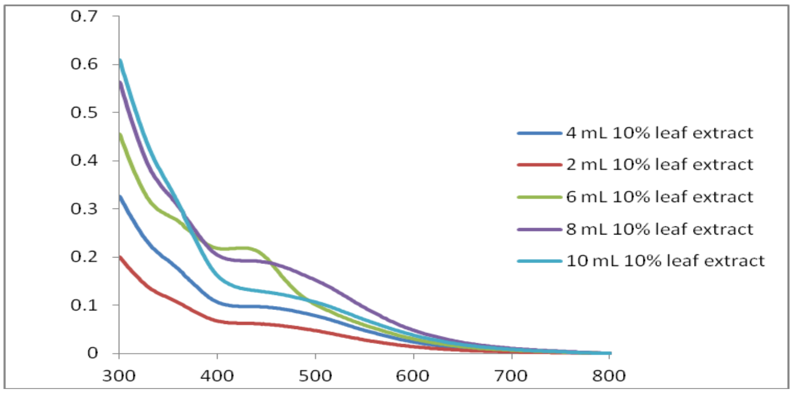


Figure 1 UV-Vis absorption spectra of synthesized silver nanoparticles using *Melicope ptelefolia* leaf extract after 60 minutes

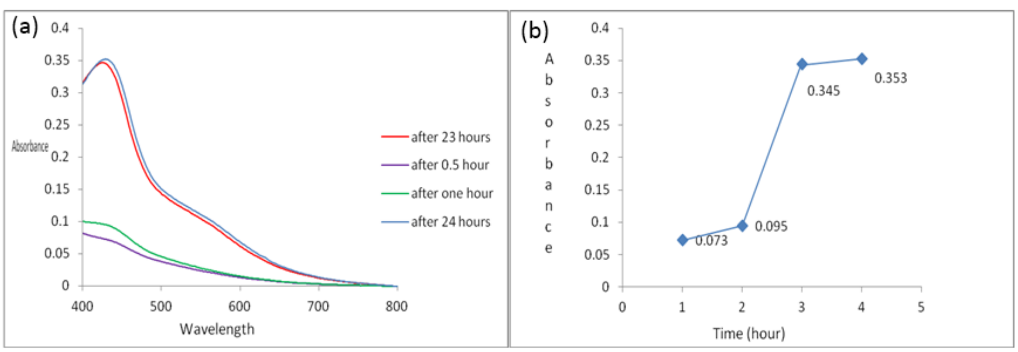


Figure 2 (a) UV-Vis absorption spectrum of synthesized silver nanoparticles using 6 mL of *Melicope ptelefolia* leaf extract and (b) Complete reduction of Ag^+ to Ag^0, optimization by time

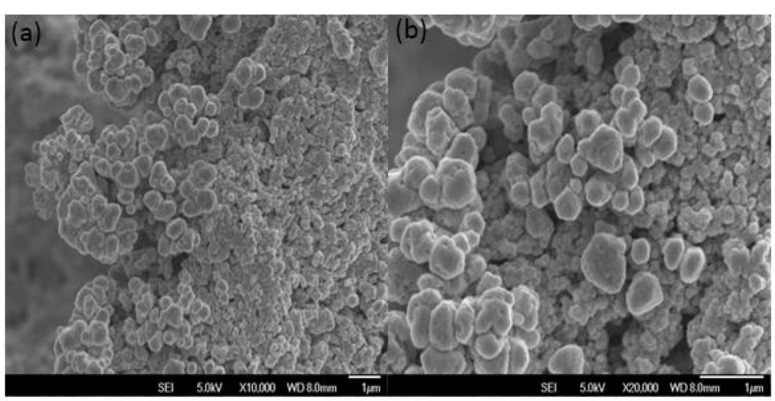


Figure 3 FESEM micrographs of silver nanoparticles of (a) 10,000X magnification and (b) 20,000X magnification

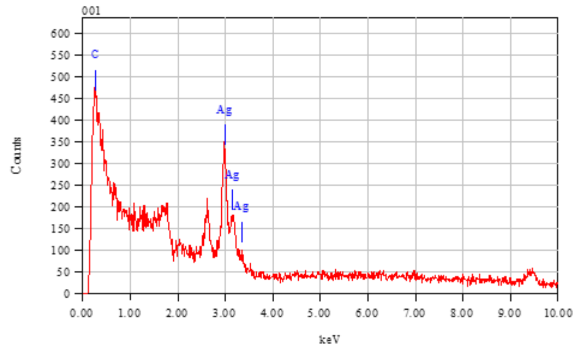


Figure 4 The spot-profile EDX spectrum of silver nanoparticles

TEM analysis in Figure 5 support the indicating of FESEM this metal is in spherical shape with average size of 17nm. XRD analysis was supported the TEM result which is AgNPs synthesis is in nano size and in mixture crystalline and amorphous nature as shown in Figure 6. Then, FTIR spectra in Figure 7 showed main absorptions of O-H stretching vibrations at 3421 cm^{-1}, C-H symmetrical stretching vibration at 2923 cm^{-1}, C=O stretching modes at 1632 cm^{-1}, C-N stretching at 1427cm^{-1} and C-O stretching at 1060 cm^{-1} indicating the nanoparticles are capped with bioactive compounds present in plant extract.

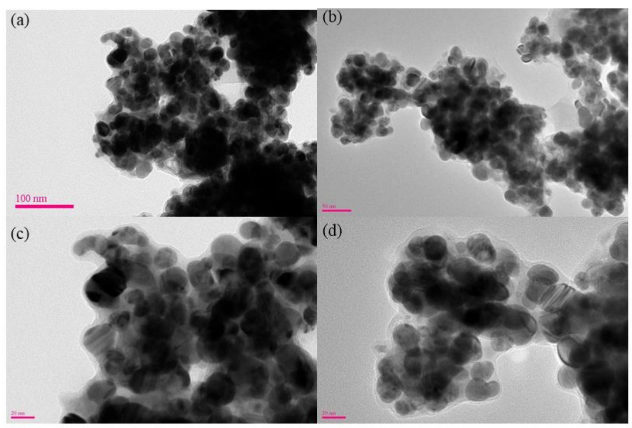


Figure 5 TEM images of silver nanoparticles low magnification (a and b) and high magnification (c and d)

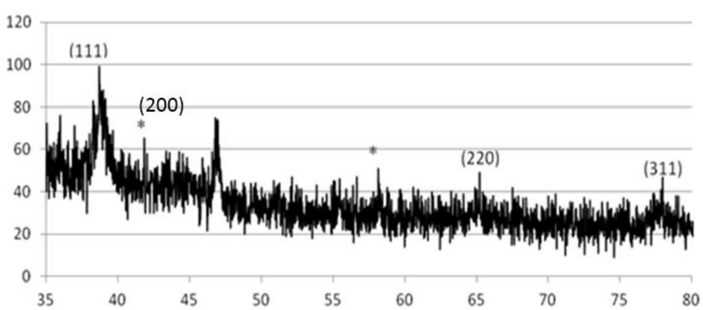


Figure 6 XRD pattern of Ag nanoparticles

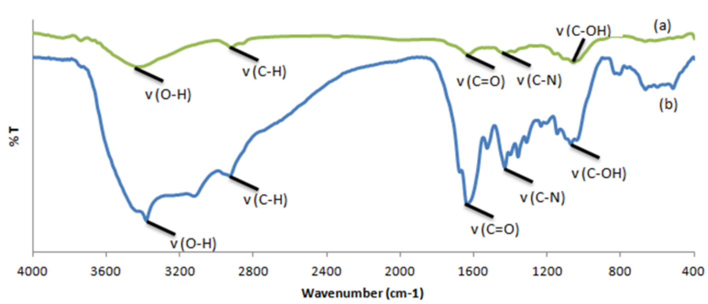


Figure 7 FTIR absorption spectra of (a) silver nanoparticles and (b) *Melicope ptelefolia* leaf extract powder

Reduction method via UV-Visible spectroscopy will be use to analyze the catalytic activity of *Melicope ptelefolia* silver nanoparticles.. These observations will prove good catalytic activity of silver nanoparticles. The reduction of 4-nitrophenol by N_2H_4 was chosen as a model reaction to investigate the catalytic activity of silver nanoparticles. At specific time intervals (1-30 mins), a small amount of the mixture was transferred into a quartz cuvette, and the UV-Visible absorption spectrum recorded in the range of 200–500 nm to monitor the progress of the catalytic reaction.

Figure 8 shows reduction of 4-NP to 4-AP in the presence and absence of Ag nanoparticles as a catalyst. After the addition of hydrazine hydrate, we can observed red shift at 406 nm due to the formation of 4-nitrophenolate ions as previous absorption of 4-NP was at 319 nm as shown in Figure 8.1. Addition of Ag nanoparticles showed the decrease in 4-nitrophenolate ions at 400 nm with gradual increase of new peak at 311 nm as shown in Figure 8.2. In the absence of Ag nanoparticles , the peak at 391 nm only shows slight decrease and proving that no significant reduction occurred without presence of catalyst as shown in figure 8.3. This study also reported by Borhamdin *et al*, (2016) which shows reduction of 4-NP to 4-AP in the presence of catalyst..

The catalytic reaction was carried out in excess of hydrazine hydrate concentration as compared to 4-NP. Therefore, the concentration of hydrazine hydrate use considered as constant and the reaction rate of the reduction dependent on 4-NP concentration. Hence, the rate was assumed to follow first order kinetics and was calculated by using equation 1,

$$K_{at} = \ln (C_t/C_0) = \ln (A_t/A_0) \quad (1)$$

Where C_t and A_t are the concentration and absorption of 4-NP at time t while C_0 and A_0 are the concentration and absorption of 4-NP at the start of the reaction. The rate constant can be calculated from the slope of the plot of ln At/A0 versus reaction time (s). As displayed in Figure 8.4, the rate constant of reaction in the presence and absence of Ag nanoparticles is 0.0013 s^{-1} and 0.0005 s^{-1} respectively. These values show the higher value of rate constant of reaction in the presence of catalyst. Thus, the rate of reaction was increased in the presence of Ag nanoparticles as surface area of active site of Ag is presence in this reaction (Borhamdin *et al.*, 2016). This trend of rate constant shows that rate of reaction will increase in the presence of catalyst.

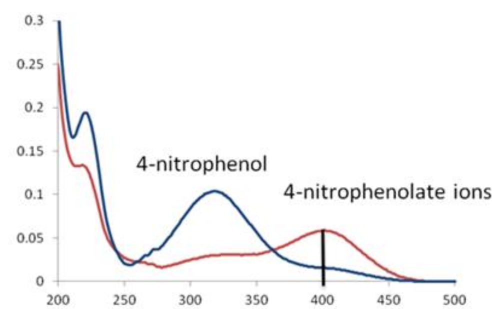


Figure 8.1 UV-visible spectra of 4-NP after the addition of hydrazine hydrate

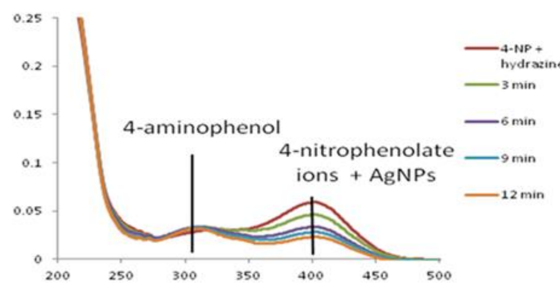


Figure 8.2 UV-visible spectra of 4-nitrophenolate ions in 12 minutes after the addition of Ag nanoparticles

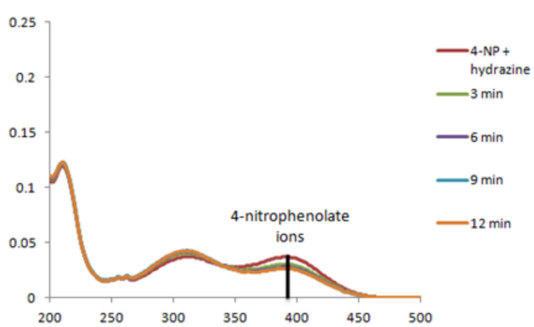


Figure 8.3 UV-visible spectra of 4-nitrophenolate ions in 12 minutes of time

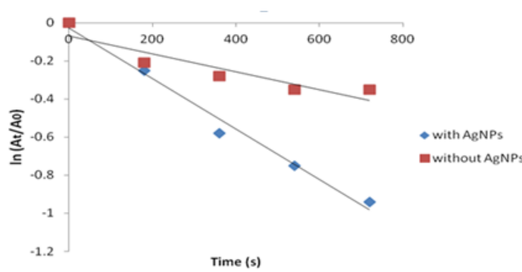


Figure 8.4 Plot of ln (A_t/A_0) versus time(t) in the absence and presence of catalyst

4. CONCLUSION

Based on this study, silver nanoparticles have been successfully synthesized via green synthesis approach. The formation of the AgNPs was easily monitored by UV-vis spectroscopy at 445 nm indicating the presence the surface plasmon resonance (SPR) band for AgNPs. FESEM micrograph of AgNPs exhibit spherical shape with high degree of agglomeration.

EDAX analyses confirm the presence of Ag metals. TEM images also shows AgNPs are in spherical with average size of 17 nm. XRD pattern indicate the presence of AgNPs, which are in nano size and in crystal face. FTIR spectra showed main absorptions that indicate the nanoparticles are capped with bioactive compounds which present in plant extract. Catalytic activity of AgNPs also successfully prove towards reduction of 4-NP to 4-AP in the excess of hydrazine hydrate.

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