Synthesis of TiO$_2$ from TiCl$_4$ Using Morinda Citrifolia Root Extract as a Molecular Template and its Photocatalytic Activity to Methylene Blue Degradation

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Abstract. TiCl$_4$ successfully as precursors for synthesised TiO$_2$ in nanometer-sized through the sol-gel method on the variation of the concentration of root extract of M. Citrifolia and have shown photocatalyst activity to degrade methylene blue with UV radiation in 365 nm. The characteristics of TiO$_2$ synthesized such as crystalline, size and morphology using SEM. SEM analysis showed that the morphology of TiO$_2$ synthesized showed the spherical shape in the nanometer-sized. Examination of the energy bandgap using UV-Vis DRS showed a decrease bandgap for TiO$_2$ synthesized (TiO$_2$ Merck = 3.2 eV; TiO$_2$ 10x = 3.16 eV; TiO$_2$ 50x = 3.1 eV; TiO$_2$ 100x = 3.08 eV). The best degradation photocatalytic activity is demonstrated by TiO$_2$ 100x until 84.07%. The reaction rate of TiO$_2$ photocatalytic for the degradation of methylene blue follow a pseudo-second-order reaction model.

1. Introduction

The textile industry is one of the largest manufacturing industries in Indonesia and the world, which produces large amounts of clothing to meet market demand. This large quantity of textile production requires synthetic dyes as dyes. Not all dyes can be used entirely in the dyeing process, but 15% of the total unused dye is discharged into the environment as waste. Among the reactive dyes available, methylene blue is a dye that is often used in the textile industry. The resulting dye waste can cause damage to the aquatic ecosystem due to the high concentration of organic compounds contained in it. In addition, the textile liquid waste cannot be decomposed naturally, so it is challenging to process it with a simple method. Therefore, an environmentally friendly waste treatment method is needed [1].

Many kinds of research on the treatment of liquid waste originating from the industry have been carried out, one of which is utilized sunlight to produce photocatalytic reactions. Sunlight producing photocatalyst reactions has become a concern because it can fulfil the concept and support innovative technologies from the application of Green Chemistry. Green synthesis offers various methods that can reduce or even eliminate harmful substances to humans and the environment [2]. Furthermore, green synthesis opens up new opportunities in particle synthesis using biomimetic mechanisms such as nanosilver manufacturing using Morinda citrifolia root extract. Among various oxide semiconductor photocatalysts, titanium dioxide is the most exciting semiconductor to be tested. Titanium dioxide (TiO$_2$) is a stable, relatively inexpensive, non-toxic and environmentally friendly semiconductor. TiO$_2$ with an energy gap of 3.2 eV in the anatase phase can be activated by ultraviolet light with a maximum wavelength of 385 nm [3].

The synthesis of nanoparticles with plant extracts provides several advantages compared to other methods, such as the process is more straightforward, cheaper, the materials are easy to obtain and tend
to produce more stable materials. Green synthesis using plant extracts can be carried out using the sol-gel route with the hydrolysis method. The synthesis of TiO$_2$ from TiCl$_4$ by a hydrolysis method with the help of none extract (Morinda citrifolia) as a particle shape guide has produced nanometer-sized TiO$_2$ and shows the stability of the solution, which remains homogeneous after the addition of ammonium. Therefore, testing the ability of the photocatalytic reaction of TiO$_2$ to decompose methylene blue dye is the idea offered in this study.

2. Method

TiO$_2$ synthesis was carried out by mixing 20 ml of TiCl$_4$ in demineralized water and dye from Morinda citrifolia root extract with various concentrations. The colloid formed was left at room temperature for 8 hours. After being allowed to stand, the colloid formed was added to 100 ml of 1M NH$_4$OH slowly into the solution while stirring using a magnetic stirrer at a speed of 300 rpm. After that, it was heated for 2 hours at a temperature of 50°C with a water bath, then allowed to stand again for 42 hours. After the colloid was formed, the solution was centrifuged at 6000 rpm for 15 minutes and then decanted. The TiO$_2$ obtained after centrifugation was then dried. TiO$_2$ characterization to analyze the energy value of TiO$_2$ band gap using UV-Vis DRS (UV-Vis Diffuse Reflectance) and surface morphology analysis by using SEM. TiO$_2$ photocatalytic activity test to decompose 100 ml methylene blue solution with a concentration of 3 ppm and pH 11. The methylene blue solution to be degraded first measured the initial absorbance value, then added TiO$_2$ with a dilution of 10x, 50x, 100x as much as 0.1 grams each. In a beaker and then measure the absorbance again.

Furthermore, the glass is irradiated with UV light for 12 hours. During the irradiation process with UV light, the solution is stirred with a magnetic stirrer. Finally, the obtained supernatant was measured its absorbance value by UV-Vis spectrophotometer at the maximum wavelength of methylene blue.

3. Results and Discussion

The synthesis of TiO$_2$ which was carried out at temperatures below 5°C for exchanging chloride ions with hydroxide ions, aims to convert TiCl$_4$ precursors into Ti(OH)$_4$ so that the TiO$_2$ particles formed are easily formed directed to nano size. This synthesis must be carried out at low temperatures because if it is carried out at high temperatures, the O-Ti-O condensation process will be fast so that the size of the crystal nucleus of the TiO2 particles formed will be more significant. This is because the condensation is determined by the hydrolysis rate affected by the system’s temperature. Therefore, during the ligand exchange process, the temperature must be conditioned to remain stable using an ice bath to change the hydrolysis reaction slowly. The following is the equation for the condensation process that occurs:

$$\text{TiCl}_4(\text{aq}) + 4\text{H}_2\text{O}(l) \rightarrow \text{Ti(OH)}_4(\text{aq}) + 4\text{HCl}(\text{aq})$$

The use of noni root extract in the synthesis process aims as a template to allow the particles that grow to be of uniform size. Stock Solution of many root extracts with water solvent in powder was obtained from a previous study [11]. Making this extract solution is by dissolving the powder into DM water until it is saturated. Then three different concentration variations were made, namely: 10x, 50x and 100x dilutions. This synthesis process was also carried out by adding 100 mmol of ammonium used to control the O-Ti-O condensation process by forming molecular clusters. This cluster can act as a squeezing agent for molecules of various sizes. The cluster formed is influenced by the number of moles of ammonium added to the colloid. The addition of ammonium can also form a salt with HCl resulting from the previous reaction with the following reaction equation:

$$\text{NH}_4\text{OH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq}) + \text{H}_2\text{O}(l)$$

The next step is heating the colloid formed at 50°C for two hours. Heating is done because energy is needed to direct the atoms to form the desired crystal arrangement during the crystal formation process. The particles that are expected to form during this synthesis are nano-sized. The nanometer-sized particles are colloidal so that the TiO$_2$ particles dispersed in water will have the characteristics of a colloidal solution [4]. The smaller the particle size formed, the more stable the colloid produced. The muscle structure formed is believed to stabilize the particles in the particle growth or ageing process, so it is expected that the particles can be arranged stably and homogeneously. Furthermore, the muscle
structure, a molecular printing agent, will provide the desired morphology and particle size with the addition of dye from non root extract and the right amount of mmol ammonium.

Figure 1 provides information on the morphology and particle size of the synthesized TiO$_2$ with 10x, 50x and 100x dilutions, showing that the morphology of TiO$_2$ is elliptical in size in the nanometer range. In Figures 1a and 1b, the morphology of TiO$_2$ particles is uniformly spherical in certain areas and overlaps each other, while Figure 1c is seen as elongated and close to each other in most certain areas. This indicates that TiO$_2$ powder has been successfully synthesized. From SEM photography, it can be seen that the TiO$_2$ particles are close together and agglomerate to form porous spaces. The effect of drying temperature and noni root extract dye on the sample caused the particles to agglomerate.

![Figure 1](image.png)

**Figure 1.** SEM micrograph of as-synthesized a. TiO$_2$ 10x, b. TiO$_2$ 50x dan c. TiO$_2$ 100x.

Determination of the energy bandgap value was carried out by UV-Vis DRS characterization. The energy band gap value of TiO$_2$ is between 3.0-3.2 eV. Determination of the energy bandgap value using the Kubelka-Munk equation where $E_g$ is obtained from the graph of the relationship between $[F(R\infty)hv]^2$ to $hv$ (eV) [5]. The energy gap is obtained from the intersection of the straight lines on the curve that intersects the x-axis. Through the UV-Vis DRS characterization, the bandgap value of the synthesized TiO$_2$ can be obtained. The energy gap value obtained from the sample characterization is the energy of the TiO$_2$ material required to create electrons and holes that will be used in photocatalytic reactions as photooxidation-reduction initiators. The addition of noni extract with a particular concentration variation affected the energy value of the bandgap on TiO$_2$. The factor of decreasing the energy gap value is also because the synthesized TiO$_2$ crystal phase is mixed. Namely, there are anatase and rutile phases.
Table 1. Bandgap energy ($E_g$) as-synthesized TiO$_2$

| No | Sample         | Bandgap energy |
|----|----------------|----------------|
| 1  | TiO$_2$ Merck  | 3.20 eV        |
| 2  | TiO$_2$ 10x    | 3.16 eV        |
| 3  | TiO$_2$ 50x    | 3.10 eV        |
| 4  | TiO$_2$ 100x   | 3.08 eV        |

Table 1 shows that the Merck TiO$_2$ band gap is 3.20 eV. This value becomes a reference for comparison with the synthesized TiO$_2$. The synthesized TiO$_2$ showed a decrease in the bandgap value compared to Merck’s TiO$_2$, where the bandgap values of TiO$_2$ 10x, TiO$_2$ 50x and TiO$_2$ 100x were 3.16 eV, 3.10 eV and 3.08 eV, respectively. With a smaller bandgap value, it can be assumed that the synthesized TiO$_2$ with the addition of noni extract will be more responsive towards visible light wavelengths.

Figure 2. Degradation data of Methylene blue: a: without TiO$_2$+UV, b: TiO$_2$, c: TiO$_2$ 10x+UV, d: TiO$_2$ 50x+UV dan e: TiO$_2$ 100x+UV.

Figure 2 shows a graph of the decrease in methylene blue concentration with TiO$_2$ 10x, 50x and 100x sharper than without TiO$_2$ with UV radiation and TiO$_2$ without UV radiation. In the first 10 minutes, when the methylene blue solution to which TiO$_2$ was added was homogenized, a very steep decrease in concentration was seen. This indicates that apart from functioning as a catalyst, TiO$_2$ also has properties as an adsorbent [6]. Titanium dioxide has a surface area that allows methylene blue to be adsorbed on the surface of TiO$_2$ with weak bonds to be released. Degradation of methylene blue increases with increasing radiation time. Table 2 shows the degradation of methylene blue with TiO$_2$ photocatalyst with various dilutions as synthesize conditions (10x, 50x and 100x), showed almost the same percentage of degradation, which were 84.07%, 84.42% and 85.10%, respectively. Successively. The graph shows that the optimum time for methylene blue degradation in the three treatments is at the 300 minute, where the graph looks straight from the 300th to the 720th minute. The highest percentage of degradation was obtained from treatment with 100x TiO$_2$ and UV radiation.

Table 3 shows various calculations for the kinetics of TiO$_2$ photocatalysis for methylene blue degradation is most suitable following the pseudo-second-order reaction model. They are plotting $t/q_t$ as the Y-axis and $t$ as the X-axis produces a straight line with the highest correlation coefficient ($R^2$), i.e. 0.9965 at 10x, 0.9971 at 50x and 0.9979 at 100x. The rate constant (k) and adsorption capacity at equilibrium ($q_e$) is generated from the modelling. This is related to the energy band gap value analyzed by the UV-Vis DRS tool that the smaller the bandgap energy value, the higher the correlation coefficient value. Therefore, the high value of $R^2$ results in this modelling ensures that the binding reaction of methylene blue by TiO$_2$ proceeds through a second-order reaction.
Table 2. Photocatalyst performance on the degradation of methylene blue.

| No | Sample          | Percentage degradation | Photocatalyst activity |
|----|----------------|------------------------|------------------------|
| 1  | TiO₂            | 48.70%                 | -                      |
| 2  | TiO₂ 10x + UV   | 84.07%                 | 35.37%                 |
| 3  | TiO₂ 50x + UV   | 84.42%                 | 35.71%                 |
| 4  | TiO₂ 100x + UV  | 85.10%                 | 36.40%                 |

Table 3. The kinetics model for TiO₂ photocatalytic reaction of methylene blue degradation.

| Kinetics Model | Parameter | 10x        | 50x        | 100x       |
|----------------|-----------|------------|------------|------------|
| Orde 1         | k (min⁻¹) | 0.0019     | 0.002      | 0.002      |
|                | R²        | 0.6826     | 0.7211     | 0.6636     |
| Orde 2         | k (mM⁻¹min⁻¹) | 0.0019    | 0.002      | 0.0021     |
|                | R²        | 0.8811     | 0.8965     | 0.8455     |
| Pseudo Orde 1  | k (min⁻¹) | 0.003      | 0.0042     | 0.0052     |
|                | R²        | 0.9437     | 0.906      | 0.8383     |
| Pseudo Orde 2  | k (mM⁻¹min⁻¹) | 0.3265    | 0.3227     | 0.3213     |
|                | R²        | **0.9965** | **0.9971** | **0.9979** |

Based on the rate law, the constant rate values listed in the table can be included in the rate law equation for the reaction. The rate law for the reaction of TiO₂ 10x is v=0.3265 (qₑ−qₜ)². TiO₂ 50x is v=0.3227 (qₑ−qₜ)² dan TiO₂ 100x is v=0.3213 (qₑ−qₜ)². Qₑ is the adsorption capacity of methylene blue at equilibrium, and qₜ is the adsorption capacity of methylene blue at time t.

4. Conclusions
We successfully synthesised TiO₂ from TiCl₄, which have high performance in catalytic activity on methylene blue degradation. TiO₂ from TiCl₄ has been successfully synthesized by the sol-gel method using noni root extract (Morinda citrifolia), which produces nanometer-sized TiO₂ crystals. The photocatalytic activity of TiO₂ 100x with UV radiation showed the most significant degradation of methylene blue at 85.10%, TiO₂ 50x at 84.42% and TiO₂ 10x at 84.07%.

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