Ag$_2$O nanoparticles fabrication by *Vernonia amygdalina Del.* leaf extract: synthesis, characterization, and its photocatalytic activities

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Abstract. Green synthesis of Ag$_2$O nanoparticle (Ag$_2$O NP) has been investigated using *Vernonia amygdalina Del.* leaf extract (VaDLE). The secondary metabolite of VaDLE plays a role as a base source and capping agents, which can be determined by phytochemical screening. The diffraction pattern and crystallinity of Ag$_2$O NP was confirmed by X-ray diffraction, while the distribution size of Ag$_2$O NP can be determined by using transmission electron microscopy. Fourier transform-infra red spectrum was used to show the interaction VaDLE and Ag$_2$O NP. FT-IR characterization showed the presence of Ag-O band at 825 cm$^{-1}$. The characterization of UV-Vis spectrophotometer showed the typical absorption of Ag$_2$O at maximum wavelength, $\lambda_{\text{max}}$ of 262 and 452 nm. The size distribution of Ag$_2$O was 22.70 nm confirmed by particle size analyser. UV-Vis DRS characterization proved the bandgap energy of Ag$_2$O at 1.56 eV. The photocatalytic activity of Ag$_2$O NP was observed on the degradation of methylene blue. The result of the degradation percentage was 71.59%.

Keywords: Ag$_2$O nanoparticle, *Vernonia amygdalina Del.*, green synthesis, methylene blue, photocatalytic activity

1. Introduction

The synthesis of nanoparticles using green synthesis method is widely developed in both science and industrial fields due to the environmentally friendly, and can be easier to combine it with the nanotechnology, especially with the one related to the plant biotechnology. Several studies have been conducted to synthesize nanoparticles with green synthesis method, such as synthesis of AuNP using *Tinospora crispa* leaves [1], synthesis of ZnO using *Imperata cylindrica* L. leaves [2], synthesis of NiO using *Physalis angulata* leaves [3], synthesis of CdO using *Parkia speciosa* seeds [4].

Silver oxide nanoparticles (Ag$_2$O NP) are metal oxides that are stable and have unique physical and chemical properties such as anti-bacterial [5] and anti-cancer agents, as well as being used for cosmetic ingredients and photocatalyst materials [6]. Ag$_2$O NP itself is a p-type semiconductor which has good photocatalyst properties with a band gap from 1.2 to 3.4 eV and a wavelength of >400 nm, which resides in visible areas [7, 8]. Recent studies reported that Ag$_2$O NP could be synthesized through several chemical methods, such as sputtering [7], hydrothermal [9], and precipitation-deposition solvothermal [10]. However, Ag$_2$O NP synthesis through chemical methods have higher toxicity than green synthesis. As a mega biodiversity country, Indonesia has plenty sources of medicinal plants with various bioactive compounds, one of which is *Vernonia amygdalina Del.* (VaD). This plant has been known for its diverse secondary metabolites such as alkaloids, flavonoids, terpenoids and saponins, which responsible for its...
various bioactivities such as anti-tumour, anti-microbial, anti-diabetic, and anti-oxidants [9]. In this research, Ag$_2$O NP was synthesized using Vernonia amygdalina Del. leaf extract (VaDLE) by green synthesis method. The photocatalytic activity of Ag$_2$O NP was performed for the degradation of methylene blue (MB) in the visible light area.

2. Materials and Methods

2.1. Materials

AgNO$_3$ as a precursor was purchased from Merck (Germany) and VaD leaf was obtained from Kebun Biofarmaka of Bogor Agricultural University (Institut Pertanian Bogor, IPB), Babakan, Dramaga, Bogor, Indonesia. All reagents were analytical grade.

2.2. Preparation of Vernonia amygdalina Del. Leaf Extract

50 g of VaD leaf was washed, dried and mashed to obtain the leaf powder. The leaf powder was macerated using methanol 1:5 (w/v) by stirring in 20 minutes every day for a week. The result was then filtered and partitioned using n-hexane to get two fractions of hexane and methanol. Each fraction was tested phytochemically. The methanol fraction was evaporated and then dissolved in distilled water as the stock solution of Vernonia amygdalina Del leaf extract.

2.3. Phytochemical screening of Vernonia amygdalina Del. Leaf Extract

The phytochemical screening was carried out to investigate the presence of alkaloid, flavonoid, tannin, terpenoid, steroid, polyphenol and saponin in methanol fraction, n-hexane fraction and VaDLE.

2.4. Synthesis of Ag$_2$O NP

0.01 M of AgNO$_3$ was reacted with VaDLE 0.167% (m/v). The mixture was stirred for 2 hours at 90°C, followed by the centrifugation process while the mixture was washed using aquadest. The result was aged for 24 hours, then dried for 3 hours at 200°C to obtain Ag$_2$O NP powder.

2.5. Characterization of Ag$_2$O NP

UV-visible spectrophotometer (Shimadzu UV-2600) was used to observe the absorption spectra and the maximum wavelength. The existence of Ag-O functional group was determined using FT-IR spectroscopy (Prestige 21 Shimadzu). Particle Size Analyser (Malvern Zetasizer 1600) was used to determine the particle size distribution and intensity of Ag$_2$O NP. The crystallinity of Ag$_2$O was confirmed using X-Ray Diffraction (Shimadzu 7000). Finally, Transmission Electron Microscopy (JEM 1400) was utilized to know the particle size distribution of Ag$_2$O NP.

2.6. Photocatalytic Activity Against MB

3 mg Ag$_2$O NP was added to the 0.00003 M MB solution and irradiated at room temperature while stirred under the visible light radiation. The time interval of this treatment was measured at 0, 15, 30, 45, 60, 75, 90, 105, and 120 minutes.

3. Results and Discussion

Phytochemical screening was carried out in order to qualitatively find out the secondary metabolite content in the VaDLE. The colour testing reaction using a colour reagent was used as the phytochemical screening method. In this research, the phytochemical screening was conducted on three fractions, namely methanol, n-hexane, and water fractions, which resulted that the stock solution of leaf extract contained of alkaloids, flavonoids, saponins, polyphenols, tannins terpenoids and steroids. These results shown the conformity with the secondary metabolite result of VaDLE from the previous study [9]. Furthermore, the phytochemical screening result was supported by the characterization using FT-IR and UV-Vis spectrophotometer. It indicated that alkaloid was contained in VaDLE. An alkaloid, which composed of C-N functional group, can be used as the base source to synthesize the metal oxide such
as ZnO and CuO [10]. Hence the presence of alkaloid in VaDLE can be used to synthesize Ag₂O as well. Furthermore, saponins in VaDLE can be utilized as biosurfactant in the formation of nanoparticle template, while the polyphenol and the flavonoid compounds can be acted as the stabilizing and capping agent to prevent the agglomeration [1].

Fig. 1a shows the Ag₂O NP and VaDLE spectra. From the visible spectrum, there were two bands of Ag₂O NP at the wavelength of 452 nm and 262 nm [11].

![Figure 1](image)

**Figure 1.** The result of UV-Vis spectra, which shown the VaDLE (red) and Ag₂O NP absorption spectrums (blue) (a) and the Tauc’s Plot of Ag₂O NP (b).

The phenomena of UV-Vis absorption of metal and metal oxide is due to Surface Plasmon Resonance (SPR). It happened during the resonance of visible light waves that collide with the electrons on the Ag₂O NP surface and produced the electron oscillations on the material surface [12]. This spectra underwent a shift from the VaDLE spectra (320 nm) to batochromic shift, indicating the formation of a new molecular structure [12], signed by the color change from white to black. Furthermore, the VaDLE spectra shown a peak at 320 nm, confirmed as the alkaloid indole spectra [13]. Fig. 1b shown the Tauc’s Plot of Ag₂O NP. The Kubelka-Munk equation was used to determine the band gap energy [10], using the % reflectance resulted from the characterization data of the Ag₂O NP. Based on the linear equation curve, the band gap energy from Ag₂O NP was observed at 1.56 eV, which shown its activity in the visible range area.

The FTIR analysis (Fig. 2a) for the leaf extract of *Vernonia amygdalina Del.* and Ag₂O NP was conducted using the wavenumber range from 4000 to 400 cm⁻¹. The FTIR spectrum on the VaDLE shown that the wavenumber absorption of 3200-3600 cm⁻¹ represented the hydroxyl (-OH) group, while at 2958 cm⁻¹ characterized the C-H absorption from alkene/alkyl groups [14]. These two functional groups indicated the presence of saponins in the VaDLE. Moreover, 1626 cm⁻¹ is an identic absorption for aromatic groups (C=C-C) and 1712 cm⁻¹ is the wavenumber for carbonyl (C=O) group [14], which likely indicate the presence of flavonoid compounds [14]. Furthermore, the absorption spectra at 1062 cm⁻¹ is an identical wavenumber of the C-N group, which refers to alkaloid compounds [15]. The Ag₂O NP absorption spectra synthesized using the VaDLE shown different wavenumbers, which was at 825 cm⁻¹ represented the presence of Ag-O bond [11]. The crystal phase analysis of Ag₂O NP was determined using XRD measurement with the diffraction pattern as shown in Fig. 2b. The diffraction peaks of 20 were at angles of 32.16°, 37.96°, 57.43° and 64.46° with the Miller index of 111, 020, 022, and 040, respectively. The XRD diffraction pattern shown the crystal structure for cubic Ag₂O NP (JCPDS No. 04-006-5378) [16]. According to the Debye-Scherrer equation, the average crystal size of the Ag₂O NP was determined at 33.55 nm.
Figure 2. FTIR spectra of the leaf extract of *Vernonia amygdalina* Del. and Ag$_2$O NP (a), XRD patterns of Ag$_2$O NP (b).

Fig. 3a shows the characterization results using PSA, which resulted that the size distribution of Ag$_2$O NP was around 22.70 nm. These results indicated that the Ag$_2$O NP had been synthesized using nano-sized leaf extract of *Vernonia amygdalina* Del. Thus, according to the Fig. 3b, the TEM analysis of Ag$_2$O NP analysis determined the particle size dispersion of synthesized Ag$_2$O NP, which revealed about 4-12 nm. From the results, the Ag$_2$O NP was determined to have cubic phase, which supports the result from the XRD.

Figure 3. Particle size distribution of the synthesized Ag$_2$O NP (a) and TEM image of Ag$_2$O NP (b).

Furthermore, Fig. 4 shown the UV-Vis absorption spectra and photodegradation efficiency of MB using 3 mg Ag$_2$O NP as the photocatalysts agent. MB has a characteristic absorption peak at a wavelength of 664 nm. The absorption of dye at this wavelength decreased during the photodegradation process, which showed the presence of dyestuff degradation. The percentage of MB solution degradation (3x10$^{-6}$ M) was obtained by converting the absorbance value into a concentration value using the Lambert-Beer equation, which degradation percentage value of 71.59% was obtained.
Figure 4. The UV-Vis absorption spectra (a) and photodegradation efficiency (b) of MB.

The photodegradation mechanism with semiconductor material involves the visible light energy, which was greater that the energy bandgap so that the electron production (e^-) in the conduction band (CB) and hole (h^+) occurred in the valence band (VB) due to the electron excitation from VB to CB. In this mechanism, the redox reaction occurred, where h^+ and e^- acted as a strong oxidizing agent and strong reducing agent, respectively. e^- on the Ag_2O surface would absorb O_{ads} to produce O_{ads}•^- and reacted with H_2O_{ads} until the OH• and H^+ were formed. Finally, the H^+ would transform to OH• and degraded MB [15, 16].

4. Conclusions
In this research, Ag_2O NP was successfully synthesized using VaDLE with the particle size distribution of 22.70 nm. The XRD characterization revealed that the synthesized Ag_2O NP has cubic-phased crystal with an average size of 33.50 nm. Moreover, the band gap value of Ag_2O NP was determined at 1.56 eV and shown a good photocatalytic activity in visible area, which can degrade 71.59% MB in 120 minutes with a maximum catalyst weight of 3 mg.

Acknowledgement
The Authors would like to thank Directorate of Research and Community Engagements, Universitas Indonesia for funding this research through Hibah PITTA Universitas Indonesia with contract No.2339/UN2.R3.1/HKP.05.00/2018; and PT DKSH (Malvern) for supporting characterization of Particle Size Analyzer.

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