# DEGRADATION OF TETRACYCLINE BY FLOATING PHOTOCATALYST $TiO_2$/Ni-COCONUT FIBER

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## Abstract
The photocatalyst process involves light (photons) as an energy source and catalysts such as $TiO_2$ to accelerate the reaction. Efforts are made to reduce the band gap energy of $TiO_2$ by shifting the absorption towards visible light using metal cation doping, such as $Ni^{2+}$, and they can float on the surface with coconut fiber. XRD characteristics with $TiO_2$ diffractogram experienced a 2θ shift as an indication that Ni has entered the $TiO_2$ structure and seen some peaks decreased in intensity after being embedded with coconut fiber as an indication that $TiO_2$/Ni has successfully attached to the fiber. The band gap energy on $TiO_2$ is 3.21 eV with a wavelength of 386.5 nm in UV light. $TiO_2$/Ni-coconut fiber experienced a shift in band gap energy to 3.09 eV with a wavelength of 400.9 nm, which is in visible light. This indicates that Ni has successfully entered the $TiO_2$ structure. The $TiO_2$/Ni catalyst embraced with coconut fiber has a higher degradation activity than the catalyst without an embrainer, with a percent degradation of 28.66% for 120 minutes of irradiation. This is influenced by the amount of light that can be absorbed during the photocatalysis process.

***Keywords**: coconut fiber, floating photocatalyst, tetracycline*

## Introduction

Tetracycline is one of the antibiotics that is often used in medicine, livestock, agriculture, and aquaculture industries to kill various types of pathogens (Wardani *et al.*, 2022). However, tetracycline is difficult to metabolize by humans and animals, causing as much as 70–90 % of tetracycline to be excreted by the body in its original form (Deswardani *et al.*, 2022). This tetracycline waste can have harmful effects on humans and the surrounding ecosystem such as joint disease, nephropathy, endocrine disorders, central nervous system defects, and can inhibit growth and development (Fan *et al.*, 2021).

Several methods have been used for the removal of pharmaceuticals from wastewater such as membrane technology (Heberer and Feldmann, 2008; Li *et al.*, 2009), bioremediation (Nguyen *et al.*, 2019), advanced oxidation processes (AOPs) (Brillas, 2023), electrocoagulation (Paredes *et al.*, 2019), adsorption (Ouyang *et al.*, 2020), and hybrid techniques (Sawunyama *et al.*, 2023). AOPs such as Ozonation (Su *et al.*, 2020), photo-Fenton (Jafari *et al.*, 2017), and UV/$H_2O_2$ (Yuan *et al.*, 2011) have been utilized for removing tetracycline in the last few years. These methods have some drawbacks, such as being incapable of resource recovery, ineffective treatment to safe levels (Manoharan *et al.*, 2022), and potentially toxic by-products (Serna-Galvis *et al.*, 2017).

Photocatalyst is an effective and eco-friendly method to degrade almost all organic pollutants, which plays an important role in wastewater treatment nowadays (Chen *et al.*, 2020; Ma *et al.*, 2020; Tang and Wang, 2018; Wang *et al.*, 2019; Zarrin and Heshmatpour, 2018). The photocatalyst method works by producing highly reactive species, namely hydroxyl radicals (•OH) which can degrade pollutants in water into small molecules that are environmentally friendly (Setiawan *et al.*, 2023). The photocatalyst process involves light (photons) as an energy source and a catalyst to accelerate the reaction (Rahmawati and Kusumawati, 2020). One of the most effective semiconductors used as a photocatalyst is $TiO_2$.

$TiO_2$ has non-toxic properties, is relatively cheap, has excellent chemical stability, and can be used repeatedly without losing its catalytic activity (Aritonang *et al.*, 2022). However, in the degradation process, $TiO_2$ has a disadvantage, namely the band gap energy is only around 3.0–3.2 eV which is equivalent to UV wavelengths (<400 nm) so it is less effective in the degradation process because UV light reaches the earth only about 5% (Pratiwi *et al.*, 2020). To overcome these problems, efforts are made to reduce band gap energy by shifting absorption towards visible light using metal cation doping. One of the metal cations used as a dopant is $Ni^{2+}$ so that it can enter the $TiO_2$ structure substitutionally or interstitially (Priatmoko and Prambasto, 2022).

Priatmoko and Prambasto (2022) researched $TiO_2$ using Ni doping with the best results of 2.51 eV so that it can absorb visible light. However, there are obstacles found in the photocatalyst process where the material conditions experience clumping or even sink to the bottom of the water due to the large density of $TiO_2$ (Mohammadi *et al.*, 2016). This condition can reduce the performance of the photocatalyst process due to less than optimal utilization of sunlight where light must penetrate a certain depth of water to make the catalyst work at the bottom of the water. The solution to overcome this problem is by conducting an embodiment between the catalyst and a material that has a lower density than water so that it can float on the surface, one of which is coconut fiber.

Coconut fiber was chosen because it has several advantages compared to other photocatalysts such as carbon materials, alumina, perlite, vermiculite, glass microbeads, and polymers (MiarAlipour *et al.*, 2018; Xing *et al.*, 2018). Coconut fiber is a natural polymer with low density, good physical and mechanical properties, non-toxic, and abundant in nature so it has the potential to be used as a floating photocatalyst material (Rachmawati and Gunadi, 2020).

Based on the description above, the synthesis of floating photocatalyst TiO2/Ni-coconut fiber will be carried out. This research will determine the density and character of $TiO_2$/Ni-coconut fiber. Photocatalyst characterization to determine the type of $TiO_2$ crystal using X-Ray Diffraction (XRD) analysis and determine the band gap energy using Diffuse Reflectance-Ultraviolet (DR-UV). Determination of degradation efficiency of tetracycline antibiotic waste using UV-vis spectrophotometer.

## Research Methods

*Materials*

The materials used are distilled water ($H_2O$), hydrogen peroxide 70% ($H_2O_2$) Smart-Lab, glycerol 85% ($C_3H_8O_3$) Merck, sodium hydroxide (NaOH) Merck, nickel acetate tetrahydrate $Ni(CH_3COOH)_2.4H_2O$ CAS, polyvinyl alcohol (PVA) Sigma-Aldrich, coconut fiber, tetracycline HCl ($C_{22}H_{24}N_2O_8.HCl$) and titanium dioxide ($TiO_2$) Merck.

*Instrumentation*

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

*Procedure*

1) Sample preparation
   The coconut fiber samples were washed using tap water and then washed using distilled water. After that, the coconut fibers were dried to a constant weight at 105°C for 24 hours in a laboratory drying oven (Abel *et al.*, 2020). The coconut fibers were then cut to a small size and filtered using a sieve shaker with a size of 3 mm. Samples that passed the sieve were taken and subjected to further treatment.
2) Coconut fiber activation
   Coconut fibers were treated with alkali (NaOH) by soaking the samples in a 10% NaOH solution for 2 hours. After that, the coconut fibers were washed and soaked using an $H_2O_2$ solution with a concentration of 3% for 1 hour to remove the remaining alkaline solution. The last stage is that the coconut fiber is dried at room temperature around 30°C for 7 days (Zulkifli *et al.*, 2020).
3) Synthesis of Ni-Doped $TiO_2$
   The synthesis of $TiO_2$/Ni uses a mass ratio of $TiO_2$: Ni which is 99: 1. A total of 2.51 grams of Ni $(CH_3COOH)_2.4H_2O$ was dissolved into 150 mL of distilled water and glycerol was added and stirred using a magnetic stirrer for 1 hour. After that, Merck $TiO_2$ was weighed as much as 79.2 g and then put into the nickel acetate tetrahydrate solution and stirred again using a magnetic stirrer for 24 hours until it formed a suspension. Next, the suspension was added 0.25 M NaOH until the pH of the solution was about 12. After that, the mixture was stirred using a magnetic stirrer for 1 day and then filtered and dried for 24 hours at 75°C and then calcined at 400°C (Priatmoko and Prambasto, 2022).
4) Synthesis of $TiO_2$/Ni-Coconut Fiber
   A total of 7 grams of PVA binder compound was dissolved into 100 mL of distilled water and then added with 2 g of coconut fiber. $TiO_2$/Ni solids with a mass of 20 wt% were added to the solution. The mixture was stirred rapidly at room temperature for 30 minutes and then filtered. The resulting residue was then oven dried at 60°C for 5 hours (Sboui, Nsib, Rayes, Ochiai, *et al.*, 2017).
5) Characterization and identification of $TiO_2$/Ni-Coconut Fiber photocatalysts
   $TiO_2$ and $TiO_2$/Ni-coconut fiber activated photocatalysts that have been synthesized are then characterized using XRD and DR-UV.
6) Tetracycline degradation activity test
   The floating activity test of $TiO_2$/Ni-coconut fiber photocatalyst was carried out by entering 200 mL of tetracycline solution at a concentration of 100 $mgL^{-1}$. Furthermore, 200 mg of $TiO_2$/Ni-coconut fiber was added. After that, the suspension was irradiated under a halogen lamp with a time range of 0, 30, 60, 90, and 120 minutes with three repetitions. The intensity of the sun was measured using a Lux Meter. The next step is 5 mL of solution was taken and tested with a UV-Vis spectrophotometer with a maximum wavelength of 355 nm.

**Result and Discussion**

Characterization using XRD aims to determine the type of crystal in the material analyzed based on the spectrum of the 2θ angle (Rosanti *et al.*, 2020). The results of the diffractogram (Figure 1) show the presence of peaks at 2θ = 25.32˚, 37.81˚, 48.08˚, 55.11˚ and 62.75˚ which corresponds to JCPDS 078-2486 which is an anatase type $TiO_2$ crystal structure. These results are also close to the research of Rachminisari *et al.* (2020) which shows peaks in anatase $TiO_2$, namely 25.4˚, 37.9˚, 48.1˚, 55.1˚ and 62.8˚. $TiO_2$ anatase phase shows better photocatalytic activity than rutile and brookite phases due to smaller particle size and slower recombination of electron-hole pairs (Phromma *et al.*, 2020).

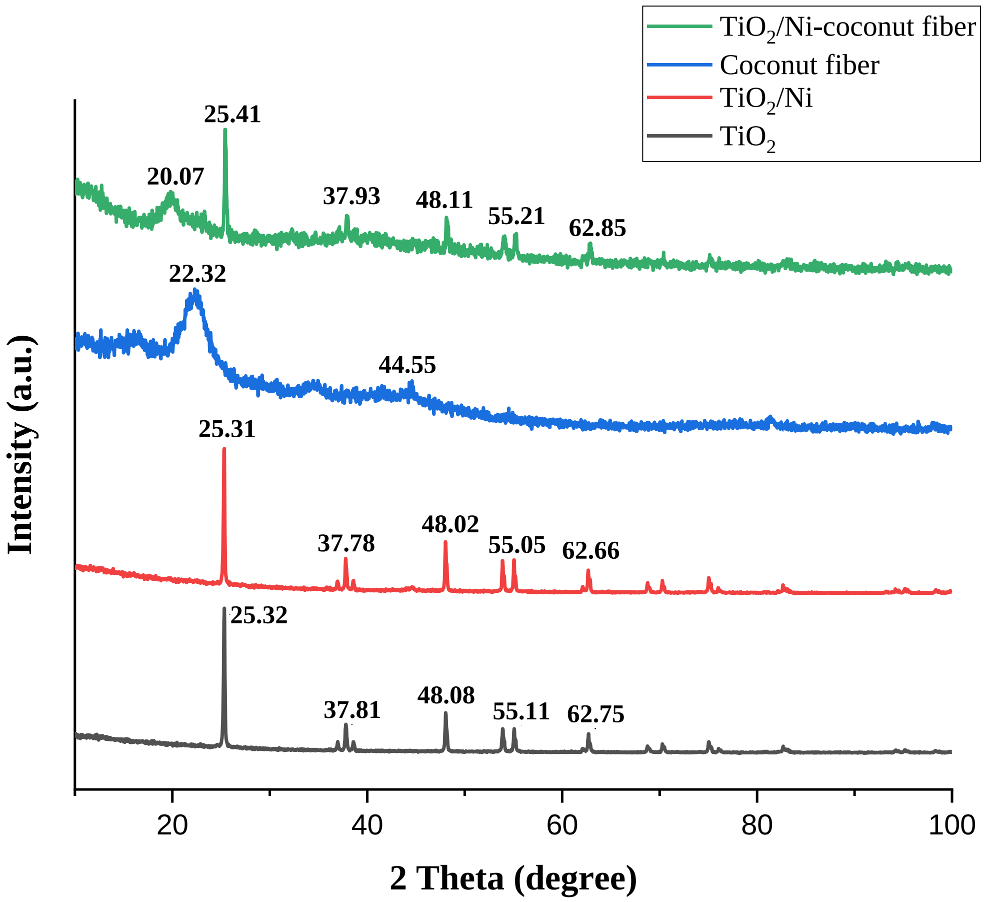


**Figure 1.** Difractograms of $TiO_2$, $TiO_2$/Ni, Coconut Fiber and $TiO_2$/Ni-Coconut Fiber

The $TiO_2$/Ni diffractogram shows a shift of $TiO_2$ at the 2θ angle towards a smaller angle, indicating that Ni has entered the $TiO_2$ crystal structure. The substitution of Ti by Ni causes a change in the distance factor between lattices because the radius of $Ni^{2+}$ ions is smaller than $Ti^{4+}$. Morin and Santi (2021) stated that Ni peaks appear at angles 2θ = 33° and 43°. However, the diffractogram on $TiO_2$/Ni after synthesizing does not show any new peaks. This is in line with the research of Liu *et al.* (2022) which shows that with no other peaks on the diffractogram, the compound has high purity because Ni has been evenly distributed on $TiO_2$.

The character of coconut fiber can be seen from the peaks 2θ = 22.32° and 44.55° which indicate the presence of cellulose compounds. This result is close to the research of Saputri and Sukmawan (2020) which shows that the peaks at angles 2θ = 14.5° and 22.2° are compounds of cellulose. Kanani *et al.* (2019) also mentioned that the sharp peak at 2θ in the range of 22° and 23° indicates the crystalline structure of cellulose. $TiO_2$/Ni which is embraced with coconut fiber does not change the type of crystal.

Shifting and decreasing the intensity of $TiO_2$/Ni when embraced with coconut fiber indicates that some of the matrix in the $TiO_2$/Ni crystal is covered by the amorphous side of the more dominant coconut fiber substrate which indicates that $TiO_2$/Ni successfully attached to coconut fiber (Sugandi *et al.*, 2023).

DRS UV-Vis characterization was performed to determine the band gap energy (Eg) value of the synthesized material (Illahi *et al.*, 2020). DRS-UV analysis is also used to determine the success of Ni dopants that enter the $TiO_2$ structure to reduce the band gap energy. The band gap value can be obtained through the Kubelka-Munk function of the Tauc equation, namely $(F(R)h\upsilon)^{1/2}$ (y-axis) against hv (x-axis). The $(F(R)h\upsilon)^{1/2}$ plot is used because the $TiO_2$ sample has an anatase phase which indicates that the catalyst is classified as an indirect band gap semiconductor, while the rutile and brookite phases are direct band gap semiconductors (Zhang *et al.*, 2014).

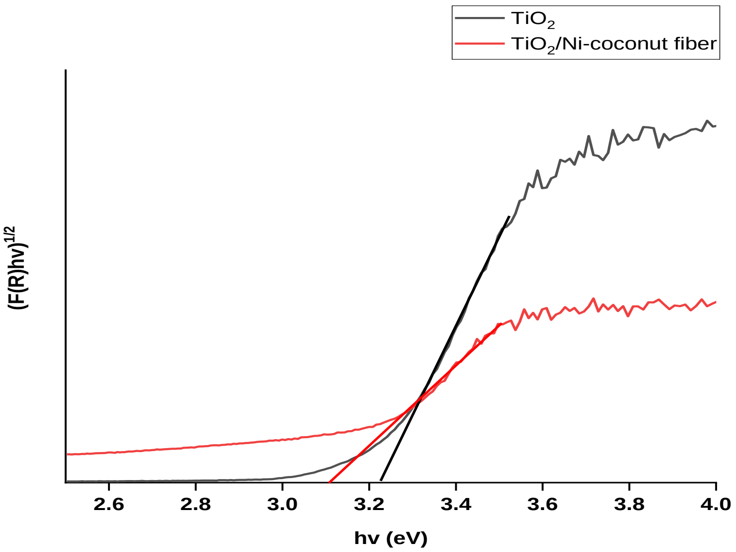


**Figure 2.** Energy Band Gap Curves of $TiO_2$ and $TiO_2$/Ni-Coconut Fiber Photocatalysts

The intersection of the resulting straight line (trendline) gives the band gap value. $TiO_2$ has a band gap value of 3.21 eV which is equivalent to a wavelength absorption of 386 nm. $TiO_2$ produced is a type of anatase $TiO_2$ because the band gap energy range in anatase $TiO_2$ is 3.20–3.30 eV, anatase structure has a large photocatalytic activity compared to rutile structure (Linsebigler *et al.*, 1995). $TiO_2$ doped with $Ni^{2+}$ produces a decrease in band gap energy to a smaller direction of 3.09 eV which is equivalent to absorption at a wavelength of 400.9 nm. The shift in band gap energy is due to $Ni^{2+}$ cations that substitute some of the $Ti^{4+}$ cations, forming a level of impurities in the form of new energy bands that can inhibit the recombination of electron hole pairs. The smaller the band gap energy, the absorption will be extended to the visible light region (Ma *et al.*, 2021).

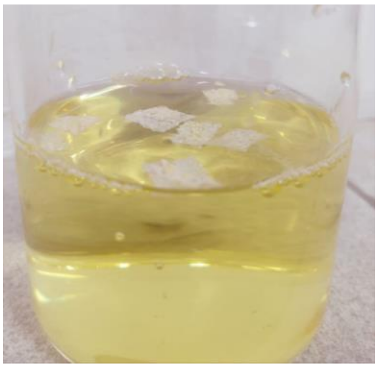

**Figure 3.** Floating Photocatalyst of $TiO_2$/Ni-Coconut Fiber

The activity of $TiO_2$/Ni-coconut fiber floating photocatalyst (Figure 3) towards tetracycline degradation was carried out using a photocatalyst reactor for 120 minutes with the addition of 20 wt% $TiO_2$/Ni to coconut fiber. Absorption measurements were made at the maximum wavelength of tetracycline that had been measured previously, namely 355 nm. The photocatalyst process in this study did not use a magnetic stirrer because when stirring is done quickly, it is feared that $TiO_2$ attached to coconut fiber will be released, thus becoming a new pollutant for the environment. Floating photocatalyst has the advantage of being able to optimize illumination and oxygenation which can result in higher radical formation and oxidation so that it is more effective in degrading waste (Sboui *et al.*, 2017). The percentage of degradation was plotted on a graph against the irradiation time (Figure 4).

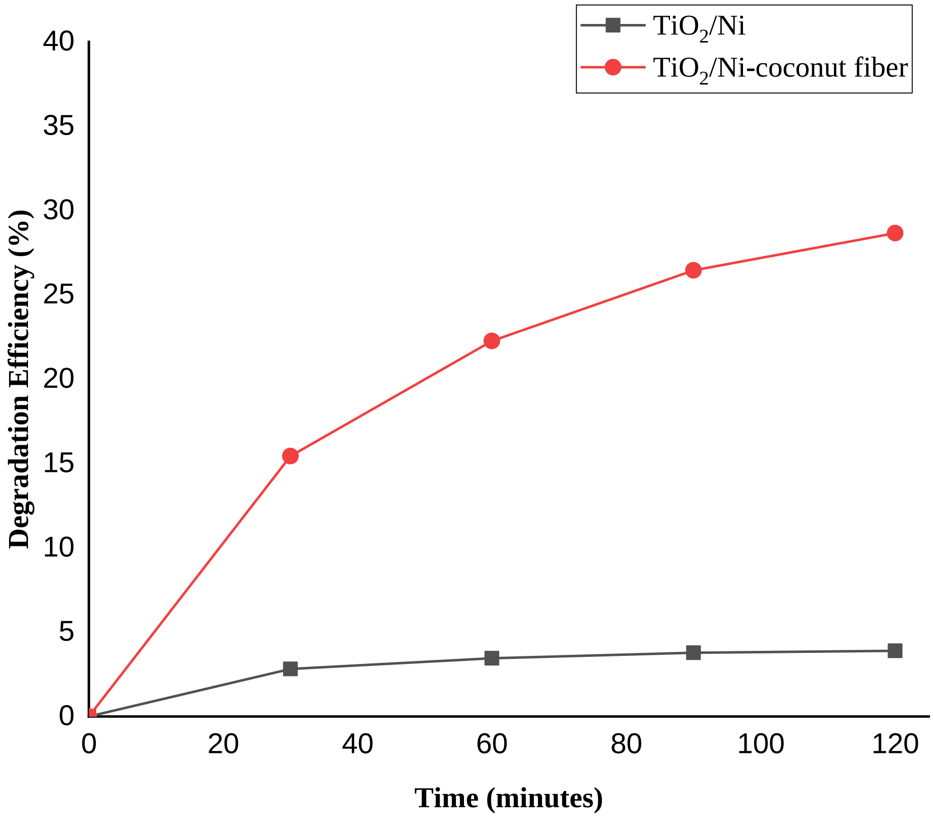


**Figure 4.** Curve of % Tetracycline Degradation versus Irradiation Time

The mechanism of the floating photocatalyst $TiO_2$/Ni-coconut fiber is that the catalyst will absorb photons from the light source that reaches the surface of the water and causes the excitation of electrons from the valence band to the conduction band if the photon energy is equal to or more than the band gap value. Simultaneously, photoelectron ($e^-$) and photohole ($h^+$) will be formed. The positive charge will then interact with water and produce •OH. The OH radical will react with the reactant and produce $O_2$ which will act as an oxidizer. The reactants will be degraded through thermochemical reactions and the resulting products are $CO_2$ and $H_2O$ (Wang *et al.*, 2016).

The results of the degradation activity test showed a percentage difference in the decrease in tetracycline levels using $TiO_2$/Ni catalysts that were embedded with coconut fiber and $TiO_2$/Ni catalysts that were allowed to sink to the bottom of the solution. $TiO_2$/Ni which is embedded with coconut fiber can degrade tetracycline as large as 28.66%, while the $TiO_2$/Ni which sinks at the bottom of the solution has a degradation activity of 3.89% during 120 minutes of irradiation. This shows that the optimum irradiation time occurs at 120 minutes because the production of OH radicals in the photodegradation process has been maximized so that the degradation of tetracycline compounds tends to be stable (Sugandi *et al.*, 2023). The high degradation activity on $TiO_2$/Ni-coconut fiber compared to $TiO_2$/Ni without a carrier is due to differences in light intensity obtained. $TiO_2$/Ni floated with coconut fiber can optimize lighting so that light only needs to get to the surface of the solution to make the photocatalyst work. While the $TiO_2$/Ni which is sunk to the bottom of the solution has less light intensity absorption. This is because light must get to the bottom of the solution to make the catalyst work (Fitri and Mora, 2018). Coconut fiber in $TiO_2$/Ni-coconut fiber also acts as a bioadsorbent in the tetracycline treatment process due to the presence of pores in coconut fiber cellulose that allows electrostatic interactions on cellulose and tetracycline (Kusuma *et al.*, 2023).

**Table 1.** Density of $TiO_2$, Coconut Fiber and $TiO_2$/Ni-Coconut Fiber

| No | Sample | Density (g/cm$^3$) |
|---|---|---|
| 1 | $TiO_2$ | 3.676 |
| 2 | Coconut Fiber | 0.673 |
| 3 | $TiO_2$/Ni-Coconut Fiber (20 wt%) | 0.713 |

The density of $TiO_2$/Ni-coconut fiber is lower than water due to the activation process on a material. Coconut fiber activated with NaOH can reduce fiber density. This is because in the activation process, the separation of lignin and hemicellulose components that exist in coconut fiber lignocellulose so that only cellulose compounds remain. The destruction of the lignin and hemicellulose components that cover cellulose makes the fiber stretch and increases the pore size, making the fiber density smaller (Lismeri *et al.*, 2016).

## Conclusions

XRD characteristics with Merck's $TiO_2$ diffractogram experienced a 2θ shift as an indication that Ni has entered the $TiO_2$ structure and seen some peaks decreased in intensity after being embedded with coconut fiber as an indication that $TiO_2$/Ni has successfully attached to coconut fiber. Band gap energy on $TiO_2$ is 3.21 eV with a wavelength absorption of 386.5 nm which is in the UV range. $TiO_2$/Ni embraced by coconut fiber experienced a shift in band gap energy to 3.09 eV which is at a wavelength absorption of 400.9 nm which is in the visible light range. This indicates that Ni has successfully entered the $TiO_2$ structure. The $TiO_2$/Ni catalyst embraced with coconut fiber has a higher degradation activity than the catalyst without an embrainer with a percent degradation of 28.66% for 120 minutes of irradiation. This is influenced by the amount of light that can be absorbed during the photocatalysis process. This research is expected to be applied as an alternative in handling antibiotic waste or other organic waste.

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