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Functionalization of titanium dioxide through dye-sensitizing method utilizing red amaranth extract for phenol photodegradation

Y S Kurniawan¹, K Anggraeni², R Indrawati^{1,2} and L Yuliati^{1,2}

¹Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Malang 65151, Indonesia

²Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Malang 65151, Indonesia

Corresponding author's email: leny.yuliati@machung.ac.id

Abstract. In this work, red amaranth (RA) extract was utilized as the source of the natural pigments for dye-sensitizing of the TiO₂. The natural pigments were isolated from the RA leaves through a maceration technique to obtain the RA extract as a red powder. Since photocatalytic efficiency of titanium dioxide (TiO₂) under visible light is negligible, further modification such as by addition of dye-sensitizer is required. The TiO₂ was sensitized using the natural pigments contained in the RA extract using (3-aminopropyl)trimethoxysilane (APTMS) as the linker agent through an impregnation method to give the dye-sensitized TiO₂ composite (RA-APTMS/TiO₂). After dye-sensitizing, new absorption peaks at 1632–1030 cm⁻¹ were detected in the Fourier transform infrared (FTIR) spectra, which were corresponded to the functional groups of chlorophyll originated from the RA extract. Furthermore, the appearance of a new absorption peak at 665 nm in the diffuse reflectance ultraviolet-visible (DR UV-vis) spectra also supported the successful sensitization of the TiO₂ by the RA extract. Photocatalytic tests showed that while the unmodified TiO₂ could not degrade phenol under visible light, the RA-APTMS/TiO₂ composites exhibited photodegradation ability in 9, 13, 22 and 7 % when using 5, 10, 20 and 30 % mass ratio of the RA extract, respectively.

Keywords: Dye sensitizing, red amaranth, phenol degradation, photocatalyst, titanium dioxide

1. Introduction

Titanium dioxide (TiO₂) has been well recognized in the material chemistry field due to its outstanding physicochemical properties [1-4]. Because of that, it has been widely applied as sunscreen, opacifier, paint, and coating materials. TiO₂ can be used as sunscreen materials because it absorbs the ultraviolet light due to its semiconductor properties having band gap energy of 3.2 eV [5]. In photocatalysis field, TiO₂ has been used since 1956 when the photocatalytic activity of TiO₂ for water splitting was discovered by Mashio and coworkers [6]. Many efforts on developing and optimizing the photocatalytic activity of TiO₂ have been reported to improve the photocatalytic activity of TiO₂ under the visible light. Dye-sensitizing of TiO₂ offers a simple solution by combining TiO₂ and dyes to broaden the absorption region of TiO₂ to the visible region [7].



Red amaranth (RA) with the scientific name of *Amaranthus tricolor L.* is a red edible plant that is abundantly found in Indonesia. The RA is rich in natural pigments such as chlorophyll, betalain, anthocyanin and carotenoid. Therefore, it may serve as the dye sensitizer agent to enhance the photocatalytic of TiO₂ under the visible light. It has been reported that the use of solvent affected the type of pigments extracted from the natural sources [8]. In order to eliminate such solvent effect, in this study the RA was processed by a slow juicer and this would make all type of pigments could be extracted and utilized for TiO₂ dye-sensitizing process. After freeze-drying [9], the isolated natural pigments were then impregnated on the commercially available TiO₂ nanoparticles, employing (3-aminopropyl)trimethoxysilane (APTMS) as the linker agent. Furthermore, the mass ratio of the added RA extract to TiO₂ was varied in 5, 10, 20 and 30 % and the composites were evaluated for photocatalytic degradation of phenol under visible light as a representation for the environmental remediation process.

2. Experimental

The RA plant was bought from a supermarket in Malang, East Java, while TiO₂ nanoparticles (TiO₂ P25) and APTMS were purchased from Evonic Industries and Sigma Aldrich, respectively. The extraction method to obtain RA extract was carried out similarly to the previously reported literature [10]. Briefly, the RA leaves were cleaned, dried and then encapsulated with maltodextrin in 5 % wt/wt. The viscous extract was dried using the freeze-drying technique to obtain the desired RA extract.

The extracted natural pigments were immobilized through an impregnation process. Briefly, as much as 0.05, 0.1, 0.2 and 0.3 g of RA extract were separately added into 50 mL of ethanol. The mixture was homogenized and then added by 1 mL of APTMS. The mixture was kept stirred for 1 day at 27 °C. Subsequently, 1 g of TiO₂ nanoparticles was added into the mixture and the mixture was stirred again for 1 day at 27 °C. The composite materials were washed with ethanol and dried to yield RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials. The obtained materials were characterized by a Fourier transform infrared (FTIR, JASCO FTIR-6800) and diffuse-reflectance ultraviolet-visible (DR UV-Vis, JASCO V-760) spectrophotometers.

Prior to the photocatalytic reaction, the adsorption process of phenol onto the surface of the composite material was performed. As much as 50 mg of RA-APTMS/TiO₂ x material was added into 50 mL of phenol 50 mg L⁻¹ and the mixture was stirred for 1 h in the dark condition. Afterwards, the mixture was irradiated using halogen lamp with a light intensity of 1.1 mmol m⁻² s⁻¹ and a cut-off filter of 420 nm for 24 h to start the photodegradation process of phenol under visible light. The concentration of phenol before ([PhOH]₀) and after ([PhOH]_t) photodegradation process was measured by using high-performance liquid chromatography (HPLC, Shimadzu LC-20 AT, equipped with a photodiode array (PDA) detector, SPD-M20A). The stationary and mobile phases used were C18 and 100 % acetonitrile (0.8 mL min⁻¹), respectively, and the column oven was fixed at 40 °C. The percentage of phenol photodegradation was calculated using the following equation.

$$\% \text{ Photodegradation} = \frac{[\text{PhOH}]_0 - [\text{PhOH}]_t}{[\text{PhOH}]_0} \times 100 \%$$

3. Results and discussion

In the present work, the natural pigments of RA were employed as the sensitizer agents for TiO₂ materials to enhance its efficiency in the phenol photodegradation process under visible light irradiation. After the dye-sensitizing process using APTMS as the linker agent, the RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials were obtained and their photographs are shown in figure 1. It was shown that the color of TiO₂ material was changed from white to green indicating that green natural pigments were successfully immobilized on the surface of TiO₂.



Figure 1. Photograph images of unmodified TiO₂ and its composite materials.

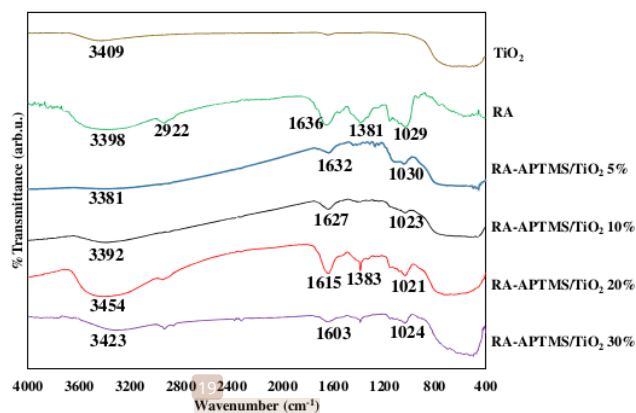


Figure 2. FTIR spectra of unmodified TiO₂, RA and the composite materials.

The obtained composite materials were characterized using FTIR spectrophotometer to identify their functional groups. The FTIR spectra of TiO₂, RA extract and RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials are shown in figure 2. The FTIR spectrum of TiO₂ shows two main absorption peaks at 3409 and 800–400 cm⁻¹ due to the presence of Ti–OH and Ti–O–Ti moieties, while the FTIR spectrum of RA shows five main absorption peaks at 3398, 2922, 1636, 1381 and 1029 cm⁻¹ for O–H, C–H, C=O, C–O and C–N functional groups, respectively. After the dye-sensitizing process, new peaks at 1603–1632, 1381–1383 and 1021–1030 cm⁻¹ were observed confirming the presence of green natural pigments on the TiO₂ composite materials.

In order to identify the effect of natural pigments on the absorption properties of the composite materials, the materials were characterized using DR UV-Vis spectrophotometer. The DR UV-Vis spectra of TiO₂, RA extract and RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials are shown in figure 3. The absorption peaks of TiO₂ were only observed at 248 and 301 nm (figure 3a), showing that the unmodified TiO₂ could not absorb visible light (400–800 nm), and is in good agreement with the reported literature [11]. In contrast, the RA gave both UV and visible light absorption peaks at 322, 439, 554 and 676 nm (figure 3b). After the dye-sensitizing process (figure 3c), the absorption peak and edge of TiO₂ at 301 nm and ca. 400 nm, respectively, were not influenced, indicating that the green natural pigments were located on the surface of TiO₂. Furthermore, a remarkable new peak was observed at 665 nm, which is the characteristic of the chlorophyll pigment [10]. Therefore, it can be suggested that the main immobilized green pigment on the RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials was chlorophyll.

The plausible structure of the immobilized chlorophylls on the surface of TiO_2 is shown in figure 4. As reported previously [12], the Ti-OH (from TiO_2) and Si-OCH_3 (from APTMS) would be condensed to form a new covalent bond of Ti-O-Si by losing of CH_3OH (methanol) as by-product. On the other hand, the chlorophylls would be mainly attached to the APTMS through ion-dipole interaction between $-\text{NH}_2$ (from APTMS) and Mg^{2+} ion (from chlorophyll). A similar ion-dipole interaction has been suggested to occur between the (3-chloropropyl)trimethoxysilane and betalain [10]. Comparison to the reported work [10], this study obviously showed that the immobilized pigment was strongly depended on the type of the linker. This fact again supported that the immobilized pigment would be attached to the linker, not the TiO_2 surface.

Since the DR UV-Vis spectra of RA-APTMS/ TiO_2 \times ($x = 5, 10, 20$ and 30%) materials show the absorption peak at visible region (665 nm), those materials are promising to be applied as photocatalyst materials under visible light irradiation. In this work, phenol was selected as the photodegradation target because phenol is well-known for its high thermal and chemical stability [13]. Furthermore, phenol pollution seizes the world's attention due to its disadvantages in generating serious diseases to the organism and aquatic environment [14]. The phenol was dissolved in distilled water at 50 mg L^{-1} concentration as the initial concentration and then irradiated for 24 h using a halogen lamp with a cut-off filter ($\lambda > 420 \text{ nm}$).

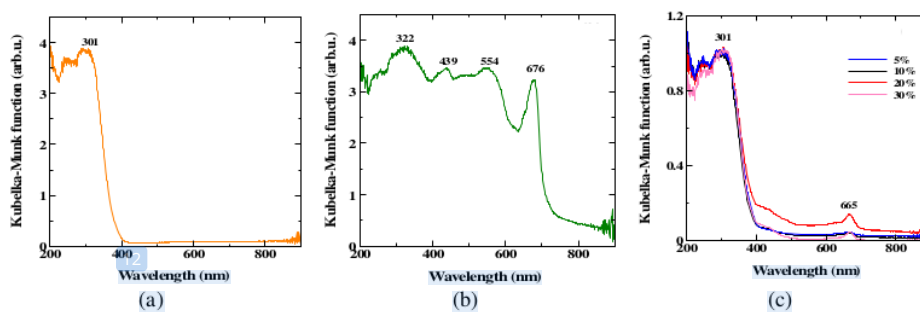


Figure 3. DR UV-Vis spectra of (a) unmodified TiO_2 , (b) RA and (c) the composite materials.

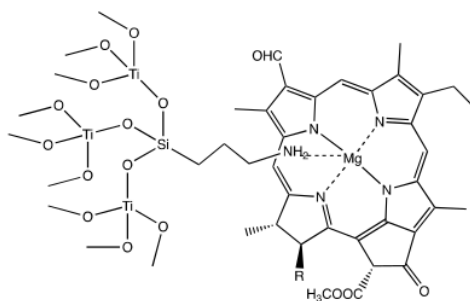


Figure 4. Plausible structure of impregnated chlorophyll as the main sensitizer on the surface of TiO_2 using APTMS as the linker agent.

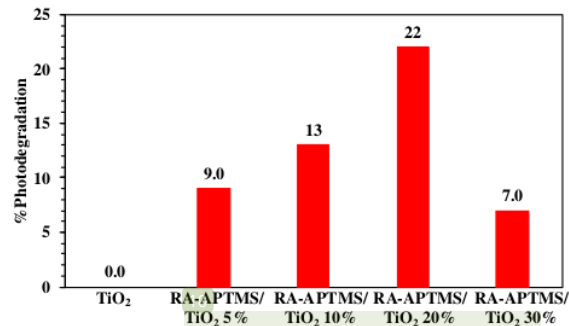


Figure 5. Photocatalytic activities of TiO₂ and the composite materials for phenol degradation process under visible irradiation.

The photocatalytic activities of TiO₂ and the composite materials for phenol degradation process under visible light irradiation are shown in figure 5. It was confirmed that the unmodified TiO₂ hardly degraded phenol under visible light (0 %), and was in good agreement with its DR UV-Vis spectrum which showed no absorption peak at above 420 nm. In contrast, after dye-sensitizing with RA extract, the RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials gave 9, 13, 22 and 7 % photodegradation of phenol, which were quite remarkable performances. The photodegradation percentage of phenol was successfully improved by increasing the amount of the impregnated chlorophylls on the RA-APTMS/TiO₂ materials up to 20 %, confirming that the chlorophyll acted as the sensitizer. However, the RA-APTMS/TiO₂ 30 % material gave a lower photodegradation percentage (7 %), suggesting that the optimum amount of RA would be ca. 20 %. The larger amount of RA might result in the formation of aggregated chlorophyll, which gave less efficiency in electron transfer and thus, inhibited the sensitizing process. However, it was clear that all the composites gave better photocatalytic activity than the unmodified TiO₂, demonstrating that RA could remarkably enhance the photocatalytic activity of TiO₂ under the visible region.

4. Conclusion

In the present work, dye-sensitizing of TiO₂ materials with chlorophyll as the major pigment on the RA extract were shown to successfully enhance the photodegradation percentage of phenol under visible light irradiation. The RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials were simply obtained as a greenish powder through an impregnation process employing APTMS as the linker agent in ethanol media. The successful impregnation of chlorophyll onto the TiO₂ surface was reflected by the presence of the FTIR absorption peaks of chlorophyll functional group, i.e. C=O, C=N, and C-N, and a new absorption peak at 665 nm in their DR UV-Vis spectra. From the phenol photodegradation experiment, it was revealed that the unmodified TiO₂ gave no photodegradation activity (0 %) while the RA-APTMS/TiO₂ x (x = 5, 10, 20 and 30 %) materials exhibited 9, 13, 22 and 7 % photodegradation activity. These findings offer open research to utilize the tropical plants as the dye sources to sensitize the TiO₂ materials for environmental remediation applications.

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