TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} nanocomposite: Synthesis via \textit{Catharanthus roseus} (L.) G. Don leaf extract, characterization and its photocatalytic activity for malachite green degradation

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Abstract. TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} nanocomposite was successfully synthesized using leaf extract of \textit{Catharanthus roseus} (L.) G. Don. (CRE), precursors of TTIP and Co(NO\textsubscript{3})\textsubscript{2}. FT-IR characterization shows that TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} has been formed due to the presence of secondary metabolites in CRE which have a major role as a weak base source for nanocomposite synthesis. Particle size analysis was employed by PSA and TEM, which were found to be 38.04 nm and 90.80 nm, respectively. Besides, the UV-Vis DRS result shows that TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} has bandgap energy at 2.8 eV. According to the morphological analysis, TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} nanocomposite has a spherical shape confirmed by SEM. The structural analysis was confirmed by XRD that TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} nanocomposite has a diffraction pattern combination of TiO\textsubscript{2} and Co\textsubscript{3}O\textsubscript{4} nanoparticle. The photocatalytic activity of TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} nanocomposite was examined for malachite green degradation. The result shows that the degradation percentage was 82.61 % under visible light illumination for 120 min.

Keywords: \textit{Catharanthus roseus} (L.) G. Don.; photocatalytic activity; TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} nanocomposite, malachite green

1. Introduction

The utilization of plant media in nanoparticle synthesis is one step to reduce the risk in the use of harmful substances to the environment. \textit{Catharanthus roseus} (L.) G. Don. is one of the plants for metal oxide nanoparticle synthesis, containing 11.11 % of alkaloids in the leaves as a source of weak base and capping agents [1]. \textit{Datura metel} L., \textit{Tinospora crispa}, and \textit{Moringa oleifera} have been reported as tropical plants for metal oxide nanoparticle synthesis [2-4].

On the other hand, TiO\textsubscript{2} is a semiconductor that has a high photocatalytic activity in the form of anatase [5] and has a high melting point, photoactivity, and thermal stability. Also, TiO\textsubscript{2} is an excellent catalyst to be applied in the environment since it is non-toxic, low cost and inert material [6]. TiO\textsubscript{2} has been reported to have a bandgap energy (E\textsubscript{g}) around 3.0–3.2 eV [7]. The value of E\textsubscript{g} is related to the maximum absorption wavelength in the range of 365–400 nm, which is confirmed to be able to work in the ultraviolet (UV) area. This condition has become one of the significant obstacles in the use of TiO\textsubscript{2}-based sunlight because only 4–5 % of the sun rays contain the UV light. There are several thoughts regarding the development of TiO\textsubscript{2} as a catalyst material under sunlight illumination. One of them is to decrease their value of E\textsubscript{g} to enhance the absorption of sunlight, especially in the visible area [8].
On the other hand, Co$_3$O$_4$ can be used for TiO$_2$ doping due to its physical and chemical property [9]. Besides, Co$_3$O$_4$ has a bandgap value of 2.07 eV, which makes it efficiently absorbs the photons of visible light [10]. TiO$_2$ was successfully prepared to modify the Au nanoparticles to decrease its bandgap value [11]. This modification has been performed for the degradation of methyl orange [12], methylene blue and crystal violet [13].

In this work, we reported the synthesis of TiO$_2$/Co$_3$O$_4$ nanocomposite using Catharanthus roseus (L.) G. Don leaf extract for the degradation of malachite green under the visible light illumination.

2. Materials and method

2.1. Materials
Catharanthus roseus (L.) G. Don. leaves were collected from Indonesia, Ti(OCH(CH$_3$)$_2$)$_4$ (TTIP) (98.9 %), Co(NO$_3$)$_2$.6H$_2$O were purchased from Sigma-Aldrich and Merck, respectively. The distilled water, methanol and hexane were in analytical grade.

2.2. Preparation of Catharanthus roseus (L.) G. Don leaf extract
Catharanthus roseus (L.) G. Don leaves were washed by distilled water, then dried at room temperature for 10 days. The dried-Catharanthus roseus (L.) G. Don was ground to obtain the powders. Fifty g of leave powders were macerated in methanol for 7 days. The extract was filtrated, and further partitioned by hexane to obtain the methanol fraction. The extract was evaporated to separate its methanol, then dissolved into distilled water to get an aqueous fraction of CRE for nanocomposite synthesis [14-15].

2.3. Synthesis of TiO$_2$ nanoparticle
TiO$_2$ nanoparticles were prepared by stirring 2.96 mL Ti(OCH(CH$_3$)$_2$)$_4$ (TTIP) and 40 mL isopropanol for 20 min. The mixture was added with 10 mL CRE and stirred for 5 h, then calcined at 500 °C for 150 min to form the nanoparticle powders [16].

2.4. Synthesis of TiO$_2$/Co$_3$O$_4$ nanocomposite
0.1 g of TiO$_2$ powders were dispersed into 25 mL distilled water, then ultrasonicated for 30 min (Part A). Meanwhile, Co(NO$_3$)$_2$.0.01 M was added with 10 mL CRE and stirred for 20 min (Part B). Subsequently, part A and B were mixed and stirred for 5 h, then calcined at 800 °C for 150 min to form the nanocomposite powders [12].

2.5. Characterization of TiO$_2$/Co$_3$O$_4$ nanocomposite
All characterizations of TiO$_2$/Co$_3$O$_4$ nanocomposite comprise UV-Vis diffuse reflectance spectrophotometry (Shimadzu 2450), spectra absorption UV-Vis spectrophotometry (Shimadzu 2600), Fourier transform infrared (FT-IR Prestige 21 Shimadzu), X-ray diffraction (XRD Shimadzu 7000), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX JEOL JSM 6510 LA), particle size analyzer (PSA Malvern Zetasizer 1600) and transmission electron microscope (TEM JEOL JEM-1400).

2.6. Photocatalytic activity
TiO$_2$/Co$_3$O$_4$ nanocomposite powder was dispersed into malachite green solution and stirred for 1 h under the visible light illumination. The malachite green degradation was observed every 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 min using a UV-Vis spectrophotometer [17].
3. Results and discussion

3.1. FT-IR analysis of Catharanthus roseus (L.) G leaf extract
FT-IR analysis was performed to determine the primary functional group of CRE. There were some functional groups such as -OH groups (3373 cm\(^{-1}\)), C-H (2945 cm\(^{-1}\)), C = C (1589 cm\(^{-1}\)), C-H (1459 cm\(^{-1}\)), and C-N (1028 cm\(^{-1}\)) [18]. The presence of alkaloids was signed by the appearance of C = C and C-N functional groups. The -OH functional group indicates the presence of flavonoids secondary metabolite compound. Figure 1 shows that there are –OH, C=C, and C-N functional group at the wavenumber of 3367, 1641 and 1028 cm\(^{-1}\), respectively. The presence of these groups illustrate that CRE can be utilized in the synthesis of TiO\(_2\)/Co\(_3\)O\(_4\) nanocomposite.

3.2. Structural analysis of TiO\(_2\)/Co\(_3\)O\(_4\) nanocomposite
The structural of TiO\(_2\)/Co\(_3\)O\(_4\) nanocomposite was analyzed by XRD. Figure 2 shows the 2\(\theta\) value of TiO\(_2\)/Co\(_3\)O\(_4\) which was a combination of the TiO\(_2\) and Co\(_3\)O\(_4\). The 2\(\theta\) values of TiO\(_2\) were at 27.63; 35.49; 36.13; 36.12 and 49.27\(^\circ\), which were well-matched to the JCPDS card no. 21-1272. Meanwhile, the 2\(\theta\) values of Co\(_3\)O\(_4\) were at 32.90; 32.94; 32.99 and 53.59\(^\circ\) which were well-matched to JCPDS card no. 43-1003.

![Figure 1. FT-IR spectrum of Catharanthus roseus (L.) G Don leaf extract.](image1)

![Figure 2. XRD pattern of TiO\(_2\)/Co\(_3\)O\(_4\).](image2)
3.3. Particle size analysis of TiO$_2$/Co$_3$O$_4$ nanocomposite

Particle size of TiO$_2$/Co$_3$O$_4$ nanocomposite was analyzed with PSA and TEM. The average particle size distribution was 38.04 nm, confirmed by PSA as presented in figure 3a. For further characterization, TEM was utilized to confirm the particle size in more details. According to figure 3b, TiO$_2$/Co$_3$O$_4$ nanocomposite exhibits the particle size around 90.80 nm.

3.4. Morphological analysis of TiO$_2$/Co$_3$O$_4$ nanocomposite

TiO$_2$/Co$_3$O$_4$ nanocomposite was characterized using SEM-EDX to determine its morphology and atomic composition. SEM image shows that TiO$_2$/Co$_3$O$_4$ nanocomposite has a spherical shape, as shown in figure 4a. Based on the EDX result, TiO$_2$/Co$_3$O$_4$ nanocomposite contained the atomic composition of Ti, Co and O, which were found to be 19.42; 3.79 and 66.21 %, respectively, as shown in figure 4b.

3.5. UV-Vis DRS analysis of TiO$_2$/Co$_3$O$_4$ nanocomposite

The UV-Vis DRS characterization was conducted to define the bandgap energy of TiO$_2$/Co$_3$O$_4$ nanocomposite by measuring the per cent reflectance, which was then converted to the bandgap value by employing the Kubelka Munk equation. According to the calculation, TiO$_2$/Co$_3$O$_4$ nanocomposite has the bandgap value of 2.80 eV, as presented in figure 5a. Meanwhile, the bandgap energy of TiO$_2$ nanoparticle was 3.2 eV, as shown in figure 5b.

![Figure 3](image1.png)

**Figure 3.** (a) Particle size distribution and (b) TEM image of TiO$_2$/Co$_3$O$_4$ nanocomposite.

![Figure 4](image2.png)

**Figure 4.** (a) SEM image and (b) EDX spectrum of TiO$_2$/Co$_3$O$_4$ nanocomposite.
3.6. Photocatalytic degradation of malachite green using TiO$_2$/Co$_3$O$_4$ nanocomposite

The photocatalytic activity of TiO$_2$/Co$_3$O$_4$ nanocomposite was tested for the malachite green degradation under the visible light illumination. The degradation was observed at the wavelength of 617 nm as a typical peak of malachite green, as shown in figure 6. The results show that the degradation percentages of malachite green using TiO$_2$/Co$_3$O$_4$ nanocomposite and TiO$_2$ nanoparticle were 82.61 % and 46.03 % for 120 min, respectively.

4. Conclusion

TiO$_2$/Co$_3$O$_4$ nanocomposite has been successfully synthesized using CRE. Alkaloids and flavonoids were the essential secondary metabolites contained in CRE for nanocomposite synthesis. The bandgap value of TiO$_2$/Co$_3$O$_4$ nanocomposite was narrower than the bandgap value of TiO$_2$ nanoparticle. Also, TiO$_2$/Co$_3$O$_4$ nanocomposite has a good photocatalytic activity rather than TiO$_2$ nanoparticle, which significantly works as photocatalysts in the visible region. The synthesized nanocomposite has been structurally formed from a combination of TiO$_2$ and Co$_3$O$_4$ confirmed by XRD characterization.
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