DEGRADATION OF HUMIC ACID BY FLOATING PHOTOCATALYST TiO_2/Cu-ARECA FIBER

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Abstract

The photocatalyst method is effective in degrading humic acid into O_2 and H_2 compounds that are more environmentally friendly. The photocatalysis process involves light and semiconductors such as TiO_2 to accelerate the reaction rate. Therefore, modification of TiO_2 is needed to shift light absorption to visible light by using Cu^{2+} doping and areca fiber. XRD characterization shows that Merck's TiO_2 has shifted at 2θ, indicating that Cu has entered the TiO_2 structure, and several peaks have reduced in intensity after being embedded with areca fiber, indicating that TiO_2/Cu has successfully attached to areca fiber. FTIR results show that TiO_2/Cu has been attached to the areca fiber, which is marked by shifting and weakening the intensity of the Ti-O-Cu wave number absorption. The test results show that TiO_2/Cu embedded in areca fiber had higher degradation activity than TiO_2/Cu without embedded, with a percent degradation of 54% for 180 minutes of irradiation. These results prove that TiO_2/Cu floated to the surface of the solution can optimize irradiation so that it is effective in the degradation process.

Keywords: *areca fiber, floating photocatalyst, peat water*

Introduction

Pontianak is a city with a large amount of peatland. Peatlands have a high enough water capacity to be used as a source of drinking water (Taufik *et al.*, 2019). However, cloudy peat water indicates a high content of organic substances, one of which is humic acid (Hawari *et al.*, 2022). Humic acid, a compound that has a yellow and black color is mutagenic, carcinogenic, difficult to degrade naturally, and acts as a substrate for the development of microorganisms (Hawari *et al.*, 2022; Zila and Zainul, 2019).

Various studies have been conducted to reduce humic acid in peat water, such as adsorption (Zhang *et al.*, 2020), coagulation (Hu *et al.*, 2024), electrocoagulation (Rahman *et al.*, 2023), and advanced oxidation processes (AOPs) (Ghazali *et al.*, 2019). Nowadays, AOPs such as photolysis, sonolysis, photo-Fenton, ozonation, and UV/H_2O_2 have been conducted to reduce organic pollutant (Zulkarnaini *et al.*, 2021). These methods have several drawbacks, such as requiring high-pressure differentials, long operating times, and expensive operating costs (Gao *et al.*, 2019; Sisnayati *et al.*, 2022). To deal with the problem of peat water containing humic acid, special attention is needed. The photocatalyst method is effective in degrading humic acid into O_2 and H_2 compounds that are more environmentally friendly (Wang *et al.*, 2015).

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Photocatalysts are a combination of photochemical reactions that utilize visible and UV light as an energy source and semiconductor catalysts to accelerate the reaction rate (Adnan *et al.*, 2021). The degradation process by light runs slowly so that to increase the rate of degradation a semiconductor catalyst such as TiO_2 is used. TiO_2 has a photocatalytic ability that, when exposed to light at a certain wavelength, the oxidizer can degrade humic acid into simpler compounds (Rahayu *et al.*, 2022). The mechanism of the photocatalyst is that when light with equal or greater energy is absorbed by TiO_2, it will produce hydroxyl radicals (•OH) which are highly reactive in attacking organic molecules due to photoexcitation or charge separation (Said, 2021).

However, pure TiO_2 has a relatively large energy gap (3.2 eV) and can only absorb 5% of ultraviolet (UV) light from the solar spectrum that reaches the earth (Ayunda *et al.*, 2022). Therefore, it is necessary to modify the TiO_2 catalyst to reduce the band gap so that it can shift the absorption of light in visible light, namely by using doping.

One of the doping agents that can improve the photocatalytic properties of TiO_2 is copper ions (Cu^{2+}) (Zainul, 2016). Copper has an ionic radius that is almost close to the radius of Ti^{4+} so that it can be incorporated into TiO_2 crystals (Vargas *et al.*, 2017). Based on research conducted by Zila and Zainul (2019), humic acid degradation using Cu-doped TiO_2 semiconductors reached 52.21%. However, photocatalysts used to degrade organic and inorganic materials in waters are usually only spread and allowed to sink so that sunlight that can be absorbed by semiconductors is very limited.

The effectiveness of photocatalysts can be enhanced by optimizing light irradiation on semiconductor catalysts. The solution to this problem has been carried out, namely to carry TiO_2 with lighter materials (floating photocatalysts), such as being carried with polymer substrates (Firmansyah *et al.*, 2019). Areca fiber was chosen because it has several advantages, such as having a lower density than water, abundant in nature, being sustainable, and being environmentally friendly (MiarAlipour *et al.*, 2018; Muhammad *et al.*, 2019; Xing *et al.*, 2018).

Based on the explanation above, it is necessary to synthesize floating photocatalyst TiO_2/Cu-areca fibers as humic acid photodegradation with the help of visible light from sunlight. This research will determine the character of TiO_2/Cu areca fiber and photocatalytic activity in degrading humic acid in peat water. Characterization of floating photocatalyst using X-ray diffraction (XRD) was carried out to determine the type of TiO_2 crystal and using Fourier Transform Infrared Spectroscopy (FTIR) to determine the functional groups. Determination of humic acid degradation activity using UV-Vis spectrophotometer.

Research Methods

Materials

The materials used were distilled water (H_2O), humic acid, perchloric acid 70–72% ($HClO_4$) Merck, sodium hydroxide (NaOH) Merck, polyvinyl alcohol (PVA) Sigma-Aldrich, areca fiber, copper sulfate ($CuSO_4$) Merck and titanium dioxide (TiO_2) Merck.

Instrumentation

The tools used in this research are stirring rod, spray bottle, burette Pyrex, quartz cup, erlenmeyer Iwaki, hot plate stirrer Scilogex, 1000 W halogen lamp KH-FD, Lux Meter Krisbow, analytical balance Bel, magnetic stirrer, pH Meter, measuring pipette Iwaki, oven Esco, spatula, test tube Iwaki, X-Ray Diffraction (XRD) PANalytical, Fourier Transform Infrared (FTIR) Shimadzu and UV-Vis Spectrophotometer Shimadzu UV-2600.

Procedure

1) Sample preparation

   Areca fiber samples were washed using clean water and distilled water. After that, the samples were dried in the sun for 48 hours and continued in a heating oven at 110 °C for 24 hours (Handayani and Taer, 2019). The next step was to cut the areca fiber to a small size to expand the surface.

2) Areca fiber activation

   Areca fibers were soaked in 5% NaOH solution for 3 hours and then washed using distilled water and dried at 60 °C (Karmuliani and Mahyudin, 2020).

3) Synthesis of Cu-doped TiO_2

   Manufacture of TiO_2/Cu photocatalyst with a mole ratio of 98:2 is carried out by the photodeposition method, namely by photoreduction of metal ions into metals that are on the surface of TiO_2. First, 23.52 grams of TiO_2 were added to 300 mL of distilled water, then perchloric acid was added until the pH became 3, and 0.96 grams of $CuSO_4$ were added as a dopant source. The mixture was stirred using a magnetic stirrer and irradiated with a UV lamp for 3 hours. The next step was to dry the mixture using an oven at 100 °C for 12 hours. The dry solid obtained was then crushed and calcined at 400°C for 6 hours to obtain TiO_2/Cu (Riyani *et al.*, 2015).

4) Synthesis of TiO_2/Cu-areca fiber

   A total of 7 grams of polyvinyl alcohol (PVA) was dissolved into 200 mL of distilled water and then added with 2 g of areca fiber. The solution was added 2 g of TiO_2 solids, stirred using a magnetic stirrer at room temperature for 30 minutes, and filtered to obtain the residue. After that, the residue was dried using an oven at 60 °C for 5 hours to obtain a floating photocatalyst TiO_2/Cu-areca fiber (Sboui *et al.*, 2017).

5) Characterization and identification of TiO_2/Cu-areca fiber

   TiO_2 and 5% NaOH-activated TiO_2/Cu-areca fiber photocatalysts were characterized using XRD and FTIR.

6) Humic acid degradation activity test

   The determination of TiO_2/Cu-areca fiber photocatalyst activity was conducted using 100 mL of water with a concentration of 30 mg/L added. Furthermore, 100 mg of TiO_2/Cu-areca fiber was added. Then, the suspension was exposed to visible light using a halogen lamp irradiation in the span of 30, 60, 90, 120, 150, and 180 minutes with 3 repetitions (triplo). The next step is that the solution is taken at 10 mL, and absorbance measurements are taken using a UV-Vis spectrophotometer at a maximum wavelength of 204 nm (Zhou *et al.*, 2019).

Results and Discussion

The XRD characterization is carried out to know the crystal analyzed in the form of crystal phase, the distance between lattices, and crystal size (Rosanti *et al.*, 2020). The use of XRD aims to determine the character of TiO_2, TiO_2/Cu, areca fiber, and TiO_2/Cu-areca fiber.

Based on the XRD diffractogram (Figure 1), which has been analyzed, the XRD diffractogram shows the characteristics of TiO_2 at peaks 2θ = 25.32°, 37.81°, 48.08°, 55.11° and 62.75°. The results of the 2θ spectrum on TiO_2 are by previous research with anatase type TiO_2 standards from JCPDS no. 21-1272, which shows peaks 2θ = 25.32°, 37.7°, 47.9°, 54.8° and 62.6° with crystal planes (101), (004), (111) and (204) (Reddy *et al.*, 2016). Anatase-type TiO_2 crystals show better photocatalytic activity when compared to rutile-type crystals due to smaller particle sizes and slower recombination of electron-hole pairs (Phromma *et al.*, 2020). The TiO_2 diffractogram shows a change in the 2θ shift to a smaller direction when the Cu^{2+} dopant is added. This indicates that Cu^{2+} has been substituted into the TiO_2 structure. The angular shift in the TiO_2 diffractogram before and after dopant addition is due to the difference in ionic radius between Ti^{4+} and Cu^{2+}, which affects the interplane distance factor in TiO_2/Cu (Kunarti *et al.*, 2018). Nuhaeroh *et al.* (2022) stated that the Cu peak appeared at a 2θ angle of 44.6°. However, TiO_2/Cu that has been synthesized does not cause new peaks. This indicates that Cu has entered and spread evenly on the TiO_2 structure.

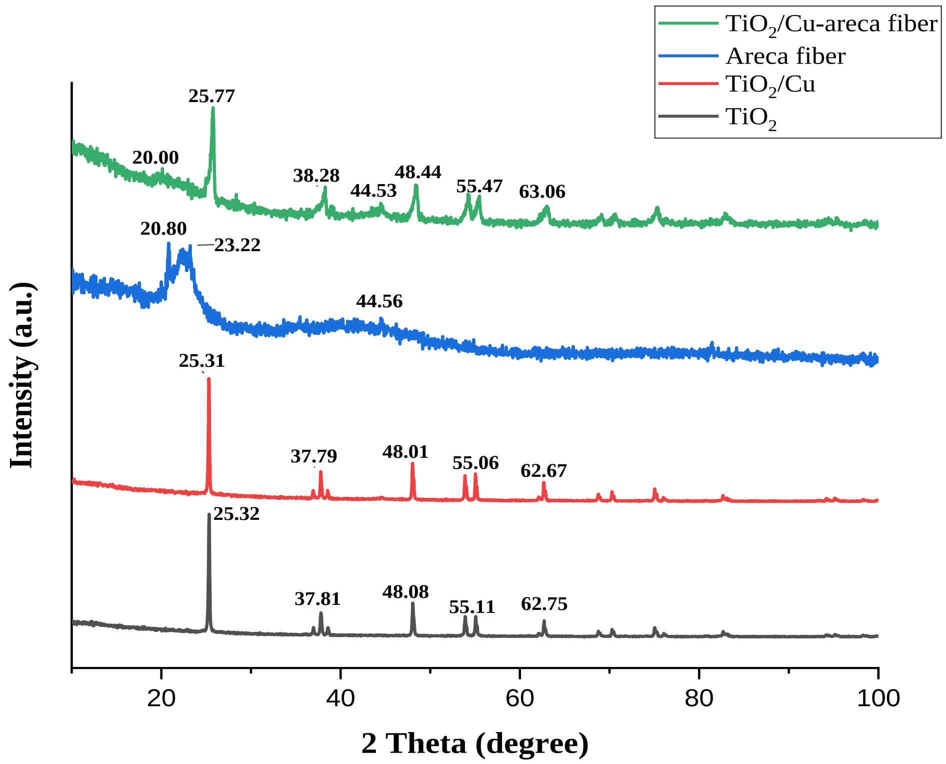

Figure 1. Difractograms of TiO_2, TiO_2/Cu, Areca Fiber and TiO_2/Cu-Areca Fiber

Areca fiber has peaks 2θ = 20.80°, 23.22° and 44.56°, which are compounds of lignocellulose and areca fiber. This result is not much different from the research of Saputri and Sukmawan (2020) which showed peaks at angles 2θ = 14.5° and 22.2°, which are compounds of cellulose. Kanani *et al.* (2019) also reported that the sharp peaks at angles 22° and 23° indicate the structure of cellulose crystals. TiO_2/Cu embraced with areca fiber shows a shift in angle and a weakening of intensity in TiO_2/Cu due to the presence of some crystal matrices covered by the amorphous side of the remaining lignin from areca fiber. This indicates that TiO_2 has successfully attached to areca fiber.

FT-IR analysis serves to determine the functional groups of TiO_2 Merck material, TiO_2/Cu, areca fiber, and TiO_2/Cu areca fiber that have been synthesized (Figure 2) (Akbar *et al.*, 2021). IR spectra on TiO_2 are identified at the absorption of wave numbers 756.10 cm^{-1} and 486.06 cm^{-1}, which indicates the vibration of Ti-O-Ti or Ti-O. The absorption range of Ti-O-Ti is 850-400 cm^{-1} (Bakre and Tilve, 2018). In addition, in the IR spectra of TiO_2, there is an absorption of 3454.51 cm^{-1} and 1649.14 cm^{-1}, which indicate the vibration of the OH group in the H_2O compound, which is absorbed on the surface of TiO_2 (Dalponte *et al.*, 2019).

The IR spectra of Cu^{2+} doped TiO_2 are characterized by an absorption wavenumber of 682.80 cm^{-1} which indicates the presence of Cu-O bond vibrations. Cu-O bond absorption peaks appear at wave numbers around 672 cm^{-1} (Hou *et al.*, 2019). The shift in TiO_2 absorption after the addition of Cu indicates the presence of crystal defects in the TiO_2 structure. The shift of the absorption peak towards the smaller wave number Ti-O-Ti from 756.10 cm^{-1} to 528 cm^{-1} indicates the presence of Ti-O-Cu bonds, which causes the absorption to shift towards smaller energy (Aritonang *et al.*, 2021).

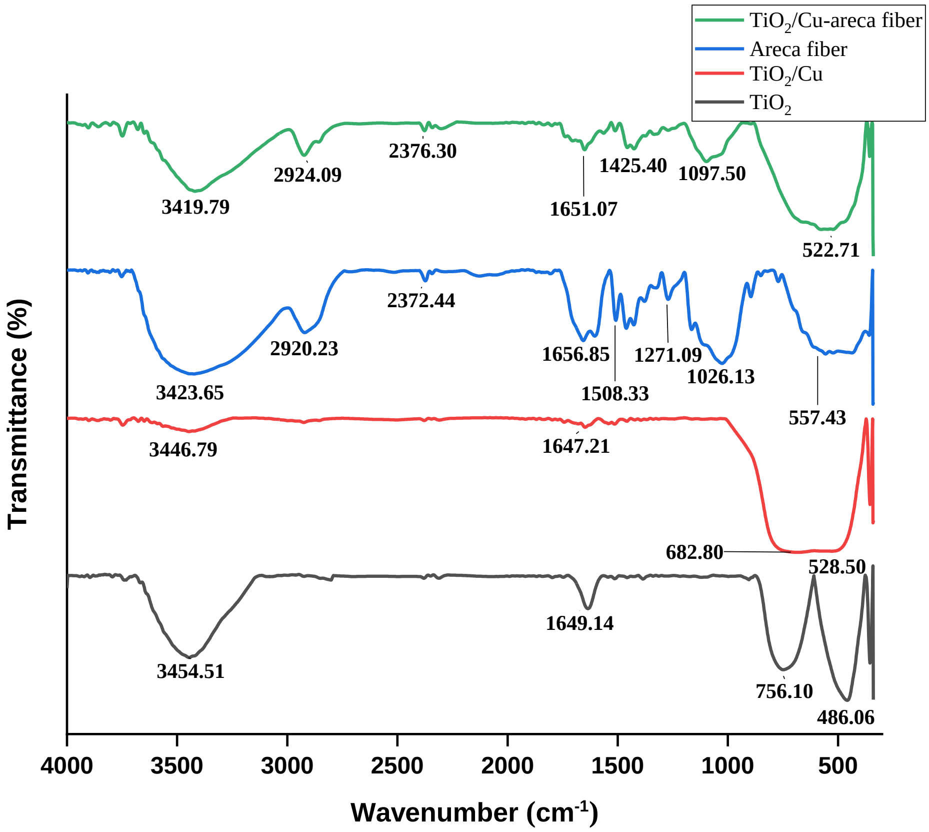

Figure 2. IR Sepctra of TiO_2 Merck, TiO_2/Cu, Areca Fiber dan TiO_2/Cu-Areca Fiber

The IR spectra of areca fiber showed the presence of the -OH group at a wave number of 3423.65 cm^{-1}, while the wave number 2920.23 cm^{-1} showed the vibration of CH_2 which is the main component of cellulose compounds reinforced by vibrations at wave number 2385.95 cm^{-1}. The -O- group that assembles cellulose appears at wave number 1271.09 cm^{-1}. Standard cellulose-specific groups are -OH, $-CH_2$, and -O- groups that appear repeatedly (Dewi *et al.*, 2017). The presence of lignin compounds is indicated by the appearance of C=C stretching vibration at a wavelength of 1508.33 cm^{-1}. The presence of hemicellulose compounds in areca fiber is indicated by the absorption peak at wavelength 1656.85 cm^{-1}. The wave number range of 1509-1609 cm^{-1} indicates the presence of lignin compounds and the wave number range around 1700 cm^{-1} indicates the identification of hemicellulose compounds (Dewi *et al.*, 2017).

IR spectra on TiO_2-areca fiber showed C-O bond vibrations at a wave number absorption of 1097.50 cm^{-1} which is a functional group of cellulose. This is close to research conducted by Darojati *et al.* (2022) which states that the 1030 cm^{-1} wave number absorption is a functional group of C-O, C=C, and C-C. IR spectra on TiO_2/Cu which is embraced with areca fiber experience a shift in absorption in the Ti-O-Cu group. It can be concluded that TiO_2/Cu successfully embraced on fiber.

The photocatalytic activity test of TiO_2/Cu-areca fiber towards humic acid degradation (Figure 3) was carried out in a lighting reactor using a halogen lamp for 180 minutes with 5% activation of areca fiber. The use of halogen lamps aims as a light source because it can produce a polychromatic light source that can reach various wavelengths (ultraviolet and visible light) (Ekasari and Yudoyono, 2013). Absorption determination was carried out at the maximum wavelength of humic acid, 204 nm. The percentage of humic acid degradation was then plotted in a curve of % degradation against irradiation time.

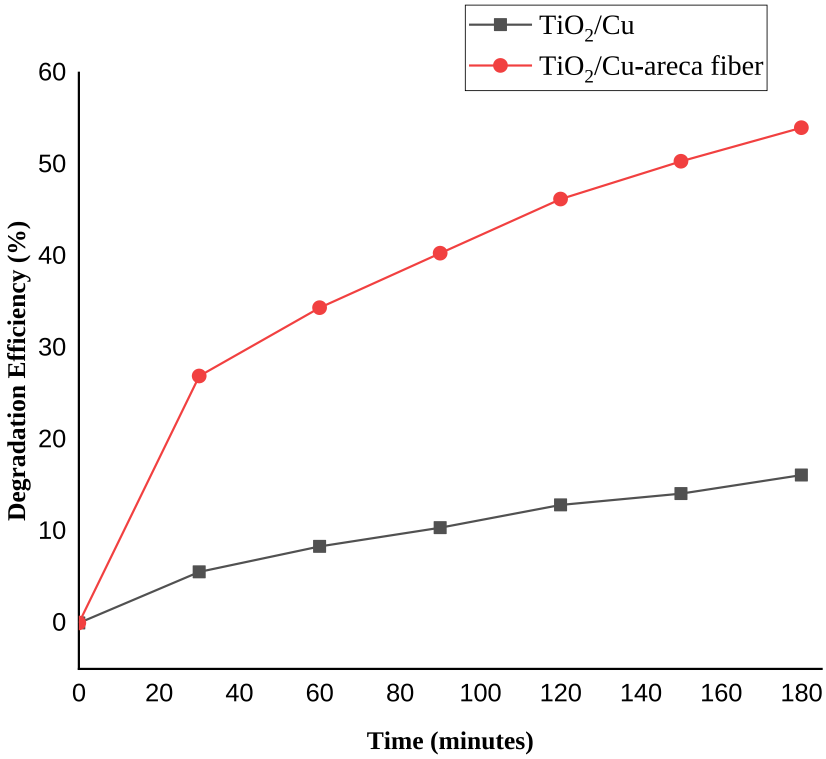

Figure 3. Humic Acid Degradation % Curve Against Irradiation Time

TiO_2/Cu with activated areca fiber can degrade humic acid by 54.00%. Meanwhile, TiO_2/Cu soaked in the base solution was only able to reduce humic acid by 16.13% for 180 minutes of irradiation. The optimum time obtained is 180 minutes of irradiation because the production of OH radicals has reached the maximum limit, so the degradation activity tends to stabilize (Sugandi *et al.*, 2023). Areca fiber on TiO_2/Cu-areca fiber also acts as a bio adsorbent due to the addition of porosity during the activation process so that it can absorb small particles in humic acid (Lubis *et al.*, 2021).

The difference in the results of reducing humic acid with floating photocatalysts is influenced by differences in catalyst density. The high density of TiO_2/Cu compared to water causes the catalyst to sink to the bottom of the solution. TiO_2/Cu that sinks will absorb less light at the bottom of the solution than a floating catalyst when embedded in areca fiber. This is due to the differences in light intensity on the surface and bottom of the waters. The intensity of incoming light will decrease as the water depth increases (Qurban *et al.*, 2017). The results of the density calculation are shown in Table 1.

Table 1. Density of TiO_2, areca fiber and TiO_2/Cu-areca fiber

No	Sample	Density (g/cm^3)
1	TiO_2	3.676 ± 0.0135
2	Areca Fiber	0.554 ± 0.0040
3	TiO_2/Cu-Areca Fiber 5%	0.890 ± 0.0058

The addition of NaOH concentration in the activation of areca fiber can reduce lignin compounds in lignocellulose so that it can increase the number of pores can reduce the density of areca fiber. The number of pores produced determines the density of the fiber. The release of lignin from lignocellulose makes areca fiber have a strain that can reduce fiber density (Septevani *et al.*, 2018).

Degradation of humic acid compounds occurs due to the interaction between the catalyst and energy from sunlight on the TiO_2 surface. If the TiO_2 material is illuminated by photons from visible light, the electron will move from the valence band (V_B) to higher energy, namely the conduction band (V_C), leaving h^+ in the valence band. h^+ in V_B from Cu will react with hydroxide ions from H_2O to produce hydroxyl radicals ($^\bullet OH$) while e^- in V_C will react with O_2 to produce superoxide radicals ($^\bullet O_2$-). Cu in TiO_2 acts as an e^- and h^+ trap, thereby slowing down the recombination of electron-hole pairs. The $^\bullet OH$ and $^\bullet O_2$- formed function in degrading organic compounds, one of which is humic acid. The approximate degradation reaction and reaction mechanism of humic acid degradation are shown in the equation (1) to (5) (Mohtar *et al.*, 2021).

$$Cu/TiO_2 + h\nu \rightarrow TiO_2\ (e^-) + Cu\ (h^+) \quad (1)$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \quad (2)$$

$$h^+ + OH^- \rightarrow {}^\bullet OH \quad (3)$$

$$e^- + O_2 \rightarrow {}^\bullet O_2^- \quad (4)$$

$$h^+ \text{ or } {}^\bullet OH \text{ or } {}^\bullet O_2^- + \text{humic acid} \rightarrow \text{degradation product} \quad (5)$$

Conclusions

Characterization using XRD showed that the Merck's TiO_2 diffractogram experienced a shift in 2θ, indicating that the Cu dopant had entered the TiO_2 crystal structure and there was a decrease in the intensity of several peaks after being attached to the areca fiber as an indication that TiO_2/Cu was successfully embedded on the surface of the areca fiber. The infrared spectra data with FTIR shows that TiO_2/Cu has been attached to the areca fiber which is marked by shifting and weakening the intensity at the Ti-O-Cu wave number absorption. The test results showed that TiO_2/Cu embedded with areca fiber had higher degradation activity than TiO_2/Cu without a carrier, with a degradation percentage of 54% for 180 minutes of irradiation. These results prove that TiO_2/Cu floated to the surface of the solution can optimize irradiation so that it is effective in the degradation process. In the future, it is hoped that this research can be applied as an alternative method for processing waste containing humic acid or other organic waste.

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