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RESEARCH PAPER

Fotocatalytic Degradation of Methylene Blue by Floating TiO_2-Coconut Fiber

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Abstract: Indonesia's expanding industrial sector has resulted in an increase in the use of dyes. Methylene blue (MB), a dye used in the batik and textile industries, has the potential to be detrimental to people and the environment. Recent research indicates that the TiO_2 photocatalyst has the ability to reduce MB. TiO_2 transported in coconut fiber can improve illumination in the photocatalysis process. The purpose of this study is to examine the properties and activity of a TiO_2-coconut fiber photocatalyst. SEM-EDX was used to characterize the morphology and composition of floating catalysts, and Fourier transform infrared (FT-IR) was used to characterize the functional groups. At 120 minutes, TiO_2-coconut fiber photocatalysis with a mass ratio of 20:80 w/w demonstrated the maximum degradation of 62.72%. The SEM-EDX data demonstrate the morphology of TiO_2 distribution on the surface of coconut fiber, which is distinguished by the presence of the main elements O, Ti, and C. The FT-IR study results demonstrate a shift and decrease in Ti-O absorption intensity from 756,09 cm1 to 721,38 cm1, indicating the presence of Ti-O-C bonds. It is hoped that this research will be useful in the treatment of MB in textile industry waste or other organic waste.

Keywords: Floating photocatalyst, TiO_2, Methylene blue, TiO_2-coconut fiber.

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INTRODUCTION

The presence of the garment industry is one of the implications of the fast growth of the industrial sector. However, if waste dyes from clothes production are not correctly handled, the textile industry can severely influence the ecosystem [1]. Methylene blue is one of the residual colors for textiles produced. Methylene blue waste has a significant environmental impact due to its high toxicity, it can induce allergies, skin irritation, and gene alterations, and is carcinogenic [2]. Special treatment is required to address the issue of color waste. Photodegradation is a process for decomposing waste organic molecules into end products such as H_2O and CO_2 that are not damaging to the environment [3].

The photodegradation method utilizes a semiconductor that performs as a catalyst with the use of light. Catalysts with names like ZnO, CdS, Fe_2O_3, and TiO_2 can be utilized [4]. TiO_2 is a non-toxic catalyst that is affordably priced [5]. The photocatalysis method uses light and a semiconductor catalyst to accelerate the reaction rate, with the light source being either visible or ultraviolet in wavelengths. When exposed to light, semiconductors release electrons/holes (e-/h+) and begin the oxidation process of organic contaminants. The photocatalyst approach has various advantages, notably that the process is easy and cost-efficient [6].

Several prior research applied TiO_2 powder to filter water from dye waste by dropping TiO_2 powder directly into wastewater [7]. The technique has one drawback in that TiO_2 can be tricky to separate once the waste purification process ends [8]. A further investigation found that TiO_2 can be composited to a porous material to absorb and decompose chemical waste [9]. However, due to the contrasted massive amount of TiO_2, the material aggregates and sinks to the bottom of the water through the photocatalysis process

[10]. These conditions may inhibit photocatalysis process efficiency due to inefficient utilization of light, therefore the light source must penetrate to a specific level of water.

Various studies have been carried out to overcome this problem, including using TiO_2 with materials that have a low density so that TiO_2 can float on the surface of the water (floating photocatalyst), including using pearlite substrates, glass microbead substrates and polymer substrates [11]. Coconut fiber is a natural polymer that is used as a carrier material because it is light, environmentally friendly and abundant in nature [12]. Previous research used coconut fiber to carry out the TiO_2 photocatalyst in the linear degradation process of alkyl benzene sulfonate in laundry wastewater with an optimum degradation percentage of 80.43% at varying mass ratios of TiO_2 and coconut fiber, namely 20:80 w/w for 120 minutes [13].

Based on the above description, the forthcoming research aims to maximize utilizing of ultraviolet (UV) light by developing TiO_2 in coconut fiber for the decomposition of methylene blue. The present research examines the mass ratio (TiO_2: coconut fiber) as well as the characteristics of TiO_2-coconut fiber. TiO_2 distribution morphology and compound composition is identified using a Scanning Electron Microscope Energy Dispersive X-Ray (SEM-EDX), functional groups are identified using a Fourier Transform-Infrared (FTIR), and the effectiveness of methylene blue degradation is measured using a UV-Vis spectrophotometer.

MATERIALS AND METHODS

Materials

The tools used in this research: hot plate SCILOGEX, measuring flask, KH-FD 1000 watthalogen lamp, Lux Meter KRISBOW ,analytical balance BEL, oven ESCO, Fourier Transform Infra-Red (FTIR) Shimadzu, Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) JEOL JSM-6510 LA and UV-Vis spectrophotometer Shimadzu UV-2600. The materials used are distilled water (H_2O), ethanol (C_2H_5OH) SMART-LAB, methylene blue ($C_{16}H_{18}ClN_3S$), titanium dioxide (TiO_2) anatase and [illegible] fiber.

Methods

Preparation sample

Coconut fiber samples were washed utilizing tap water, and then alongside distilled water. Afterwards, it is air-dried in an oven at 105°C for 24 hours to diminish the water content and volatile components [14]. After being dried, the coconut fiber is cut to a small size of 1 to 4 mm in addition to sorted through a sieve shaker with sizes of 4 mm and 1 mm. The fibrous material from coconuts that undergoes a 1 mm sieve is then collected.

Coconut fiber activation

This delignification of coconut fiber is carried out over a method of organosolv. Organosolv is a useful technique to eliminate lignin and hemicellulose from natural fibers [15]. Coconutfiber is soaked in awater/ethanol solvent with a volume proportion of 2:1 for 2 hours prior to being ultrasonically applied using a 40 kHz frequency sonicator to eliminate impurities, increase the number of pores, and lessen both hemicellulose and lignin in the lignocellulosic structure of coconut fiber [16]. Right after that, the coconut fiber fiber is filtered to obtain the treated coconut fiber.

Synthesis of TiO2-coconut fiber

The TiO_2-coconut fiber production was carried out by adding 5 g of coconut fiber and 5 g of TiO_2 in a volume ratio of 2:1 distilled water/ethanol. The mixture was then stirred for two hours using an magnetic stirrer to form a homogeneous suspension. The remaining material follows by being filtered and dried over 4 hours at 90°C resulting in TiO_2-Coconut Fiber. Subsequently, TiO_2-coconut fiber is separated using a sieve shaker with a 100 mesh sieve to separate TiO_2 which is partially attached to the coconut fiber [13]. The TiO_2-coconut fiber photocatalyst was made with mass ratios of 80:20, 70:30, 60:40, and 50:50 by weight (coconut fiber: TiO_2).

Methylene blue degradation activity test

The photocatalyst test of TiO_2-coconut fiber and pure TiO_2 anatase as a comparison (control) was conducted by placing 100 mL of 10 ppm of methylene blue in a beaker and adding 100 mg of TiO_2-coconut fiber. Immediately after that, the suspension was illuminated with a halogen lamp over 0, 30, 60, 90, and 120 minutes. A solution of 10 mL was collected. The UV-Vis spectrophotometer has been utilized for measuring the absorbance at a maximum wavelength within 664 nm to determine the concentration of methylene blue.

Characterization and idntification of TiO2-coconut fiber photocatalyst

TiO_2 and photocatalyst TiO_2-coconut fiber with a mass ratio (TiO_2: coconut fiber) of 50:50 w/w were characterized using FTIR and SEM-EDX.

RESULTS AND DISCUSSION

Scaning electrorn microscope energy dispersive x-ray (SEM-EDX)

SEM-EDX characterization intends to observe the morphology and composition of TiO_2 embedded in coconut fiber. In accordance with the results, coconut fiber (Figure 1) has a morphology of fibers that tightly bind linked together. Because the structures of cellulose, hemicellulose, and lignin are still restricted, those sporadic ties suggest that the bonds between lignocellulosic compounds are very restrictive [17]. The morphology of TiO_2 embedded in coconut fiber (Figure 2) illustrates how TiO_2 is spread on the surface of the coconut fiber, covering the fiber morphology. TiO_2 dispersed on the surface of the fiber is round and lumpy, with pore cavities indicating agglomeration. The process of combining small particles that have accumulated into larger particles is recognized as agglomeration.

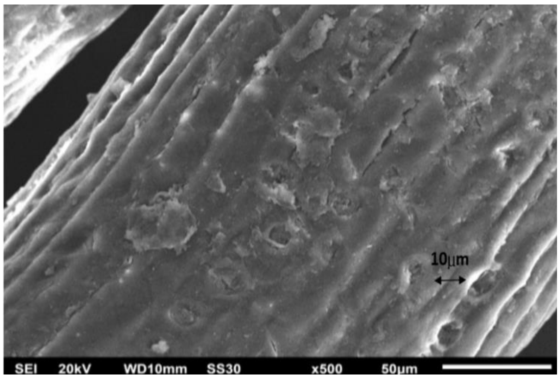

Figure 1. Morphology of coconut fiber

The aggregation in TiO_2 is caused by precipitation and excessive stirring, resulting in collisions between particles [18]. The occurrence of aggregates during the adsorption process decreased the photocatalytic properties. This is stipulated that TiO_2 clumps, reducing the surface area and inhibiting some of TiO_2's active sites from absorbing MB as well as the light during the photocatalysis process.

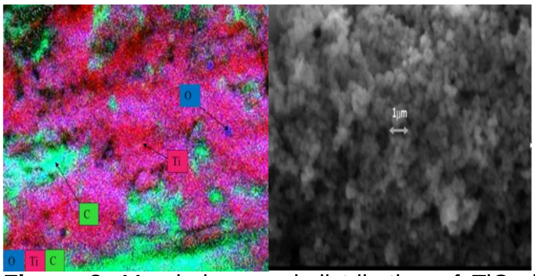

Figure 2. Morphology and distribution of TiO_2 in TiO_2-coconut fiber at 10.000x magnification

The elements in the material to be analyzed through EDX data. The EDX analysis results of TiO_2-coconut fiber in Table 1 show that the TiO_2-coconut fiber material consists of three dominant elements: O, Ti, and C. The amount of oxygen element was 51.27%, meaning it's a constituent element in TiO_2 and coir fiber. So that more of the catalyst's are detectable. The 23.36% carbon element tends to come from natural fibers, one of which is coconut fiber. Natural fibers are materials the fact that is mainly made up of oxygen and carbon [19]. Mineral elements in coconut fiber, such as aluminum, calcium, and copper, have been identified in relatively small amounts once contrasted to carbon and oxygen [20]. The existence of titanium elements (23.09% and oxygen) in the TiO_2-coconut fiber catalyst indicates the presence of TiO_2 compounds [21].

Table 1. Percentage of elements in TiO2-coconut fiber based on EDX analysis

Element	Weight %	Atom %
O	51.27	56.53
C	23.36	34.30
Ti	23.09	8.50
Zr	1.17	0.23
Cu	0.64	0.18
K	0.25	0.11

Fourier transform indra red (FTIR)

This research utilizes FT-IR to identify the functional groups of the TiO_2 anatase material, coconut fiber, and TiO_2-coconut fiber that were synthesized (Figure 3). TiO_2 IR spectra have been observed at absorption wave numbers 756.09 cm^{-1} and 486.06 cm-1, indicating Ti-O-Ti or Ti-O vibrations. Ti-O-Ti absorbs between 850 and 400 cm^{-1} [22]. Aside from that, absorptions at wave numbers 3454.51 cm^{-1} and 1649.14 cm^{-1} in the TiO_2 IR spectrum reveal that H_2O has been absorbed on the TiO_2 surface. Additional study shows strong absorption at 3300 cm-1 and weak absorption at 1633 cm^{-1}, confirming the presence of OH (hydroxyl) groups on the surface[22].

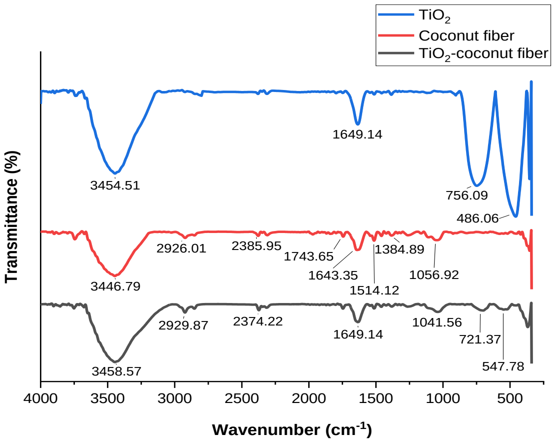

Figure 3. IR spectra of TiO_2 merck, coconut fiber and TiO_2/coconut fiber

The presence of -OH groups is shown by a wave number of 3446.79 cm^{-1} in the infrared spectrum of coconut fiber fiber, whereas a wave number of 2926.01 cm^{-1} suggests the vibration of CH_2, which is the main component of cellulose compounds as well as is further emphasized by vibrations at a wave number of 2385.95 cm^{-1}. The -O- group, which assembles cellulose, has a wave number of 1384.89 cm^{-1} [23]. remarkably typical cellulose groups are -OH, $-CH_2$, and -O- groups [24].

The C=C stretching vibration is distinguished by the appearance of absorption at wavelengths of 1643.35 cm^{-1} and 1514.12 cm^{-1}, indicating the presence of lignin compounds. Peak absorption at wave number 1743.65 cm^{-1}, which corresponds to the acetyl or ester group in hemicellulose compounds, implies the presence of hemicellulose compounds [25]. The existence of lignin compounds is indicated by the wave number range 1509 - 1609 cm^{-1}, and the presence of hemicellulose compounds is pointed out by the wave number range 1700 - 1740 cm^{-1} [24]. The TiO_2-coconut fiber IR spectrum shows a shift and decrease in intensity in the Ti-O-Ti group from absorptions of 756.09 cm^{-1} and 486.06 cm^{-1} to 721.38 and 547.78 cm^{-1}, implying the presence of bonds. Ti-O-C is formed by the reaction of TiO_2 and carbon.

Methylene blue activity test

The results of the floating photocatalyst degradation test (Figure 5) clearly demonstrate that the optimum degradation percentage raised more with a decline in TiO_2 mass at varying catalyst mass ratios (TiO_2: coconut fiber) during 120 minutes of exposure. The TiO_2-coconut fiber (20:80) ratio yields the highest percentage of methylene blue dye degradation (62.72%).

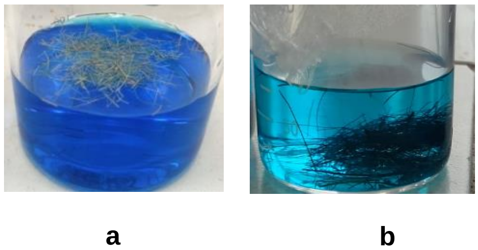

Figure 4. Floating photocatalyst TiO_2-coconut fiber (a) before and (b) after the degradation process

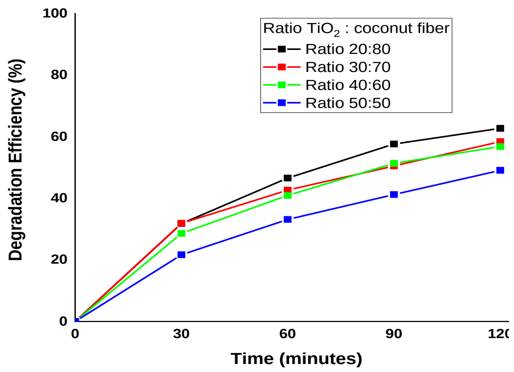

Figure 5. The effect of TiO_2 and coconut fiber mass ratio on methylene blue degradation efficiency

The density of the catalyst affects differences in degradation results on floating photocatalysts with mass variations. The higher the density of the TiO_2-coconut fiber catalyst, the faster the floating catalyst sinks to the bottom of the solution, reducing the degradation efficiency at certain times. At an exposure time of 120 minutes, TiO_2-coconut fiber with a variation of 20:80 (w/w) demonstrated the highest degradation activity. The greater the addition of TiO_2 composition to the mass variation, the lower the degradation activity with the length of lighting time. The addition of TiO_2 composition reduces degradation activity because the density of the floating catalyst increases, causing it to sink faster to the bottom of the solution.The more TiO_2 is bound to the fiber, the higher the density of TiO_2-coconut fiber [13]. This result is consistent with the theory, which states that the larger the volume of a constituent with a high density, the higher the density of the catalyst composite formed, and vice versa [26].

TiO_2 photocatalyst at the optimum mass ratio, namely TiO_2/coconut fiber (20:80), was compared to the control TiO_2 photocatalyst (without support), which was allowed to sink to the bottom of the solution and photolysis (without catalyst). The comparison aims to assess if whether there's a difference in photocatalytic activity between TiO_2 carried with coconut fiber and immersed in the bottom of a solution degrading methylene blue.

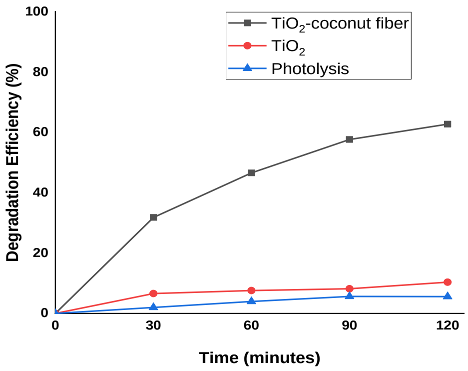

Figure 6. Curve of floating photocatalyst versus control

The results (Figure 6) reveal that degradation activity fluctuates. Within 120 minutes, the TiO_2 catalyst immersed in water produced a degradation percentage of 10.37%, while the TiO_2 encased in coconut fiber produced a degradation activity of 62.72%. This difference can be attributed to the various intensities of light received. TiO_2 that sinks absorbs less light than a catalyst embedded in coconut fiber. This is because the difference in light intensity that penetrates water depth decreases with increasing water depth [27].

CONCLUSION

The Ti-O-C functional group is identified by a shift and weakening of the intensity of Ti-O absorption from 756.09 cm^{-1} and 486.06 cm^{-1} to 721.38 cm^{-1} and 547.78 cm^{-1}, indicating that TiO_2 has attached to the coconut fiber. SEM-EDX results show the distribution of TiO_2 on the surface of coconut fiber. This is supported by EDX data containing the dominant elements O, Ti, and C, which are components of TiO_2 and coconut fiber. Photocatalyst on TiO_2-coconut fiber with a mass ratio of 20:80 w/w exhibited optimum photocatalytic activity at 120 minutes, with the highest degradation of 62.72%. The smaller TiO_2 composition allows the catalyst to float longer, optimizing illuminating.

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