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SYNTHESIS OF $Bi_4Ti_3O_{12}$/ALGA FOR CIPROFLOXACIN DEGRADATION

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Abstract

Antibiotic waste has become a serious issue for ecosystems, and one method that offers great potential to address this problem is photocatalysis. To enhance the photocatalytic activity, one approach is to impregnate the photocatalytic compound onto a supporting material and become composite material. In this study, $Bi_4Ti_3O_{12}$/Algae (Spinossum cottonii, Euchema spinossum, and Sargassum *sp*) composite compounds were synthesized with various algae, including Sargassum and Spinosa. The diffractogram and IR spectra data indicate that the composite compounds were successfully synthesized. The photocatalytic activity test results demonstrate good potential for the $Bi_4Ti_3O_{12}$/Euchema spinossum composite in the degradation of ciprofloxacin, as it was able to degrade 30% of ciprofloxacin within 60 minutes.

INTRODUCTION

Antibiotic drugs have played a major role in treating infectious diseases in humans. However, excessive use has caused new environmental problems, namely the emergence of antibiotic waste [1]. One type of antibiotic waste that has also been reported is ciprofloxacin antibiotic waste. This waste has been reported to be harmful to humans and is difficult to break down by microorganisms. Therefore, efforts are needed to address this issue. Some methods that have been developed to treat ciprofloxacin antibiotic waste include adsorption, oxidation, activated sludge, and photocatalysis [2].

One method with great potential for treating antibiotic waste is photocatalytic technology, as it is inexpensive, efficient, and does not produce new waste [3]. Photocatalytic technology can degrade antibiotic compounds because its mechanism generates reactive oxygen species (ROS) that react with antibiotic compounds [4]. Photocatalyst compounds reported for their ability to degrade antibiotic compounds include TiO_2, $BiFeO_3$, and Cu_2O [5]. One group of compounds reported as having potential for use in photocatalytic technology are Aurivillius-structured compounds. An interesting property of these compounds is their ferroelectric nature, which can slow down the recombination rate of electron (e^-)-hole (h^+) pairs [6]. This property makes these compounds advantageous for use in photocatalytic technology, as they provide good photocatalytic activity.

Aurivillius-structured compounds have the general formula $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{-2}$ which is arranged alternately between bismuth layers $(A_{n-1}B_nO_{3n+1})^{-2}$ The A site is occupied by large cations such as Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+}, while the B site is filled with high-charge cations like Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, or Mo^{6+}. The value of *n represents the number of pseudo-perovskite layer*s [7]. Aurivillius group compounds that have been reported to exhibit good photocatalytic properties include Bi_2WO_6, $Bi_4Ti_3O_{12}$, and $Ca_2Bi_4Ti_5O_{18}$ [8-10].

As a photocatalytic material, $Bi_4Ti_3O_{12}$ has been reported to have a band gap energy of 3.1 eV (400 nm) [11]. The use of the photocatalyst compound $Bi_4Ti_3O_{12}$ to degrade organic compounds/dyes such as rhodamine B and methyl orange has been reported by Liu et al., (2017) [12]. The utilization of this compound to degrade antibiotic compounds has also been reported by several researchers. However, reports on the ability of $Bi_4Ti_3O_{12}$ to degrade antibiotic compounds remain very limited, indicating that further study of this property is still highly needed.

Photocatalytic activity is influenced by several factors, one of which is the surface area of the particles. This is because reactions in photocatalyst compounds occur on their solid surface; therefore, a larger surface area leads to more interaction with the compounds being degraded [4]. One method to increase the surface area of photocatalyst compounds is by embedding

them on supporting materials such as activated carbon or zeolite [13]. One type of biosorbent reported to have a high surface area and used as a supporting material for photocatalyst compounds is algae of the Sargassum sp. group [14]. Thus, the degradation ability of the $Bi_4Ti_3O_{12}$ compound can be enhanced by embedding it or creating a composite with algae. Therefore, in this study, a $Bi_4Ti_3O_{12}$/algae composite will be synthesized and applied to degrade the antibiotic compound ciprofloxacin.

EXPERIMENT

Material

Materials used in this research include Bi_2O_3 (Sigma Aldrich), TiO_2 (Sigma Aldrich), NaCl (Sigma Aldrich), KCl (Sigma Aldrich), $AgNO_3$ (Sigma Aldrich), Acetone (Merck), and Etanol (Merck).

Instrumentation

Materials used in this research include XRD, FTIR,and UV-Vis DRS.

Procedure

Synthesis $Bi_4Ti_3O_{12}$

The Aurivillius compound $Bi_4Ti_3O_{12}$ is synthesized using a mixed salt melt method with NaCl-KCl in a molar ratio of 1:7 for the product compound and salt. Precursors are weighed according to the stoichiometry of the reaction, with the target compound mass set to 3 grams. Next, the precursors Bi_2O_3, TiO_2, and the NaCl/KCl salt mixture are placed in an agate mortar and ground for 1 hour, with acetone added for better homogeneity. The precursor and salt mixture are then calcined at 750 and 820°C for 6 hours, after which it is removed from the furnace. In the following stage, the salt in the sample is removed by washing with hot water. Residual NaCl-KCl salt is identified by adding $AgNO_3$ solution to the wash water until no more white precipitate forms. In the final step, the sample is dried in an oven to remove moisture content.

Synthesis $Bi_4Ti_3O_{12}$/Algae

The algae used in this study include types such as Spinossum cottonii, Euchema spinossum, and Sargassum. In the initial stage, the algae samples are dried and then ground. Next, 0.5 g of $Bi_4Ti_3O_{12}$ and 4 g of algae are dissolved in 60 ml of ethanol. At 73°C, the mixture is stirred for one hour. Then, 6 ml of ethanol and 1.58 ml of diethanolamine are added to the solution, with stirring continued during the addition. The solid is then dried in an oven at 90°C [15].

Characterization

The characterization techniques used are as follows: (a) XRD Characterization using an XRD instrument with Cu-Kα radiation at 40 kV and 30 mA over a 2θ range of 10-90°. The obtained diffractogram is compared with the $Bi_4Ti_3O_{12}$ compound diffractogram database in the Inorganic Crystal Structure Database (ICSD). (b) IR spectroscopy to identify vibration mode of samples, (b) SEM Characterization using an SEM instrument, followed by analysis with ImageJ software to calculate particle size distribution. (c) UV-Vis DRS Characterization using an instrument measured over a wavelength range of 200-800 nm. Data analysis from the UV-Vis DRS instrument is conducted using the Kubelka-Munk equation

Photocatalytic Activity Test

In this test, 100 milligrams of $Bi_4Ti_3O_{12}$/algae composite is added to a beaker containing 100 mL of 5 ppm ciprofloxacin solution. Next, the following tests are conducted:
(a) Adsorption Capacity Test of the $Bi_4Ti_3O_{12}$/algae composite, performed by stirring the test solution for two hours and calculating the change in concentration at the end of the test.
(b) Catalytic Activity Test, conducted by stirring and irradiating the test solution with UV light for 120 minutes, followed by measuring the final concentration after testing. For photocatalytic testing, five commercial UV lamps are used. Ciprofloxacin concentration measurements are performed using UV-Vis spectroscopy. The degradation test is conducted in a homemade photocatalytic reactor measuring 40x40x40 cm, equipped with five commercial UV lamps. The commercial reactor used in the photocatalytic activity test for degrading ciprofloxacin is shown in **Figure 1.**

Figure 1. Homemade photocatalyst reactor.

RESULT AND DISCUSSION

The diffractogram of the synthesized $Bi_4Ti_3O_{12}$ compound is shown in **Figure 2.** When compared to the standard data from the Joint Committee on Powder Diffraction Standards (JCPDS) no. 01-073-2181 for $Bi_4Ti_3O_{12}$, it can be observed that the sample diffractogram matches the standard. This indicates that the target compound has been successfully synthesized. The diffractogram also shows that no additional peaks are present, suggesting the absence of impurity compounds.

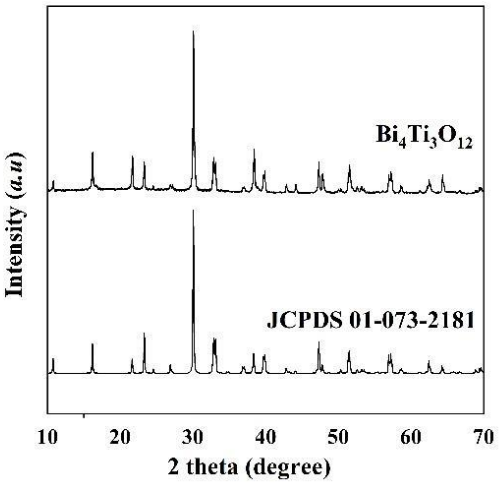

Figure 2. Diffractogram of $Bi_4Ti_3O_{12}$.

The SEM micrograph is shown in **Figure 3,** where it can be observed that the obtained particle morphology is plate-like/sheet. From the scale bar on the SEM image, it is clear that the particles have a plate-like shape, which aligns with other research reports stating that the characteristic morphology of Aurivillius compounds is plate-like/sheet [16]. Plate-like $Bi_4Ti_3O_{12}$ particles have been reported to exhibit good photocatalytic activity [3].

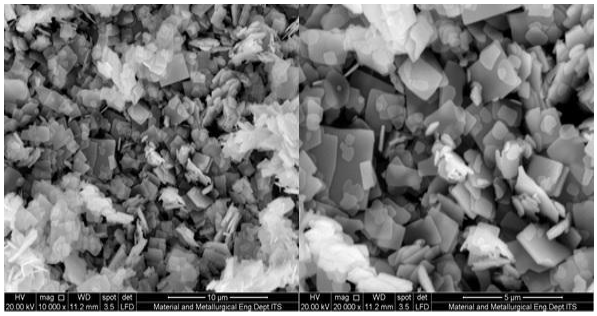

Figure 3. SEM image of $Bi_4Ti_3O_{12}$.

The reflectance spectrum of the $Bi_4Ti_3O_{12}$ sample is shown in **Figure 4**, while the band gap energy calculation using the Kubelka-Munk equation is displayed in **Figure 5**. The calculation results indicate that the $Bi_4Ti_3O_{12}$ compound has a band gap energy of 3.12 eV (397.7 nm). This suggests that the compound operates in the UV region. The electronic transition involved includes electrons from the 6*s* orbital of Bi and 2*p* in the valence band, and 3*d* orbitals of Ti in the conduction band [3].

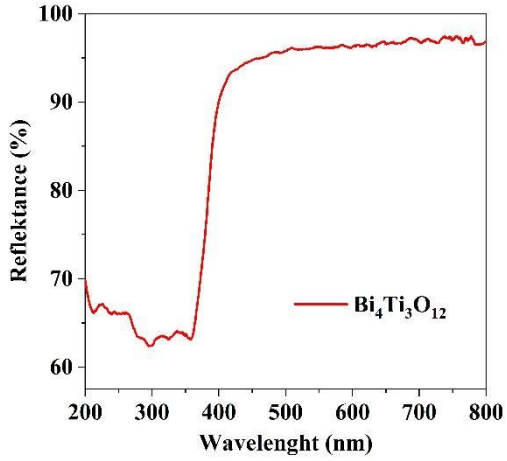

Figure 4. Reflectance spectrum of $Bi_4Ti_3O_{12}$.

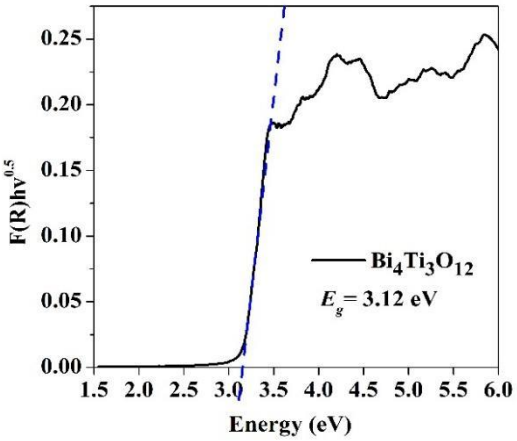

Figure 5. Plot tauc of $Bi_4Ti_3O_{12}$

The IR spectra of the three algae samples are shown in Figure 6, where IR vibration peaks are found in the following regions: (a) ~3400 cm^{-1}, which corresponds to OH vibration, (b) ~2900 cm^{-1}, which corresponds to C-H stretching vibration, (c) 1633 cm^{-1}, which corresponds to asymmetric and symmetric stretching of COOH, (d) ~1418 cm^{-1}, which corresponds to C-OH deformation vibration with contributions from O-C-O vibration, (e) ~1100 cm^{-1}, which corresponds to S=O vibration, (f) 1150 cm^{-1}, which corresponds to C-O vibration, (g) and in the range of ~600-900 cm^{-1}, which corresponds to vibrations from ester sulfate in the structure of 3,6-anhydro-L-galactose, agar-specific band, galactose 4-sulfate, and galactose 6-sulfate, which are characteristic structures of algae [17].

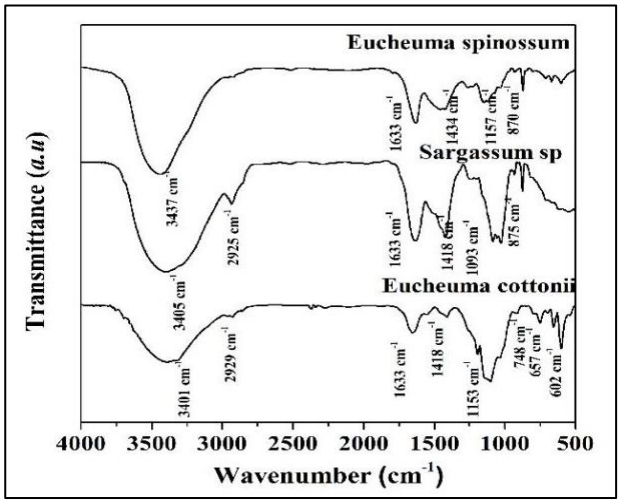

Figure 6. IR spectra of Algae.

The diffractogram of the synthesized $Bi_4Ti_3O_{12}$/algae composite is shown in **Figure 7.** When compared with the diffractogram in **Figure 2**, it shows a match with the $Bi_4Ti_3O_{12}$ sample diffractogram. This indicates that the sample contains the $Bi_4Ti_3O_{12}$ compound. The diffraction peaks from algae/seaweed do not appear because the diffraction instrument is based on electron diffraction, and the seaweed sample consists mainly of atoms like C, O, and H, which have fewer electrons compared to Bi, Ti, or Fe, and thus do not appear in the diffractogram. The diffractogram also shows that no impurity compounds were formed during the composite formation process.

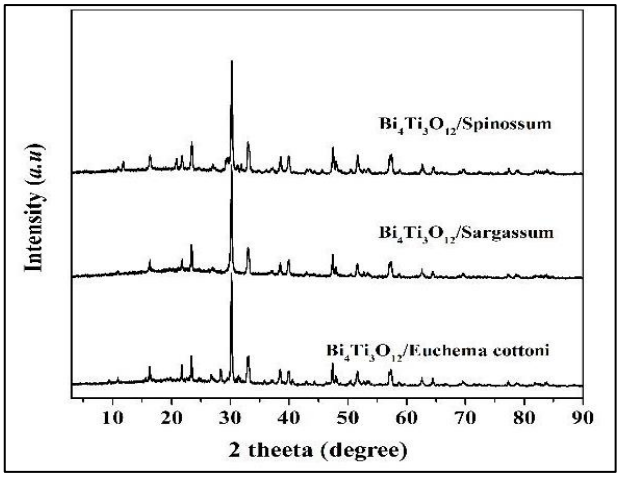

Figure 7. Diffractogram of $Bi_4Ti_3O_{12}$/Algae.

The IR spectrum of the $Bi_4Ti_3O_{12}$/algae composite is shown in Figure 8. When compared with the IR spectrum of algae/seaweed in Figure 13, a match is observed. This indicates that the sample contains algae/seaweed, which is one of the components of the composite. The IR spectrum also shows a new peak in the region of ~550 cm^{-1}, which is related to the Ti-O vibration from the octahedral TiO_6 structure [18].

The degradation ability test of ciprofloxacin by the $Bi_4Ti_3O_{12}$/Algae composite material was conducted on two samples, namely $Bi_4Ti_3O_{12}$/Euchema spinossum and $Bi_4Ti_3O_{12}$/Euchema cottoni. The absorbance spectra of ciprofloxacin after interaction with the $Bi_4Ti_3O_{12}$/algae composite are shown in **Figures 8-10**.

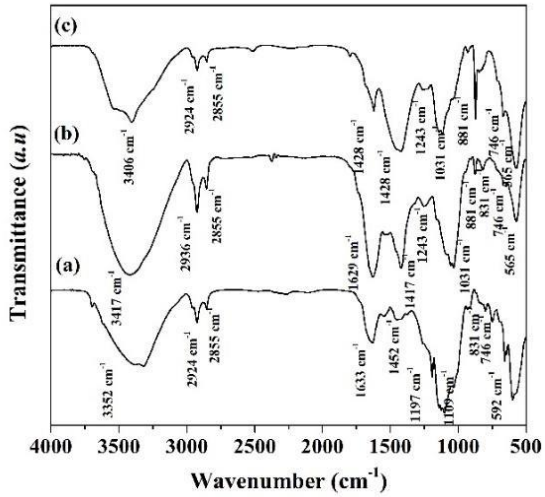

Figure 8. IR spectra of $Bi_4Ti_3O_{12}$/Algae: (a) $Bi_4Ti_3O_{12}$/Euchema cottoni, (b) $Bi_4Ti_3O_{12}$/Sargassum sp, and (c) $Bi_4Ti_3O_{12}$/Euchmea spinossum.

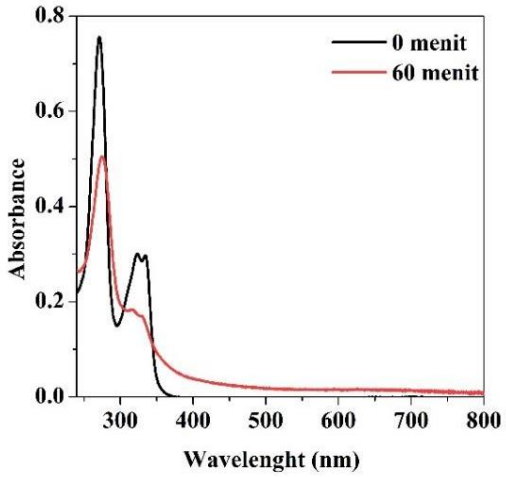

Figure 9. Ciprofloxacin degradation by $Bi_4Ti_3O_{12}$/Euchema spinossum.

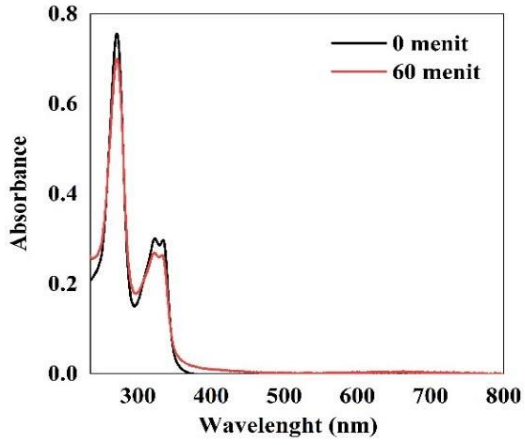

Figure 10. Ciprofloxacin degradation by $Bi_4Ti_3O_{12}$/Euchema cottoni.

Figure 8 shows that the $Bi_4Ti_3O_{12}$/Euchema spinossum composite is capable of reducing ciprofloxacin concentration by approximately 30% over 60 minutes. This indicates that the composite has good potential in reducing the antibiotic ciprofloxacin. However, the $Bi_4Ti_3O_{12}$/Spinossum cottoni composite did not show good results (**Figure 10**). This may be due to aggregation during the measurement, which hindered the photocatalytic process. Similarly, the $Bi_4Ti_3O_{12}$/Sargassum sample showed no significant results during the measurement, likely due to excessive aggregation, which interfered with UV light transmission [19-22].

CONCLUSION

The $Bi_4Ti_3O_{12}$/algae composite has been successfully synthesized, as evidenced by the diffractogram and IR spectrum data. The degradation results show that the $Bi_4Ti_3O_{12}$/Euchema spinossum can reduce the ciprofloxacin concentration by 30%, whereas the other composites did not exhibit good performance. This may be due to significant aggregation during the photocatalytic activity test, which hindered their effectiveness.

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