Synthesis, characterisation and catalytic activity of V₂O₅ nanoparticles using *Foeniculum vulgare* stem extract

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1. Introduction

Metal oxide nanoparticles have become an interesting research subject due to their potential application as catalyst [1-4]. Vanadium pentoxide (V₂O₅) is a transition metal oxide that has an important role in the development of science and technology [5], for instance as a catalyst [6,7], electronic devices [8] and biomedical application[9].

Vanadium generally has different oxidation numbers that give some oxide structures such as VO, V₂O₃, VO₂ and V₂O₅. Among of them, V₂O₅ is probably the most studied one, due to its thermodynamic stability [10]. Synthesis of V₂O₅ nanoparticles has been successfully carried out by conventional chemical methods using hazardous compounds [11] as base source and capping agent. Along with the advancement in science and technology, V₂O₅ nanoparticles can be synthesized by green chemical methods. This method usually uses extracts from microorganism or parts of plant [12]. Conceptually, this method has an approach such as physico-chemical synthesis method [13]. The development of this method in synthesis of V₂O₅ nanoparticles is still limited, for example by using *Saccharomyces cerevisiae* [14] and rambutan peel [9]. Unfortunately, synthesis of nanoparticles using plants from Indonesia has not been widely reported.

*Foeniculum vulgare* grows wildly on the plateau with an alkaloids content of 119.37 μg/mg [15] and the other compounds such as flavonoids, steroids, and saponins. Secondary metabolite compounds plays a vital role as an alternative base sources, stabilizer, and capping agent in the synthesis of metal oxide nanoparticles [16]. Phytochemical tests were used to confirm the secondary metabolite compounds in *Foeniculum vulgare* qualitatively.

**Abstract.** A green synthesis route of metal oxide has been developed to synthesize the V₂O₅ nanoparticles. V₂O₅ was synthesized using *Foeniculum vulgare* stems extract (FSE) and ammonium monovanadate as precursors. The role of secondary metabolite compounds affect the particle size of V₂O₅. The crystalline phase and crystallite size of V₂O₅ were investigated by X-ray Diffraction (XRD) with the orthorhombic crystalline phase and the average crystallite size around 78.6 nm. The presence of functional groups was evaluated by Fourier Transform Infrared (FT-IR). The morphology, particle size, and chemical composition of V₂O₅ were analyzed by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy Dispersive X-Ray (EDX). V₂O₅ nanoparticles show a good catalytic activity for the reduction of methylene blue (MB).

**Keywords:** V₂O₅, *Foeniculum vulgare* stems, catalytic activity, methylene blue
In this study, synthesis of V.O. nanoparticles was performed using *Foeniculum vulgare* stems extract. In addition, V.O. nanoparticles have been characterized by UV-Vis spectrophotometer, Fourier Transform Infrared (FT-IR) spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), and Transmission Electron Microscopy (TEM). The catalytic activity of V.O. nanoparticles was investigated for reduction of methylene blue (MB).

2. Experimental

2.1. Materials

*Foeniculum vulgare* stems were obtained from Pasuruan, East Java, Indonesia. Ammonium monovanadate (NH,VO,) was purchased from Merck chemicals. All reagents and solvents were analytical grade.

2.2. Preparation of stems extract

The *Foeniculum vulgare* stems extraction was adapted from the previous report with some modifications [17,18]. 50.0 g of dried *Foeniculum vulgare* stems was macerated in 250 mL of methanol for a week. The filtrate was partitioned by *n*-hexane. The methanol fraction was evaporated with a rotary vacuum evaporator. The concentrated methanol fraction was dissolved in distilled water to obtain aqueous *Foeniculum vulgare* stems extract (FSE). The presence of secondary metabolite compounds was identified qualitatively by phytochemical test.

2.3. Phytochemical test

Preliminary phytochemical test was conducted to determine the presence of alkaloids, flavonoids, terpenoids, steroids, tannins, saponins, and phenolic as described by Beyazen et al. [19]. For alkaloids identification test: 1.0 mL of FSE was reacted with 3.0 mL of 2N HCl and 4.5 mL of Wagner’s reagent sequentially. Brownish red solution indicates the presence of alkaloids. For flavonoids test: 2.0 mL of FSE was reacted with 2.0 mL of 0.1M NaOH and then added HSO, dropwise. The fading color indicates the presence of flavonoids. For phenolic test: 2.0 mL of FSE was reacted with 1.0 mL distilled water and then added 5 % FeCl, dropwise. Dark green solution indicates the presence of phenolic. For saponins test: 1.0 mL of FSE was mixed and shaken with 3.0 mL of distilled water. The appearing bubbles indicate the presence of saponins.

2.4. Synthesis of V.O. nanoparticles

1M NH,VO, solution was reacted with FSE by stirring for 2 h at 80 °C and then incubated at room temperature for 7 days. The orange powder was obtained after the calcination at 600 °C for 4 h.

2.5. Characterization of V.O. nanoparticles

The UV-Vis absorption of V.O. nanoparticles was analyzed using UV-Vis spectrophotometer (Shimadzu 2600) at wavelength range 200–800 nm. The functional groups of FSE and V.O. nanoparticles were recorded by FT-IR (Prestige-21 Shimadzu). The structural properties of V.O. nanoparticles were identified by XRD (PANalytical Empyrean) using Cu Kα as radiation (1.5406 Å). The morphology and composition information of the V.O. nanoparticles were characterized by SEM-EDX (Zeiss Evo MA10). The particle sizes of V.O. nanoparticles were analyzed by TEM (Tecnai D2360 S-Twin).

2.6. Catalytic activity

The catalytic activity of V.O. nanoparticles was examined by monitoring of methylene blue (MB) reduction using NaBH, as a reducing agent. The amount of V.O.and 1 mM MB was mixed with 0.1M NaBH, and then stirred for 5 min. The MB’s concentration was determined through observation of the decreasing absorbance at 664 nm using UV-Vis spectrophotometer.

3. Results and discussion

The phytochemical test was performed to investigate the presence of alkaloids, flavonoids, phenolic, and saponins in FSE. The methanol filtrate showed the positive result for all secondary metabolites. However, FSE only showed the presence of alkaloids, flavonoids, and phenolic (table 1).

3.1. UV-Vis absorption spectra analysis
Table 1. Phytochemical test of FSE

| Secondary metabolite compound | Methanol | Aqueous |
|------------------------------|----------|---------|
| Alkaloids                    | +        | +       |
| Flavonoids                   | +        | +       |
| Phenolic                     | +        | +       |
| Saponins                     | +        | -       |

*+ to indicate presence, - to indicate absence*

The UV-Vis absorption spectra of V$_2$O$_5$ nanoparticles (black line) are shown in figure 1. For the comparison, the spectrum of NH$_4$VO$_3$ solution (blue line) and FSE (red line) were also analyzed. The maximum wavelength of NH$_4$VO$_3$ solution, FSE, and V$_2$O$_5$ nanoparticles were appeared at 276, 265, and 452 nm, respectively. The maximum wavelength of V$_2$O$_5$ nanoparticles is in accordance with the previous report [20].

3.2. FT-IR analysis
FT-IR analysis aims to reveal the functional groups of FSE and V$_2$O$_5$ nanoparticles. Figure 2 presents the wavenumber changes of FSE and V$_2$O$_5$ nanoparticles. The characteristic bands of alkaloids occur at 1625 cm$^{-1}$, 1386 cm$^{-1}$ and 1271 cm$^{-1}$ at the spectrum of FSE (black line) and these results were in accordance with previous report [21]. However, the band of alkaloids was not appeared at the spectrum of V$_2$O$_5$ nanoparticles (blue line). The characteristic vibration of V=O and V-O-V bond is shown at 940 cm$^{-1}$, 835 cm$^{-1}$, and 718 cm$^{-1}$. These results have the conformity with the previous report [22].

3.3. Structural and morphology
The crystalline properties of V$_2$O$_5$ nanoparticles were examined by XRD. As can be seen from figure 3, the diffraction patterns of V$_2$O$_5$ nanoparticles show the orthorhombic crystalline phase indexed to (ICDD No. 96-101-1292, space group Pmn21). There are 2 peaks at 2θ = 20° and 26° with the structural plane (001) and (101) indicating the presence of V$_2$O$_5$ nanoparticles [9]. The crystallite size of V$_2$O$_5$ nanoparticles was estimated by Debye-Scherrer equation obtained 78.6 nm. The morphology of V$_2$O$_5$ nanoparticles prepared by a green synthesis method was characterized by SEM, as depicted in figure 4a. V$_2$O$_5$ nanoparticles reveal a form of cubic agglomeration with particle size on a scale bar of 200 nm. The corresponding EDX spectrum is shown in figure 4b indicating the elemental composition of vanadium and oxygen with the mass percentage of 11.77 % and 25.80 %, respectively.
Figure 3. XRD pattern of V₂O₅ nanoparticles

Figure 4. (a) SEM image and (b) EDX spectrum of V₂O₅ nanoparticles

Figure 5. TEM image of V₂O₅ nanoparticles

For further characterization on the morphology of V₂O₅ nanoparticles, the TEM image exhibits cubic-like agglomerated morphology, which has an average diameter of around 70 nm as shown in figure 5.
The catalytic performance of synthesized V.O. nanoparticles reduced MB to leuco methylene blue (LMB) using NaBH₄. The reaction was observed by UV-Vis spectrophotometer in wavelength range of 450-800 nm at room temperature as shown in figure 6. MB shows the UV-Vis absorption peak at maximum wavelength of 664 nm. Figure 6a shows slightly decrease of MB absorbance. Figure 6b exhibits the decreasing absorbance of MB peak at 664 nm using V.O. nanoparticles catalyst. The decreasing of MB concentration using V.O. nanoparticles catalyst is faster than without catalyst as shown in figure 7a. V.O. nanoparticles help the electron transfer from BH₄⁻ to MB. A linear correlation between \( \ln \left( \frac{C_0}{C_t} \right) \), where \( C_t \) was concentration at various times and \( C_0 \) was concentration at the initial time, against reduction time (\( t \), min) indicates that the MB reduction follows pseudo-first order kinetics. The observed rate constant (\( k_{\text{obs}} \)) was calculated from the slope of the straight line and obtained 0.075 min⁻¹ as shown in figure 7b.

4. Conclusions
The V.O. nanoparticles have been successfully prepared using *Foeniculum vulgare* stems extracts by green synthesis methods. According to XRD characterization, the crystalline phase of V.O.
nanoparticles shows an orthorhombic shape with the crystallite size of 78.6 nm. This result was strengthened by the supporting data from SEM, TEM, and EDX. The obtained V₂O₅ nanoparticles show the catalytic activity for MB reduction in 50 min. The reduction of MB followed pseudo-first order kinetics with \( k_c \) value of 0.075 min⁻¹.

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