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Catalytic Reduction of 4-Nitrophenol and Methylene Blue with Silver Nanoparticles Decorated with *Drymoglossum pilosselloides* Extract

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Abstract

Drymoglossum pilosselloides is one of the epiphytic plants that is commonly found in Southeast Asia region. In this study, the ethanol extract of *D. pilosselloides* plant has been used in the green synthesis of silver nanoparticles. The synthesized silver nanoparticles were characterized by ultraviolet-visible (UV-Vis) spectrophotometry, X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, and transmission electron microscopy (TEM) measurements. The UV-Vis spectrum of silver nanoparticles showed a maximum wavelength at 453 nm. The XRD measurement showed the silver nanoparticles peaks at 38.38°, 44.60°, 64.76°, and 77.62°. The FTIR spectra provided evidence of the interaction between silver and chemicals in the plant extract as a weak signal at 682 cm^{-1}. Meanwhile, TEM revealed an average size of 12.63 nm. The synthesised silver nanoparticles were utilised for the reduction of 4-nitrophenol with a conversion percentage of up to 100% with a reduction reaction rate constant of 7.104 s^{-1}. In addition, methylene blue was also successfully reduced with the synthesised silver nanoparticles as the catalyst with a reduction reaction rate constant (k) of 21.150 s^{-1}. This study highlights the superior advantage of utilizing ethanolic extract of *D. pilosselloides* to prepare silver nanoparticles with promising catalytic reduction purposes.

Keywords: *Drymoglossum pilosselloides*, green synthesis, catalytic reduction, silver nanoparticles, 4-nitrophenol, methylene blue

1. INTRODUCTION

Nanotechnology is a crucial domain in industry, environment, and pharmaceutical fields. Recently, nanotechnology has been attracting the world's attention uet o its wide applicability [1]-[4]. One of the fascinating aspects of nanotechnology is the use of nanoparticles. Nanoparticles are defined as particles with dimensions between 1 to 100 nm [5] [6]. These nanoparticles display unique properties and stand out when compared to materials on a larger scale [7]. In particular, metallic nanoparticles have taken centre stage uet o their excellent characteristics in terms of electrical, chemical, optical, antibacterial, and catalytic properties associated with their enormous surface area [8][9].

These metal nanoparticles have a wide range of applications, especially regarding precious metal nanoparticles. In the last decade, silver nanoparticles have become a major focus of research due to their outstanding special characteristics, as well as their capabilities in various modern technological applications [10].

Unfortunately, the advanced development of nanoparticles has generated toxic and negative damage to environmental sustainability. Therefore, recent developments in nanoparticle research have emphasised the development of more environmentally friendly technologies [11]. The focus is on silver nanoparticle synthesis processes that reduce the use of harmful chemicals and use more efficient production methods, resulting in products with minimal environmental impact. One of the approaches used by researchers is the use of plant extracts in a green synthesis approach [12]-[14]. Several types of plants have been reported to have the potential to be used in the synthesis of silver nanoparticles, such as *Camelia sinensis* [15], *Parkia speciosa* [16], and *Tragopogon collinus* [17].

The plant that is the focus of this research is *Drymoglossum pilosselloides*, an epiphytic fern. This plant grows naturally in lowland areas, mangroves,
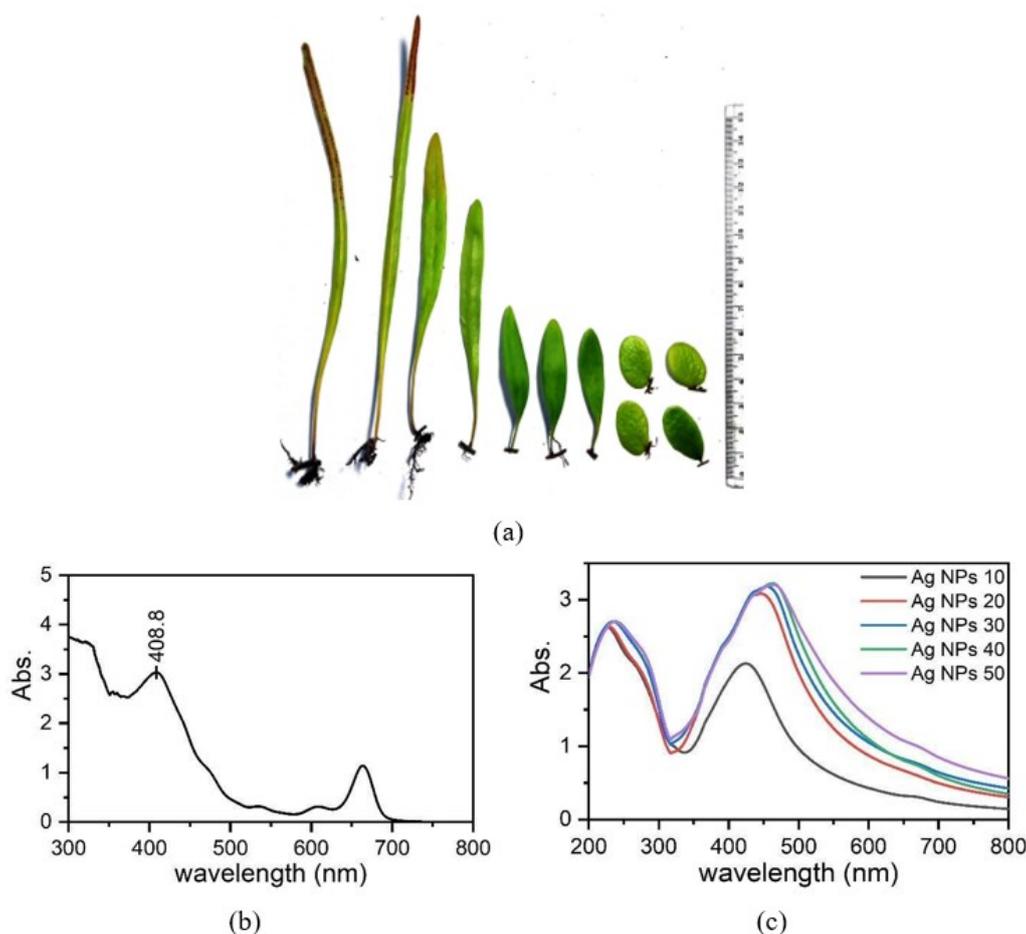
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Figure 1. (a) The photograph of *Drymoglossum piloselloides* leaves, (b) UV-Vis spectrum of the ethanolic extract of *Drymoglossum piloselloides,* and (c) the UV-Vis spectra of the synthesised silver nanoparticles using various amount of NaBH$_4$ as the reducing agent.

open areas, and gardens [18]. *D. piloselloides* is widespread in India, Southeast Asia, Papua New Guinea, and Northern Australia, documented to have various active compounds such as flavonoids, tannins, steroids, essential oils, phenols, and saponins [19]. Extraction methods using ethanol are commonly used to obtain chemical compounds from *D. piloselloides* [20]. Extracts from this plant, which contain active phytochemical substances, have potential in the formation of polydisperse nanoparticles. The resulting nanoparticles tend to vary in size and display interesting nanocatalytic properties.

The 4-nitrophenol, which is initially toxic in the aquatic environment, can be converted through the reduction process into 4-aminophenol with lower toxicity [21][22]. Furthermore, 4-aminophenol plays important applications in the photographic industry, textile dyeing, and pharmaceutical industry as the active substance used [23]. In the reduction of 4-nitrophenol, silver nanoparticles have demonstrated remarkable efficiency. The reduction process involves the transfer of electrons from a reducing agent to the nitro group of 4-nitrophenol, resulting in the formation of 4-aminophenol. Current trends show that an environmentally friendly approach can produce silver nanoparticles that are capable of reducing 4-nitrophenols such as *Poria cocos* [24]*, Diospyros malabarica* [25]*, Stachys lavandulifolia* [26]*,* and *Dolichos lablab* [27]. On the other hand, methylene blue, as a colouring agent with environmental impacts, can be reduced to leucomethylene blue through a catalytic process [28]. Similarly, silver nanoparticles exhibit notable catalytic activity in the reduction of methylene blue [29]. This conversion has the potential to produce compounds that are more environmentally friendly. This paper will emphasise the application of silver nanoparticles synthesised using *D. piloselloides* extract in the

context of catalysis application. Silver nanoparticle was used as homogeneous catalysts and the results showed excellent catalytic properties in the reduction process of 4-nitrophenol and methylene blue compounds.

2. MATERIALS AND METHODS

2.1. Materials

Dragon's scales (*Drymoglossum piloselloides*) leaves were collected from peat soil areas of Palangkaraya city and Pulang Pisau district, Central Kalimantan, Indonesia. Laboratory-grade chemicals such as silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), 4-nitrophenol ($C_6H_5NO_3$), methylene blue ($C_{16}H_{18}ClN_3S$) and ethanol (C_2H_6O) were purchased from Merck Sigma-Aldrich Reagent Pte, Singapore without additional purification steps.

2.2. Methods

2.2.1. Preparation of Ethanolic Extract of D. piloselloides

As much as 1 g of powdered samples of *Drymoglossum piloselloides* leaves were added into 40 mL of ethanol. This extract underwent heating at 60 °C for 30 min. Subsequently, the solution cooled naturally and underwent filtration through a Whatman filter paper, collecting the filtrate. This resulting solution served as the foundational stock for synthesizing silver nanoparticles.

2.2.2. The Synthesis of Silver Nanoparticles

Silver nanoparticles were synthesized through a green synthesis approach. Specifically, 18 mL of a 1 mM $AgNO_3$ solution was combined with $NaBH_4$ and 1 mL of *D. piloselloides* extract. Diverse volumes of $NaBH_4$, labeled as AgNPs10 to AgNPs50, spanning from 10 to 50 µL, were utilized in this process. The resulting mixture underwent stirring in an ice bath for a duration of 15 min. The acquired silver nanoparticles underwent characterization using a UV-Vis spectrophotometer to determine the peak of surface plasmon resonance (SPR) value. Subsequently, the silver nanoparticles exhibiting the most pronounced SPR were further analyzed using transmission electron microscopy (TEM). Characterization of the synthesized nanoparticles was also carried out using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) instruments.

2.2.3. Catalytic Reduction of 4-Nitrophenol and Methylene Blue

In the reduction process of 4-nitrophenol employing silver nanoparticles as the catalyst, a mixture of 2000 µL of 0.01 mM 4-nitrophenol and 500 µL of 0.4 M $NaBH_4$ was introduced to the previously synthesized silver nanoparticle catalyst, ranging from 10 to 50 µL. Distilled water was added to reach a total volume of 3.5 mL in a cuvette. The transformation from 4-nitrophenol to 4-aminophenol was monitored using a UV-Vis spectrophotometer, scanning the range of 250–550 nm at 30-second intervals. The concentration was
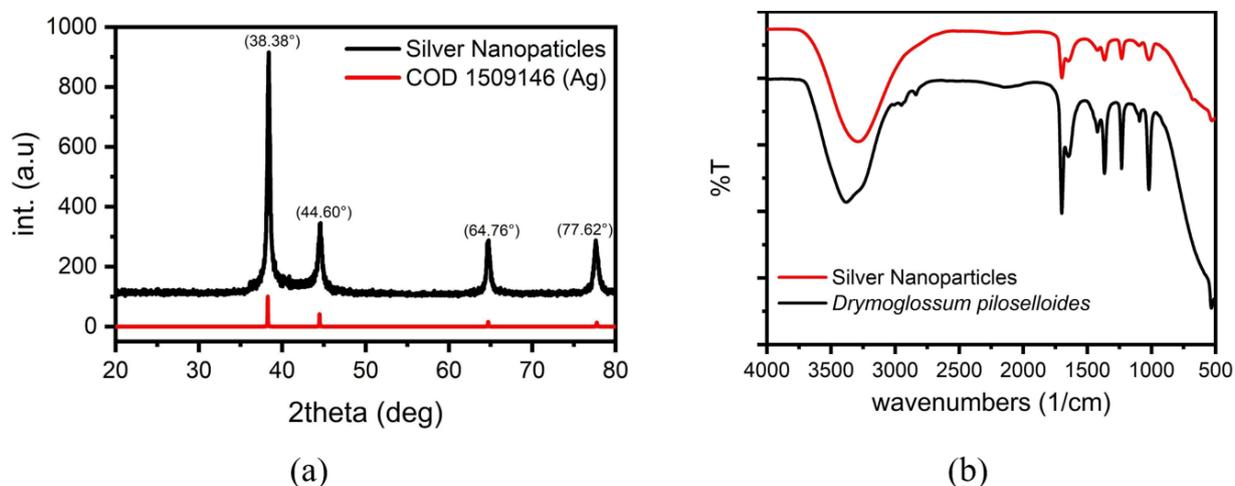

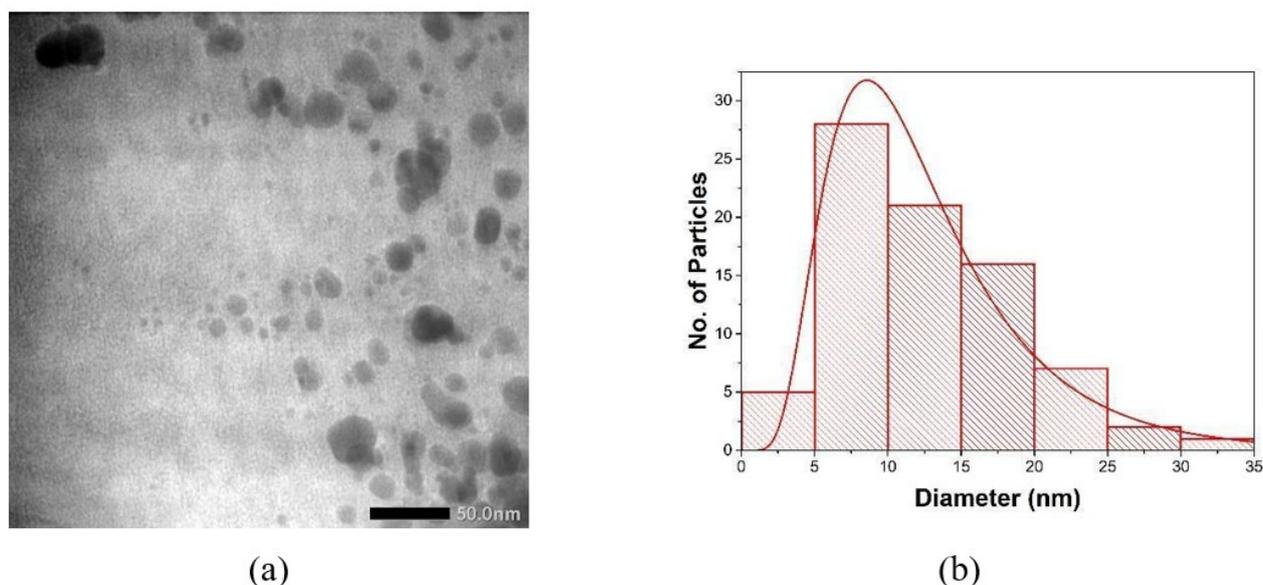**Figure 2.** Characterization data of silver nanoparticles using (a) XRD and (b) FTIR.

Figure 3. (a) TEM image and (b) histogram of obtained silver nanoparticles.

monitored at the maximum wavelength of 403 nm. The percentage conversion was determined based on Equation 1;

$$Percentage\ Conversion\ (\%) = \frac{(C_0 - C)}{C_0} \times 100\%$$ (1)

where C_o is the initial concentration and C is concentration at time. Through these observations, the reaction rate (k) of the catalytic reduction (s^{-1}), following pseudo-first-order kinetics due to the diminishing concentrations of 4-nitrophenol, could be determined from the results following the previous descriptions [30][31]. In the reduction reaction involving methylene blue, the procedural steps closely mirrored those of the 4-nitrophenol reduction, with a notable adjustment in the quantity of silver nanoparticles introduced. Specifically, the range of silver nanoparticle addition varied from 50 to 100 μL. The reaction rate (k) of methylene blue reduction was determined based on the first-order kinetics equation (Eq. 2) [32][33].

$$ln\frac{A_t}{A_0} = -kt$$ (2)

where A_t is the concentration at time t, A_0 is the concentration at time 0, and k is the first-order reaction rate constant (s^{-1}).

3. RESULTS AND DISCUSSIONS

3.1. Synthesis and Characterization of the Synthesized Silver Nanoparticles using D. piloselloides Extract

The synthesis process of silver nanoparticles exhibits a gradual alteration in color, transitioning from a colorless state to a distinct red-violet hue. This observable alteration serves as a clear indicator of the existence of SPR from the silver nanoparticles' structure. The extracts used in the synthesis of silver nanoparticles were from various types of *D. piloselloides* leaves as pictured in Figure 1(a). The extract was characterized by the UV-Vis spectroscopy, delineated in Figure 1(b) and 1(c) showcasing the UV-Vis spectrum of the extract and the synthesized silver nanoparticles, respectively. Based on the UV-Vis spectra, the silver nanoparticles with the highest absorbance were nanoparticles coded AgNPs 40 (equal to the usage of 40μL NaBH₄) with an absorbance of 3.222. Within the spectrum of AgNPs 40, the silver nanoparticles distinctly manifest a robust and widened peak, precisely at the 453 nm wavelength, an attribute absent in the dragon's scales extract. The expansive nature of the SPR spectra can be attributed to the formation of notably significant anisotropic structures within the nanoparticles [34][35]. Furthermore, the red swift on the UV-Vis spectrum, transitioning from 408 to 453 nm, stands as a compelling indication of a dimensional reduction within the environment conducive to

silver nanoparticle formation [36].

The synthesized silver nanoparticles were also tested using XRD to determine whether the silver reduction was successful. The XRD results were compared with COD 1509146 presented in Figure 2 (a). The results obtained showed that zero valence silver was successfully formed by the observation of four dominant peaks at 38.38°, 44.60°, 64.76°,

and 77.62°. As reinforcement proof for the evidence of an interaction between *D. piloselloides* extract with silver, FTIR analysis was conducted and the results are shown in Figure 2(b). Several signals, i.e., hydroxyl signals at 3000–3750 cm⁻¹, carbonyl and C=C aromatics at 1500–1750 cm⁻¹, as well as ether and alkyl groups at 1000–1300 cm⁻¹, were similar to the FTIR spectrum of the extract. A new
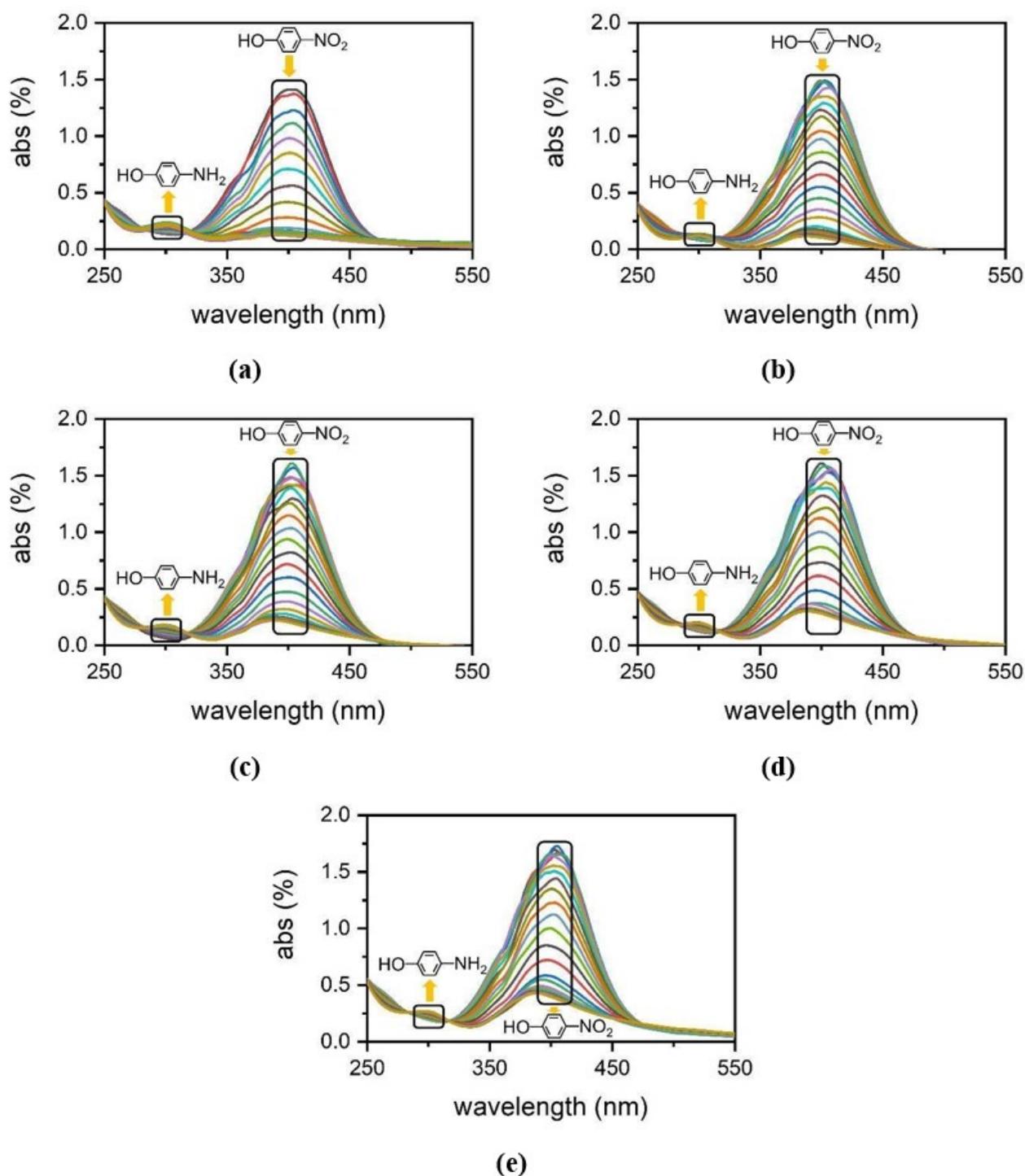

Figure 4. Time-dependent UV-Vis spectra of the reaction mixture of 4-nitrophenol with (a) 50, (b) 75, (c) 100, (d) 125, and (e) 150 µL of synthesized silver nanoparticles.
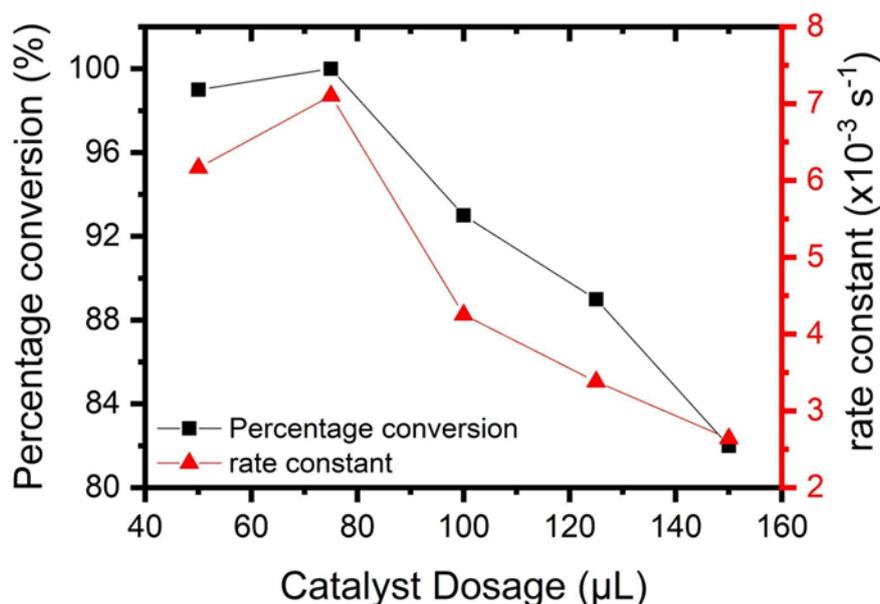
Figure 5. The comparison of percentage conversion and reaction rate constant value of the reduction of 4-nitrophenol.
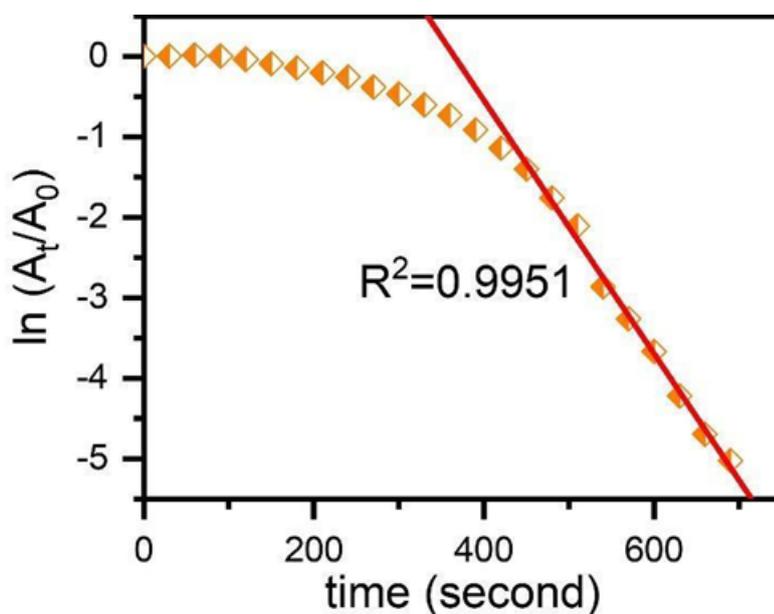

Figure 6. Linear plot analysis of $\ln(A_t/A_0)$ vs time for the 4-nitrophenol reduction using 75 µL of silver nanoparticle as the catalyst.

absorption signal at 682 cm^{-1} came from the interaction between *D. piloselloides* extract with silver as reported in the previous study [37].

Figure 3(a) provides a comprehensive depiction of the distinctive anisotropic configurations observed within the prepared silver nanoparticles. Additionally, Figure 3(b) illustrates the distribution pattern of nanoparticle diameters, showcasing a prevalent diameter spectrum spanning from 5 to 10 nm. Notably, the range encompasses a recorded maximum diameter of 31.52 nm and a minimum diameter of 3.43 nm, signifying the diverse size variations present within the samples. In summary, the average diameter size of the observed silver nanoparticles remains consistent at approximately 12.63 nm, and the standard deviation stands at 6.23 nm, indicating the degree of variability within the observed nanoparticle sizes. Additionally, the TEM image reveals instances of nanoparticle agglomeration, attributed to localized size

increments within the sample set.

The average size of the successfully synthesized silver nanoparticles was 12.630 nm, in agreement with findings in several previous studies showing that nanoparticles with diameters of less than 15 nm generally display remarkable catalytic properties, particularly in the context of reduction catalysis because of their large surface area [38]. The reduction process is an electron transfer mechanism involving a reducing agent, with NaBH$_4$ chosen as the reducing agent within the scope of this study. One of the widely studied reduction reactions is the conversion of 4-nitrophenol to 4-aminophenol. In Figures 4(a) to 4(e), the spectrum of 4-nitrophenol as it interacts with the homogeneous catalyst of silver nanoparticles every 30 seconds is clearly illustrated. In these spectra, there is a significant decrease in the wavelength around 403 nm, which
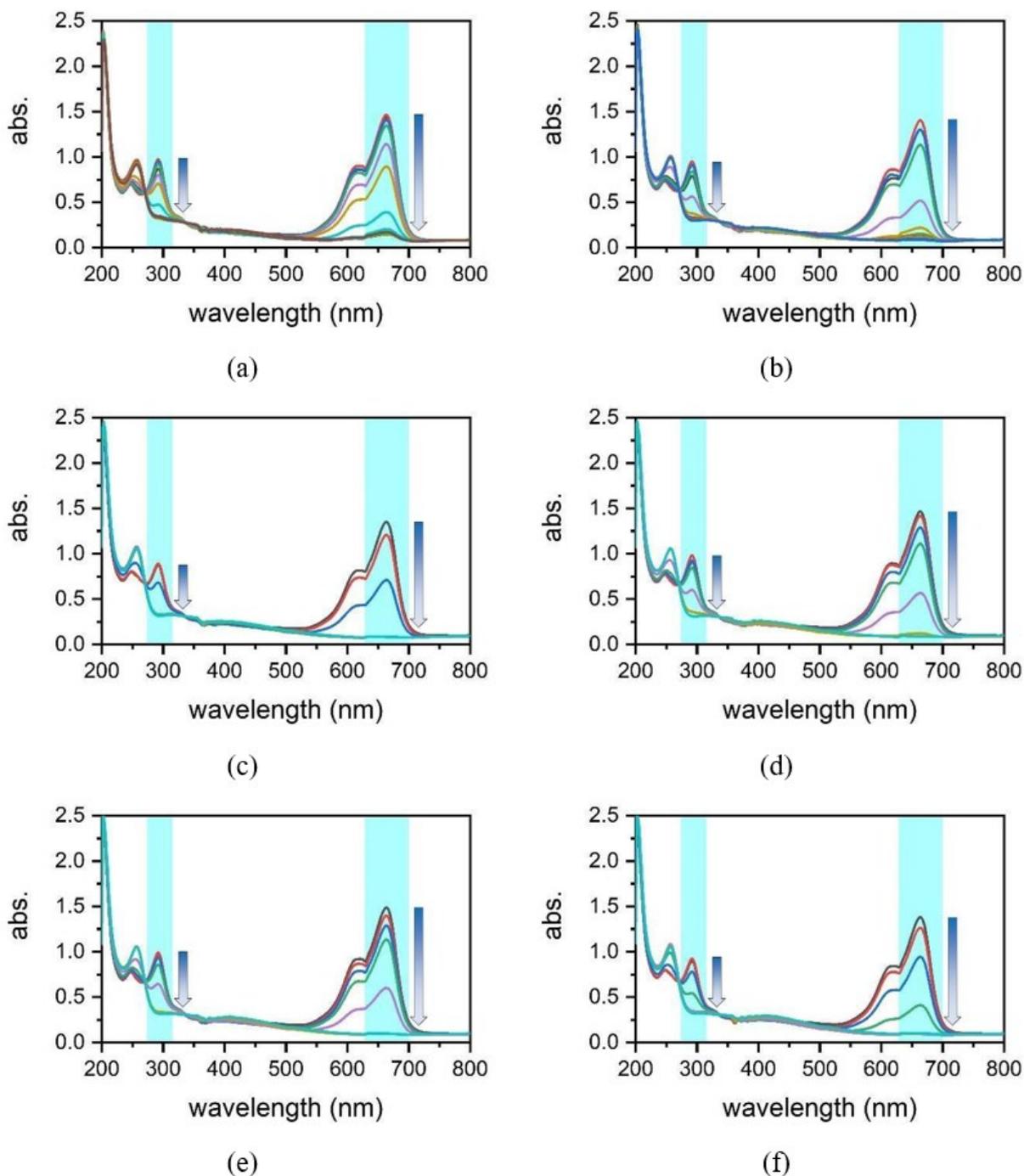

Figure 7. Time-dependent UV-Vis spectra changes of methylene blue with the addition of (a) 50, (b) 60, (c) 70, (d) 80, (e) 90, and (f) 100 μL of silver nanoparticles.

is the characteristic peak of 4-nitrophenol. The decrease in the intensity of the 4-nitrophenol peak is in line with the increase in absorbance at around 302 nm, which is a typical peak of 4-aminophenol.

3.2. Catalytic Reduction of 4-Nitrophenol and Methylene Blue

The reduction of 4-nitrophenol levels through the addition of silver nanoparticle catalyst at variant concentrations showed that the optimal volume of homogeneous catalyst was 75 µL, resulting in conversions up to 100%. This conversion of 4-nitrophenol compares favorably with previous studies using plant extract approaches as shown in Table 1. The pattern observed when adding the homogeneous catalyst was an increase from 50 to 75 µL, followed by a decrease in conversion from 100 to 150 µL. Figure 5 displays the comparison of percentage conversion and reaction rate constant (k)

value of adding silver nanoparticles in the reduction process of 4-nitrophenol with the highest k value being 7.104 s^{-1}. The k value refers to previous studies showing that the reduction of 4-nitrophenol with silver nanoparticles catalyst fits well to a pseudo-first-order model. This is supported by the linear plot analysis of $\ln(A_t/A_0)$ vs time as shown in Figure 6.

The reduction of methylene blue was also carried out by adding a certain amount of silver nanoparticles together with NaBH$_4$ as the reducing agent. As seen in Figure 7, there is a decrease in the absorbance of methylene blue at 293 nm indicating the transition from π to π^* in methylene blue, as well as absorbance at 665 nm as the maximum wavelength of methylene blue indicating the n to π^* transition. The absorbance value at 665 nm was used to calculate the percentage reduction of methylene blue to leucomethylene blue. As shown

Table 1. Comparison study of the percentage conversion of 4-nitrophenol by silver nanoparticles.

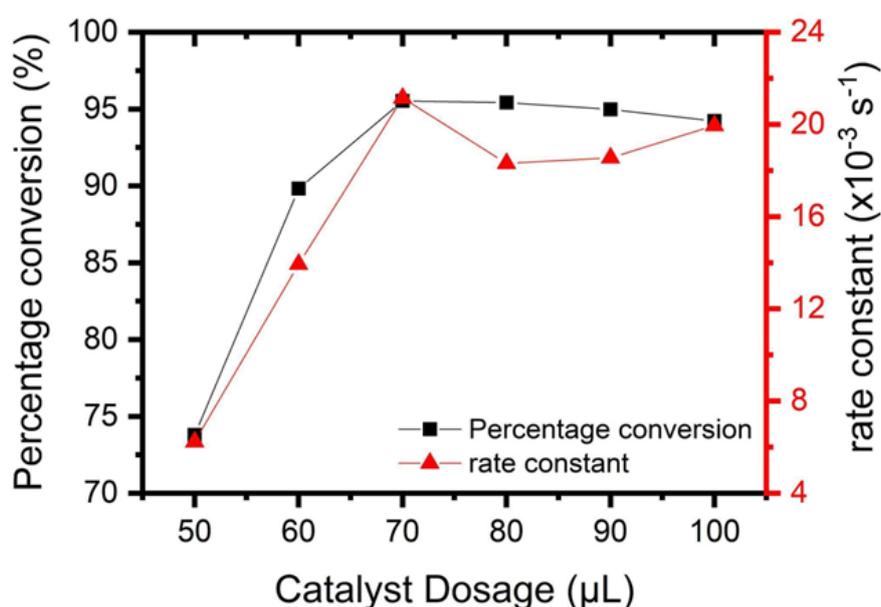| Stabilizing Agent	Catalytic Efficiency (%)	Reaction Time (min)	Ref.
Poria cocos	96.7	10	[24]
Ocimum tenuiflorum leaves	100	30	[25]
Moringa oleifera seed	75.0	75	[39]
Terminalia arjuna leaves	88.8	20	[40]
Drymoglossum piloselloides leaves	100	10	Present Study

Figure 8. Comparison of percentage conversion and reaction rate constants in methylene blue reduction at various amount of silver nanoparticles.

Table 2. Comparison study of the percentage conversion of methylene blue by silver nanoparticles.

Stabilizing Agent	Catalytic Efficiency (%)	Reaction Time (min)	Ref.
Achillea millefolium L.	100	30	[41]
Picrasma quassioides	100	30	[42]
Convolvulus arvensis	100	20	[43]
Trigonella foenum-graecum seeds	100	8	[44]
Gmelina arborea	100	10	[45]
Drymoglossum piloselloides leaf	95.53	10	Present Study
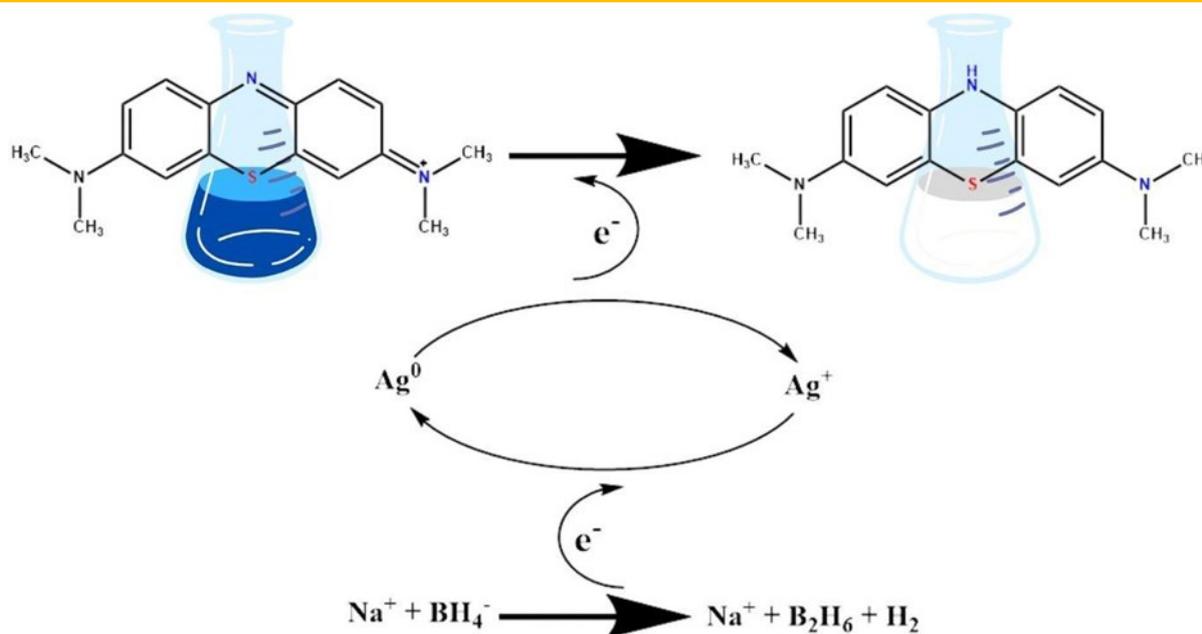
Figure 9. Proposed reduction mechanism of methylene blue to leucomethylene blue using silver nanoparticles.

in Figure 8, a 95.538% change ensued alongside the highest recorded reaction rate constant of 21.150 s^{-1} at 70 µL of silver nanoparticles. The methylene blue conversion results obtained in this study were quite high (95.53%) but did not reach 100% which was less effective than some previous studies using plant extracts as listed in Table 2. However, the reaction time was shorter in this study compared with the previous reports on *Achillea millefolium* L. extract, *Picrasma quassioides* extract, and *Convolvulus arvensis* extract [41]-[43]. A decrease in the concentration of methylene blue indicates the formation of leucomethylene blue. The proposed mechanism of leucomethylene blue formation using silver nanoparticles in this study is presented in Figure 9. This result opens a new application of *D. piloselloides* to prepare metal nanoparticles for wastewater treatment in the future.

4. CONCLUSIONS

Silver nanoparticles have been successfully synthesized with the help of ethanolic extract of *Drymoglossum piloselloides*. The prepared silver nanoparticles showed the highest SPR peak at 453 nm. The XRD and FTIR data also confirmed the formation of silver nanoparticles. TEM results showed the average size of the nanoparticles was 12.63 nm with a maximum diameter of 31.52 nm. Silver nanoparticles exhibited good catalytic activity for the reduction of 4-nitrophenol and methylene blue with reduction reaction rate constants of 7.104 and 21.150 s^{-1}, respectively.

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Conflicts of Interest

The authors declare no conflict of interest.

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