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MORALITY BEFORE KNOWLEDGE

Enhanced photocatalytic degradation of methylene blue in textile wastewater using high-crystallinity TiO_2 nanotubes synthesized by post-hydrothermal treatment

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ABSTRACT

Background: The textile industry has seen rapid progress but is also responsible for wastewater pollution, especially from dye substances such as methylene blue, which are difficult to degrade. The need for efficient wastewater treatment is crucial in addressing environmental issues related to textile production. Photocatalysis is one promising method for wastewater treatment, utilizing titanium dioxide (TiO_2) as a photocatalyst. One approach to enhance the photocatalytic activity of TiO_2 is to modify its structure into nanotubes, which offer a high surface area-to-volume ratio. This study aims to synthesize TiO2 nanotubes with high crystallinity for improved photocatalytic performance. **Methods**: TiO_2 nanotubes were synthesized using a post-hydrothermal treatment process, followed by characterization using scanning electron microscopy (SEM) to evaluate the morphology of the nanotubes. The degradation of methylene blue was used as a model for evaluating the photocatalytic activity of the synthesized TiO_2 nanotubes under optimal conditions. **Findings:** The SEM characterization revealed that TiO_2 nanotubes synthesized at 100°C exhibited the best structure, leading to superior photocatalytic performance. These nanotubes were effective in degrading methylene blue, demonstrating a higher degradation rate compared to other conditions. **Conclusion**: The post-hydrothermal synthesis of TiO_2 nanotubes at 100°C results in enhanced photocatalytic activity, making it a promising material for textile wastewater treatment, specifically for methylene blue degradation. **Novelty/Originality of this article:** This study presents a novel application of TiO_2 nanotubes synthesized through post-hydrothermal treatment to address the degradation of methylene blue in textile industry wastewater. The use of optimized synthesis conditions for improved photocatalytic performance contributes new insights into the field of wastewater treatment technologies.

KEYWORDS: TiO2 nanotubes; post-hydrothermal; methylene blue wastewater.

1. Introduction

Technological advancements in Indonesia have significantly accelerated, driving the emergence of numerous industries producing various products to meet daily needs, including food, beverages, pharmaceuticals, clothing, and more. However, many of these industries generate liquid waste, often containing pollutant concentrations that exceed the minimum permissible thresholds. Among these pollutants is methylene blue, a dye frequently used in the textile industry. The widespread use of synthetic dyes in this sector is primarily due to their affordability, durability, availability, and ease of application.

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Nevertheless, synthetic textile dyes pose a significant environmental challenge, as the resulting wastewater remains colored and difficult to degrade. Such wastewater must undergo proper treatment before being discharged into water systems (Naimah et al., 2014).

Several conventional methods for treating textile wastewater have been extensively developed by researchers, including chlorination, ozonation, and biodegradation. Despite their effectiveness, these methods are associated with high operational costs and implementation challenges, particularly in Indonesia. Adsorption processes, although commonly employed, are less effective as the organic waste adsorbed accumulates in the adsorbent, potentially causing secondary environmental problems over time (Utubira et al., 2006). This limitation necessitates exploring alternative methods that are both efficient and environmentally friendly.

An alternative approach to treating textile wastewater is the photocatalytic method (Parent et al., 1996). This method involves oxidation-reduction reactions facilitated by electron-hole pairs, resulting in the production of hydroxyl radicals (OH), which are capable of degrading harmful organic pollutants. Compared to conventional methods, photocatalysis offers distinct advantages, including non-hazardous waste by-products, reduced chemical and energy usage, and greater efficacy in degrading both organic and inorganic compounds. The process leverages the dual roles of photocatalysts as reductants and oxidants, providing a versatile solution to wastewater treatment challenges.

Titanium dioxide (TiO_2) is a commonly used photocatalytic material. Naturally occurring as titanium oxide, TiO_2 possesses several advantages: excellent optical properties, non-toxicity, affordability, robust photocatalytic activity, a wide band gap, and abundant natural availability. To further enhance its photocatalytic activity, structural modifications are necessary, such as the development of nanotubes. These modifications aim to improve the material's performance and adaptability in wastewater treatment applications. The objectives of this study include investigating the effects of temperature variation on the characteristics of synthesized TiO_2 nanotubes, evaluating the impact of temperature variation on reducing methylene blue concentrations in liquid waste, and synthesizing TiO_2 nanotubes with high crystallinity and low band gap energy to enhance their degradation rates for methylene blue. Additionally, this research seeks to reduce liquid waste in Indonesia through innovative treatment methods.

Nanotubes are increasingly favored for morphological modifications due to their high surface area-to-volume ratio. This feature enhances light scattering, leading to increased light absorption. Titanium nanotubes with ordered structures have been successfully synthesized using various methods, including deposition within nanoporous alumina templates (anodizing reaction) (Kasuga et al., 1998), sol-gel reactions (Gao et al., 2009), and hydrothermal processes (Hayashi & Hakuta, 2010). Each method offers distinct advantages that contribute to the development of highly efficient photocatalytic materials.

This study employs the hydrothermal method to fabricate nanotubes with smaller diameters, thinner walls, and high crystallinity. These properties enhance their potential as catalysts for accelerating the degradation of textile wastewater pollutants like methylene blue. Previous studies, such as that by Yuwono et al. (2011), demonstrated that combining pre-annealing treatment at 300°C for six hours with post-hydrothermal treatment at 100–150°C significantly improved the nanocrystallinity of TiO2 anatase phases, resulting in nanotubes with a maximum crystal size of 18.30 nm and a minimum band gap energy of 3.21 eV.

2. Methods

This research was conducted at the Chemistry Laboratory of Universitas Bhayangkara Jakarta Raya, Campus II Bekasi. The study spanned one year, from April 2019 to April 2020. The extended timeframe was due to difficulties in acquiring the required equipment, the lengthy experimental process, and disruptions caused by the COVID-19 pandemic in

Indonesia. The research focused on synthesizing and evaluating TiO_2 nanotubes through various treatments and testing their efficacy in degrading methylene blue in wastewater.

The study involved three types of variables. The independent variable, which was not explicitly defined, allowed comparisons between commercial TiO_2 P25 Degussa and processed ilmenite mineral. The dependent variable included the processes involved in synthesizing TiO_2 nanotubes, such as pre-hydrothermal treatment, rinsing, drying, pre-annealing, and post-hydrothermal treatment. Control variables were maintained to ensure consistency, such as the sequence of synthesis procedures and the criteria for evaluating successful nanotube formation.

The equipment utilized included autoclave hydrothermal reactors, beakers, Erlenmeyer flasks, measuring cylinders, aluminum foil, Whatman filter paper, glass funnels, pH meter paper, a hot plate magnetic stirrer, a Memmert UN55 oven, digital scales, oven trays, droppers, stirring rods, scissors, syringes, general stationery, and Scanning Electron Microscopy (SEM). Materials used were TiO_2 P25 Degussa, distilled water, NaOH, HCl, and methylene blue.

The procedure began with material preparation to ensure all components met the requirements for accurate analysis. TiO_2 P25 Degussa powder, distilled water, NaOH pellets, HCl solution, and methylene blue were measured and prepared. One gram of TiO_2 was mixed with 12 grams of NaOH pellets and 30 ml of distilled water to form a 10 M solution. This mixture was stirred using a magnetic stirrer for one hour to achieve homogeneity and then transferred to a Teflon-lined hydrothermal reactor.

The pre-hydrothermal process involved sealing the solution in the reactor and heating it at 150°C for 48 hours in a Memmert oven. Afterward, the autoclave was cooled naturally to room temperature before cautiously opening it. The resulting thick gel-like product was poured into a funnel lined with filter paper, allowing excess water to drain. The product was rinsed alternately with distilled water and 0.1 M HCl solution three times until its pH reached neutrality, as confirmed using pH meter paper.

The filtered product was dried in an aluminum foil-lined tray at 110°C for 12 hours. Once dried, it was returned to the hydrothermal reactor for pre-annealing, which involved heating at 150°C for 6 hours. Subsequently, post-hydrothermal treatment was performed at varying temperatures (80°C, 100°C, 120°C, and 150°C) for 24 hours. During this stage, the samples were placed carefully in the reactor to avoid direct contact with water, creating a controlled environment by adding a small amount of water to the reactor.

The morphology of the synthesized TiO_2 nanotubes was analyzed using SEM at the Department of Metallurgical and Materials Engineering, Universitas Indonesia. Photocatalytic testing was conducted using a 1% methylene blue solution, prepared by mixing 5 ml of methylene blue with 500 ml of distilled water. After stirring for 10 minutes, 75 ml aliquots were placed in containers labeled according to treatment conditions (80°C, 100°C, 120°C, 150°C, and a standard solution without TiO_2 nanotubes). These solutions were exposed to direct sunlight for three cycles of 8 hours each to evaluate the degradation performance of the TiO_2 nanotubes.

3. Results and Discussion

3.1 Characteristics of TiO_2 nanotubes

The characteristics of the synthesized TiO_2 nanotubes were examined using Scanning Electron Microscopy (SEM) to investigate the morphology and structure under varying post-hydrothermal treatment conditions. The SEM images provided detailed observations of the tube-like structures, which were influenced by the temperature and duration of the post-treatment process. These morphological observations revealed distinct tube-like structures that formed under different post-hydrothermal treatment conditions, with varying degrees of uniformity and structural integrity.

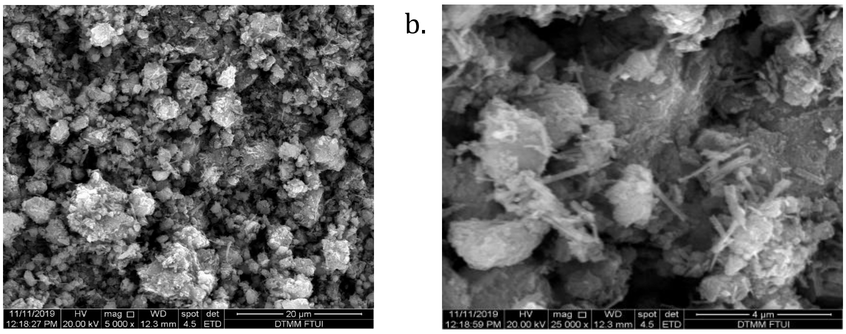

Fig 1. (a) Sample A result in SEM post-hydrotermal for 80ºC after 24 hours (b) Magnified picture of sample A result

Sample A, treated at 80°C for 24 hours, showed the presence of some tubular structures scattered around the TiO_2 surface. However, the distribution of these structures was not uniform, with some areas displaying a lack of well-defined tube formation. The irregularities in structure suggest that the formation process at this temperature was incomplete, likely due to insufficient thermal energy to promote the growth of uniformly distributed nanotubes. This finding indicates that a lower temperature may not provide the necessary conditions for the formation of high-quality TiO_2 nanotubes, limiting their potential applications in various fields.

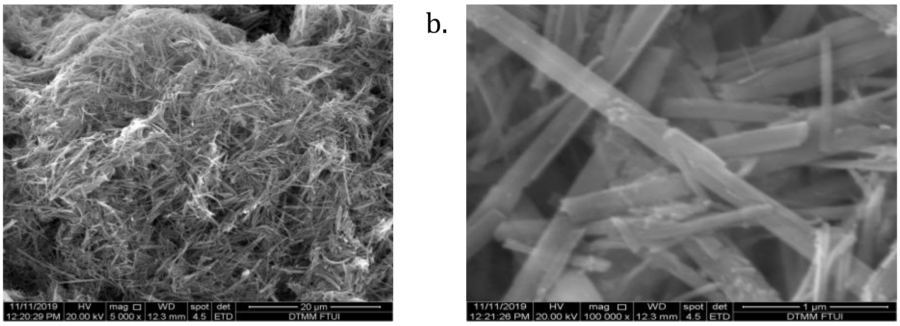

Fig 2. (a) Sample B result in SEM post-hydrotermal for 80ºC after 24 hours (b) Magnified picture of sample B result

Sample B, subjected to a post-hydrothermal treatment at 100°C for 24 hours, exhibited well-developed and highly organized nanotube structures. The SEM images revealed a high density of tube-like formations, which were distributed uniformly across the entire TiO_2 surface. This uniform distribution of the nanotubes indicates that 100°C is the optimal temperature for forming TiO_2 nanotubes, as it promotes the consistent growth of nanotubes across the surface without compromising their structural integrity. The high density and organization of the nanotubes observed in Sample B suggest that the post-hydrothermal treatment at 100°C effectively supports the formation of well-defined and highly ordered TiO_2 nanotubes, in agreement with prior research findings.

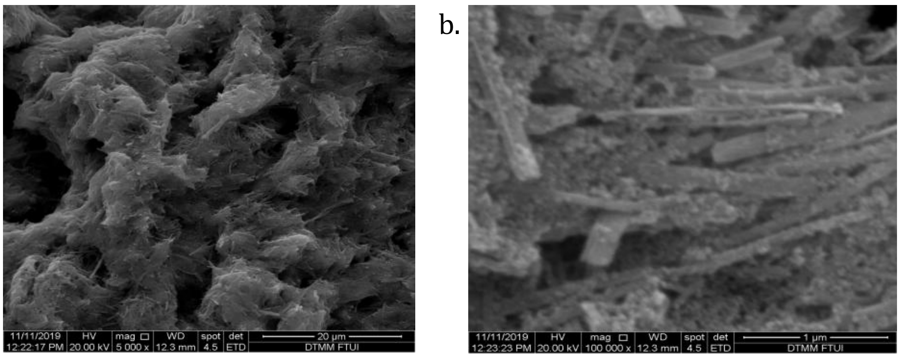

Fig 3. (a) Sample C result in SEM post-hydrotermal for 80ºC after 24 hours (b) Magnified picture of sample C result

Sample C, treated at 120°C for 24 hours, displayed fewer tubular structures compared to Sample B, indicating a decrease in nanotube formation at higher temperatures. The SEM analysis revealed areas where the nanotube structures appeared to have collapsed or become denser and more compact, suggesting that the higher temperature compromised the structural integrity of the nanotubes. These observations align with the hypothesis that elevated temperatures may lead to the collapse or deformation of the nanotube structures, potentially due to excessive thermal energy that disrupts the delicate formation process. Thus, the results suggest that while higher temperatures may still produce some nanotubes, they may not maintain the same level of uniformity and structural quality observed at lower temperatures.

a. b.

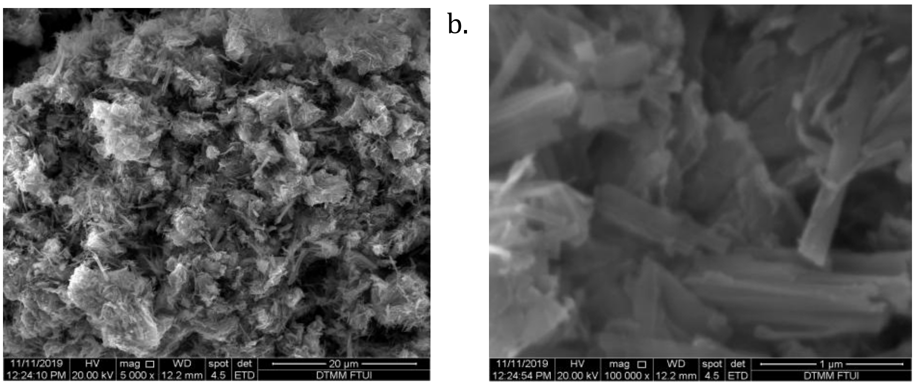

Fig 4. (a) Sample D result in SEM post-hydrotermal for 80^{o}C after 24 hours (b) Magnified picture of sample D result

Sample D, treated at 150°C for 24 hours, showed limited tubular formations, which were similar to the results observed in Sample C. However, the structural compactness observed in Sample C was less pronounced in Sample D, indicating that the higher temperature treatment at 150°C further diminished the formation of well-defined nanotubes. While some nanotube structures were still present, their density and organization were much lower compared to those formed at 100°C. These results suggest that post-hydrothermal treatment at 150°C is less effective in producing high-quality TiO_2 nanotubes, as the nanotubes formed at this temperature were less structured and more compact. This finding supports the conclusion that excessively high temperatures may hinder the optimal formation of TiO_2 nanotubes.

The findings from this study highlight that post-hydrothermal treatment at 100°C for 24 hours is the most favorable condition for producing high-quality TiO_2 nanotubes. The uniformity, high density, and structural integrity observed in Sample B demonstrate that this treatment temperature yields the best results in terms of nanotube formation. The results from the higher temperature treatments (120°C and 150°C) further emphasize that temperatures above 100°C lead to compromised structural integrity and less effective nanotube formation. These conclusions are consistent with prior research, which suggests that temperatures around 100°C are optimal for achieving high-quality TiO_2 nanotubes, making this post-hydrothermal treatment condition highly suitable for potential applications in various technological and industrial fields.

3.2 Photocatalytic activity of TiO2 nanotubes

The results from the analysis of TiO_2 P25 Degussa nanotubes using a photocatalytic method to degrade methylene blue dye are as follows.

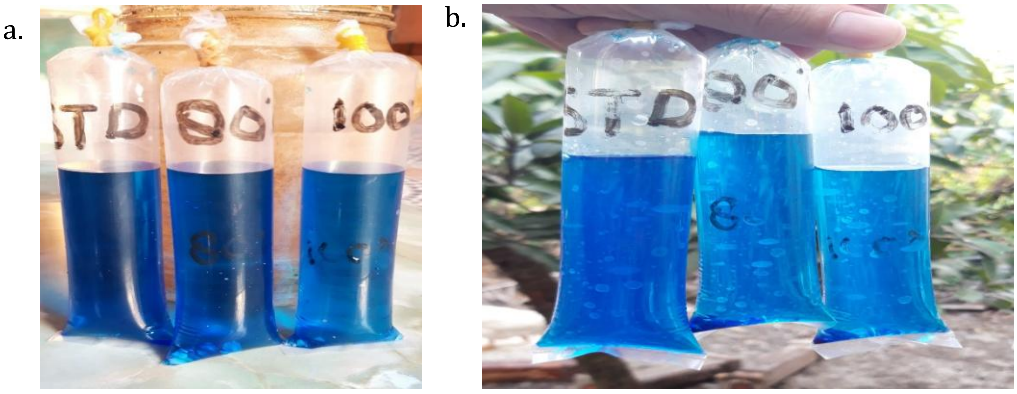

Fig 5. (a) All three samples before sun exposure (b) All three samples after sun exposure for the first round of 8 hours

After the first sun exposure, the methylene blue dye in the sample showed minimal fading. This indicates that the dye undergoes some degradation when exposed to direct sunlight, although the effect is slight, as observed in the figure. In comparison, the samples labeled 80 and 100 also showed fading of the dye, and the differences were visible when compared to the STD sample, suggesting that the photocatalytic process may be starting to take effect, even with limited exposure.

Fig 6. All three samples after sun exposure for the second round of 8 hours

Following the second round of sun exposure, the methylene blue dye in the STD sample showed almost no change compared to the first exposure. In contrast, the dye in the 80 and 100 samples continued to fade more significantly, indicating an ongoing improvement in the degradation process. This suggests that extended sun exposure enhances the photocatalytic activity, and the effect becomes more pronounced with each cycle.


Fig 7. All three samples after sun exposure for the third round of 8 hours

After the third round of sun exposure, the methylene blue dye in the STD sample showed minimal fading compared to the previous two cycles. However, the 80 and 100 samples exhibited even more noticeable fading, indicating further degradation of the dye. The water in these samples became progressively clearer, demonstrating the increasing effectiveness of the TiO_2 nanotubes in degrading methylene blue dye over time.

Fig 8. The difference in color of the samples before and after the first to the third sun exposure

In conclusion, TiO_2 nanotubes showed significant potential in degrading methylene blue dye. The degradation increased progressively with each sun exposure cycle, with the 80 and 100 samples showing a marked improvement in dye fading compared to the STD sample. This confirms the efficacy of TiO_2 nanotubes in photocatalytically degrading methylene blue, with the process being enhanced by prolonged exposure.

3.3 Analysis of temperature effects on TiO_2 nanotube synthesis

The effect of temperature on the synthesis of TiO_2 nanotubes was clearly demonstrated by the differences observed in the morphology and photocatalytic performance of the samples. At lower temperatures, such as 80°C, the tubular structures were incomplete and inconsistently distributed across the TiO_2 surface. This uneven distribution of nanotubes at lower temperatures resulted in lower photocatalytic activity, as the incomplete structures provided limited surface area for sunlight-driven degradation.

As the temperature increased to 100°C, the formation of nanotubes became more uniform and structurally intact, resulting in the highest photocatalytic performance among the samples. The optimal nanotube morphology at 100°C, with well-defined and densely packed structures, contributed to a larger reactive surface area for efficient photocatalysis. These observations support the conclusion that a post-hydrothermal treatment at 100°C for 24 hours yields the most desirable TiO_2 nanotube characteristics for photocatalytic applications, aligning with previous findings that suggest this temperature is ideal for promoting the formation of high-quality nanotubes.

However, as the temperature continued to rise to 120°C and 150°C, the structural integrity of the nanotubes deteriorated, leading to a decrease in photocatalytic efficiency. The SEM analysis of these samples revealed signs of structural collapse and compactness, which likely hindered their photocatalytic performance by reducing the surface area available for interaction with sunlight. These findings emphasize the critical role of temperature in determining the quality and functionality of TiO_2 nanotubes. The optimal synthesis conditions—specifically, a post-hydrothermal treatment at 100°C—are essential for producing nanotubes with both superior structural integrity and photocatalytic properties, making them highly effective for environmental remediation purposes.

The results underscore the importance of carefully controlling synthesis parameters, particularly temperature, to achieve TiO_2 nanotubes with the most desirable characteristics. The trade-off between higher temperatures and structural integrity highlights the need for precise temperature optimization in the synthesis process to ensure the production of TiO_2 nanotubes with optimal photocatalytic performance. By maintaining these controlled conditions, it is possible to enhance the efficiency of TiO_2 nanotubes for a wide range of environmental applications, including wastewater treatment and air purification.

4. Conclusions

Based on the research conducted, it can be concluded that the TiO_2 nanotubes formed from the synthesis of Titanium Dioxide P25 Degussa have the following results: The TiO_2 nanotubes formed were proven to be applicable in degrading the dye methylene blue. It is expected that TiO_2 nanotubes can be used for waste management, particularly for liquid waste in the textile industry, which commonly uses methylene blue as a dye for fabric before discharging it into the environment. The TiO_2 nanotubes that produced the best results were formed at the final stage of the post-hydrothermal process, with a temperature of 100°C for 24 hours. The best reduction in dye concentration was observed in Sample B, which underwent post-hydrothermal treatment at 100°C for 24 hours. The influence of temperature and process duration on the characteristics of the synthesized TiO_2 nanotubes resulted in different outcomes.

Based on the findings of this study, several recommendations are put forward for future research. Further analysis and testing of the TiO_2 nanotubes are necessary, including X-ray diffraction, UV-Vis, transmission electron microscopy (TEM), and the use of a photocatalytic reactor with ultraviolet lamps as testing equipment for subsequent research. It is also important to consistently use personal protective equipment during the research process. Lastly, prayers to God Almighty are recommended to ensure the smooth progress of the research.

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Author Contribution

The authors is responsible for the conception, design, data collection, analysis, and interpretation of the research. Additionally, the author drafted and revised the manuscript, ensuring its final approval for publication.

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Conflicts of Interest

The authors declare no conflict of interest.

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