Synthesis of V$_2$O$_5$ nanoparticles using *Calophyllum inophyllum* leaf extract as photocatalyst under visible light irradiation

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Abstract. Synthesis of V$_2$O$_5$ nanoparticles (NPs) using *Calophyllum inophyllum* leaf extract (CILE) as an eco-friendly material has been investigated. V$_2$O$_5$ NPs were prepared using NH$_4$VO$_3$ as precursor. The typical absorption peak of V$_2$O$_5$ NPs has been characterized using UV–Vis spectrophotometer at 204 nm. V$_2$O$_5$NPs have the band gap value of 2.42 eV confirmed by UV-Visible Diffuse Reflectance Spectroscopy (UV-vis DRS). X-ray diffraction (XRD) analysis shows that an average crystal size of V$_2$O$_5$NPs was 68 nm. Identification of functional groups was characterized by Fourier-Transform Infrared (FTIR) spectroscopy. The absorption band at 1023 cm$^{-1}$ shows the V=O bond and the V-O-V bond at 849 and 578 cm$^{-1}$, respectively. Size distribution of V$_2$O$_5$ NPs was characterized by particle size analyzer (PSA). Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) Spectroscopy analysis was used to determine the morphological and the element composition of V$_2$O$_5$ NPs. The degradation percentage of methylene blue (MB) using V$_2$O$_5$ NPs was 74.83 % under visible light irradiation for 120 min.

1. Introduction

Nanomaterials are the pillar of nanoscience and nanotechnology. One form of nanomaterials is the metal oxide V-O-V. Metal oxide nanoparticles have significant contributions in many application fields, namely in chemistry, physics and materials. In technological applications, metal oxide nanoparticles are used in water treatment photocatalysts [1]. On the other hand, photocatalyst has become a new technology for solving the environmental pollution problems. Photocatalyst has been used for degradation of organic pollutants in wastewater by the presence of sunlight or visible light sources [2].

Among the various oxide-based semiconductors, V$_2$O$_5$ is especially interesting one due to its widely applications like electrochemical devices and catalyst [3]. In addition, V$_2$O$_5$ has narrow band gap (Eg), which is susceptible to photoactivation in visible light area, and has been used in semiconductor-type photocatalyst for degradation of water pollutants under visible light area.

Several methods have been used for the synthesis of nanomaterials in a relatively short time. However, conventional nanomaterial synthesis such as top-down approach and bottom-up approach leads to the adsorption of toxic chemicals on the material surface that may have adverse the effects on various applications [4]. The use of biological materials such as bacteria [5], mushrooms [6], enzymes [7], and plant leaf extracts [8] for the synthesis of nanomaterials offers many benefits such as being environmentally friendly, and are suitable for pharmaceutical and other biomedical use as well as does not involve harmful substance in synthesis procedures. In our previous reports, some metal oxide nanoparticles were synthesized using plant extract such as ZnO-CuO, Nd$_2$O$_3$, CuO, and La$_2$O$_3$ [9–12].
3.1. Synthesis.

Based on phytochemical screening, saponin, polyphenols, and flavonoid can be isolated from *Calophyllum inophyllum* leaves. Susanto et al. [13] have reported that phytochemical compounds in *Calophyllum inophyllum* leaves contain alkaloids, tannins, polyphenols, triterpenoid, flavonoid, and saponin.

In this research, synthesis of V.O.NPs was done using *Calophyllum inophyllum* leaves extract as a weak base source and a capping agent. Furthermore, the synthesized nanoparticles were evaluated in the photocatalytic activity for degradation of methylene blue (MB) as model pollutants under visible light irradiation.

2. Materials and experimental procedures

2.1. Preparation of *Calophyllum inophyllum* leaves extract

*Calophyllum inophyllum* leaves were washed and grounded to form powders. Powders were macerated using distilled methanol (1:5 (m/v)) for 7x24 hours by stirring for 20 min per day. The compound was filtered and partitioned with n-hexane (1:1 (v/v)). The methanol fraction was evaporated and dissolved in distilled water. The result was then filtered to obtain a stock solution of *Calophyllum inophyllum* leaves extract (CILE) for nanoparticles synthesis [14]. In addition, phytochemical screening was carried out for qualitative determination of flavonoid, terpenoid, steroid, alkaloid, tannin, polyphenol, and saponin in CILE using the method as reported by Saraswathi and Santhakumar [15].

| Secondary metabolites | Flavonoid | Terpenoid | Steroid | Alkaloid | Tannin | Polyphenol | Saponin |
|-----------------------|-----------|-----------|---------|----------|--------|------------|---------|
| Results               | +         | -         | -       | +        | -      | +          | +       |

+ : positive result, - : negative result

The potential of plants in Indonesia as biological materials for synthesis of nanomaterials has not been fully explored yet. *Calophyllum inophyllum* is one of the most extensively distributed plants in Indonesia and has many benefits. Susanto et al. [13] have reported that phytochemical compounds in *Calophyllum inophyllum* leaves contain alkaloids, tannins, polyphenols, triterpenoid, flavonoid, and saponin.

2.2. Synthesis of V.O. NPs

10 mL of 1.31% CILE was added into 100 mL of 0.025M NH.VO. (Merck) and stirred at 80 °C for 4 hours. The solutions were then aged for 24 hours to form colloids. Finally, the result was dried at 100 °C then calcined at 500 °C for 4 hours to obtain the powder of V.O.NPs.

2.3. Characterization

The diffraction pattern of V.O.NPs was identified by X-Ray Diffraction (XRD, Shimadzu) at 20 range of 0–80°. The morphology of V.O.NPs was investigated by Scanning Electron Microscopy (SEM, Zeiss). Elemental analysis of V.O.NPs was confirmed by Energy Dispersive X-Ray (EDX, Bruker). UV-Vis absorption spectra were recorded by UV-Vis spectrophotometer (Shimadzu 2600) at the wavelength between 200–800 nm. Size distribution of V.O.NPs was characterized by Particle Size Analyzer (PSA, Malvern Zetasizer 1600). Identification of functional groups was characterized by Fourier Transform Infrared (FTIR, Prestige 21 Shimadzu) spectroscopy and the band gap value measurement was determined by UV-Vis Diffuse Reflectance Spectroscopy (DRS, Shimadzu 2600).

2.4. Photocatalytic activity analysis

Photocatalytic activity was evaluated in MB degradation. 5.0 mg of V.O.NPs were added into 25 mL of 2.0x10−M MB solution. The mixture was sonicated for 30 min and further stirred for 2 hours under sodium lamp irradiation. UV-Vis absorption spectra were recorded every 30 min to observe the decrease of MB absorbance.

3. Results and discussion

Based on phytochemical screening result as shown in table 1, CILE has positive results for alkaloids, saponin, polyphenols, and flavonoid, which can act as hydrolyzing and capping agent in nanoparticles synthesis.

3.1. Characterization of V.O.NPs
FTIR spectra of CILE and V\textsubscript{2}O\textsubscript{5}NPs are shown in Figure 1a. CILE shows the vibration of C-N stretching and N-H bending at wavenumber of 1061 and 1607 cm\textsuperscript{-1}, respectively. These two vibrations indicate the presence of alkaloid. The presence of polyphenol and flavonoid are shown by the vibration of O-H stretching at 3316 cm\textsuperscript{-1}. The vibration of C-O stretching at 1284 cm\textsuperscript{-1} and the vibration of C-H stretching at 2939 cm\textsuperscript{-1} indicates the presence of saponin [16]. In fact, the vibration at 1023 cm\textsuperscript{-1} is attributed to the V=O stretching (vanadyl oxygen). Both vibrations at 849 and 578 cm\textsuperscript{-1} are corresponded to V-O-V deformation modes.

Figure 1b shows diffraction patterns of V\textsubscript{2}O\textsubscript{5}. The 2\textdegree{} value of V\textsubscript{2}O\textsubscript{5} has conformity with COD of V\textsubscript{2}O\textsubscript{5} No. 96-101-1292. V\textsubscript{2}O\textsubscript{5} has diffraction peaks at 2\textdegree{} value of 15.31\textdegree{}, 20.22\textdegree{}, 21.65\textdegree{}, 26.09\textdegree{}, 30.96\textdegree{}, 32.31\textdegree{}, 32.80\textdegree{}, 34.25\textdegree{}, 51.15\textdegree{}, and 62.05\textdegree{}. The average of crystal size was calculated using the Debye-Scherrer equation:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where D is crystalline size, \( \lambda \) is wavelength of the X-Ray radiation (0.1541 nm), K is generally taken as 0.89, \( \beta \) and \( \beta_0 \) are the peak widths at half-maximum height of sample and the broadening of equipment. According to the calculation, the average crystals size of V\textsubscript{2}O\textsubscript{5} is about 68 nm.

Optical properties of V\textsubscript{2}O\textsubscript{5}NPs are characterized by UV-Vis spectrophotometer as shown in figure 2a. The strong absorption peak occurs at maximum wavelength of 204 nm due to the transition of...
Table 2. Elemental composition of V2O5 NPs.

| Element | C  | V    | O  |
|---------|----|------|----|
| Atomic % | 17.72 | 39.95 | 42.29 |

Figure 3. PSA result of V2O5 NPs

Figure 4. (a) SEM image and (b) EDX spectra of V2O5 NPs

holes between vanadium and oxygen [17]. Figure 2b shows the Tauc’s plot of V2O5 NPs as resulted from UV-Vis DRS characterization to find out the band gap value. The band gap value of V2O5 NPs was obtained by calculating from the Kubelka-Munk equation. The calculation result shows the band gap value of V2O5 NPs was 2.42 eV.

PSA characterization aims to know the average of particles size distribution of V2O5. Figure 3 shows the average of particles size distribution of V2O5 NPs is 66.55 nm.

Figure 4a shows that the SEM image of V2O5 NPs morphology has an agglomerate shape. Further analysis about elemental composition on V2O5 NPs is illustrated in figure 4b. The EDX spectra of V2O5 NPs clearly confirm the presence of vanadium and oxygen. The elemental composition is shown in details in table 2. The presence of C happens due to the remains of organic compounds from CILE.

3.2. Photocatalytic performances of V2O5 NPs

UV-Vis absorption spectra of MB degradation were observed in the decrease of absorbance at maximum wavelength of 664 nm as shown in both Figure 5a and 5b. In addition, Figure 5c illustrates that MB degradation percentage with and without V2O5 NPs were 18.65 and 74.83 %, respectively after 120 min under visible irradiation. This result demonstrates that V2O5 NPs has an efficient photocatalytic activity to degrade organic pollutant such as MB.
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Figure 5. UV-Vis absorption spectra of MB degradation (a) with and (b) without V. O. NPs and (c) Degradation percentage of MB

4. Conclusions
V. O. NPs were successfully synthesized using Calophyllum inophyllum leaf extract (CILE) with average particles size distribution of 66.55 nm. V. O. NPs have a typical absorption peak at maximum wavelength of 204 nm and an average crystals size of 68 nm. V. O. NPs show V=O bond at 1023 cm$^{-1}$ and the V-O-V bond at 849 and 578 cm$^{-1}$. The band gap value of V. O. NPs was 2.42 eV. The degradation percentage of MB was 74.83% for 120 min. According to the results and discussions, we report that an eco-friendly based V. O. NPs has good photocatalytic activity in MB degradation under visible light irradiation.

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