Removal Ciprofloxacin Through Adsorption-Photocatalyst Properties of $CaBi_4Ti_4O_{15}$

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***Abstract*-. $CaBi_4Ti_4O_{15}$ is one of the four-layer Aurivillius compound family and reported having photocatalytic properties. In this research, we synthesized $CaBi_4Ti_4O_{15}$ by molten salt method, and then the reducing ciprofloxacin concentration ability by adsortion-photocatalysis process was studied. The diffractogram sample showed that $CaBi_4Ti_4O_{15}$ was successfully synthesized with no additional peaks detected which indicates the absence of impurities compound. The micrograph results showed that $CaBi_4Ti_4O_{15}$ has a plate-like morphology with an average particle size of 150 µm. UV-Vis DRS results showed a bandgap energy of 3.148 eV (394.16 nm). The adsorption test showed that the ciprofloxacin concentration decreased 17.61% in 30 minutes. Meanwhile, the adsorption-photocatalyst test results showed that $CaBi_4Ti_4O_{15}$ reduced the concentration of Ciprofloxacin at around 35% for 90 minutes.**

Keywords; $CaBi_4Ti_4O_{15}$, Adsorption-Photocatalyst, Ciprofloxacin

I. INTRODUCTION

Antibiotics are drugs that can cure bacterial infections so that they are widely consumed, causing more and more antibiotic waste that pollutes the environment (Abdurahman, et al, 2021). The toxic side effects of drugs on resources such as cipro are very dangerous and have serious consequences for human, animal, and plant health. Several methods that have been used to handle antibiotic waste include (a) using the microorganism Xylaria longipes, (b) fenton oxidation, (c) oxidation with the help of UV light and chlorine gas, and (d) photocatalysts (Rusch, 2018, Giri, 2014, Deng, 2019, and Ansori, 2016). The photocatalyst method is an environmentally friendly and effective method when degrading liquid waste, especially dye waste (Yahya et al, 2018).

One of the compounds that has the potential to degrade antibiotic compounds is the Aurivillius structured compound (Borg, et al, 2002). Aurivillius compounds reported to function as antibiotic and rhodamine B degraders include the $Bi_7Fe_2Ti_2O_{17}Cl$ compound which degrades tetracycline and rhodamine B antibiotics by 90% for tetracycline antibiotics and 98% for rhodamine B with degradation efficiency achieved in 90 minutes and 60 minutes (Gu, et al., 2022). $CaBi_4Ti_4O_{15}$ is a four-layer Aurivillius compound reported to have a $CaBi_4Ti_4O_{15}$ band gap energy value of 3.06 eV (Nayak, et al., 2017).

The adsorption properties of photocatalysts play a crucial role in the degradation process of organic pollutant compounds. The adsorption process is one of the physical methods that has better properties compared to other wastewater treatment technologies due to its low cost, convenient design, greater availability, and high dye purity at high concentrations (Ziyaadini, et al., 2020). However, the adsorption-photocatalytic activity of the $CaBi_4Ti_4O_{15}$ compound in reducing the concentration of antibiotic compounds has not been reported therefore this study become important. In this resarch, $CaBi_4Ti_4O_{15}$ compound was synthesized by molten salt method and then the adsorption-photocatalyst activity of $CaBi_4Ti_4O_{15}$ for ciprofloxacin concentration decreasing was studied.

II. MATERIAL AND METHODS

Materials

$CaCO_3$ (Merck, 99% powder), TiO_2 (Aldrich, 99% powder), Bi_2O_3 (Himedia, 99% powder), NaCl (Merck, 99.5% powder), KCl (Merck, 99.5% powder), $AgNO_3$ (Merch, 2.5% solution), acetone (Merck), ciprofloxacin, and distilled water.

Synthesis

The precursors of TiO_2, $CaCO_3$, Bi_2O_3, were ground in agate mortar for 1 hour and then acetone was added to homogenize the sample and the was mixed with NaCl/KCl salt with a salt ratio of 1:1 and a sample and salt ratio of 1:7. Then it was ground again and homogenized with an agate mortar for 1 hour. Then the product was calcined at a temperature of 750 and 820 °C for 6 hours. Then the product was removed from the furnace and washed repeatedly with hot water to remove the salt. The presence of salt can be detected by dripping $AgNO_3$ solution onto the filtrate, after the salt is removed the product is dried.

Characterization

The characterization techniques used are The characterization technique: (a) X-ray diffraction (XRD) characterization was carried out to determine the phase of compound (b) Scanning electron microscopy (SEM) was used to determine the morphology of the synthesized compound, (c) Ultraviolet-Visible diffuse reflectance spectroscopy (UV-Vis DRS) was used to determine the light absorption area and used to calculate the band gap energy

Adsorption-photocatalytic activity test

100 mg of $CaBi_4Ti_4O_{15}$ was mixed with 100 ml of an 8 ppm ciprofloxacin solution in a 100 ml beaker glass and stirred for 30 minutes. After that, the mixture was then filtered using filter paper to separate the catalyst residue from the supernatant. The supernatant was subsequently transferred to a cuvette for absorbance measurement using UV-Vis spectroscopy.

The Adsorption-Photocatalytic activity test used 100 mg catalyst and ciprofloxacin 8 ppm and mixed in beaker glass and thet put to homemade photoreactor (exposure with lamp: 80 LEDs 220 V E27 UV) for 90 minutes. After that, the mixture was then filtered using filter paper to separate the catalyst residue from the supernatant. The supernatant was subsequently transferred to a cuvette for absorbance measurement using UV-Vis spectroscopy.

III. RESULT AND DISCUSSION

A. *Characterization Results*

The sample diffractogram was shown in Figure 1 and compared to the standard data in the Joint Committee on Powder Diffraction Standards (JCPDS) $CaBi_4Ti_4O_{15}$ with the number 96-152-8631. It can be seen that there is a match between the peaks of the product and the JCPDS standard diffractogram peaks. It indicates that the $CaBi_4Ti_4O_{15}$ compound was successfully synthesized and the absence of additional peaks indicates the absence of impurity compounds. The typical peaks of the $CaBi_4Ti_4O_{15}$ compound were found at 2θ (°); 12.82; 16.90; 21.56; 27.97; 30.57; 32.90; 39.9; 44.56; 47.47; 52.72; 57.38; 62.04; 63.79; 66.70.

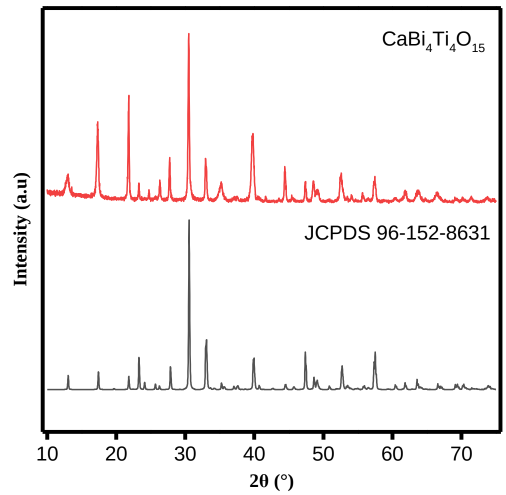

Figure 1 Diffractogram of $CaBi_4Ti_4O_{15}$ compound

The SEM image results shown in Figure 2 of the $CaBi_4Ti_4O_{15}$ product compound can be seen that the sample has a plate-like morphology with a non-uniform size. This morphology is typical of the Aurivillius compound reported by many parties (Zulhadjri, et al., 2022). Figure 3 shows the results of particle size distribution measurements and the particle have size at around 150 μm.

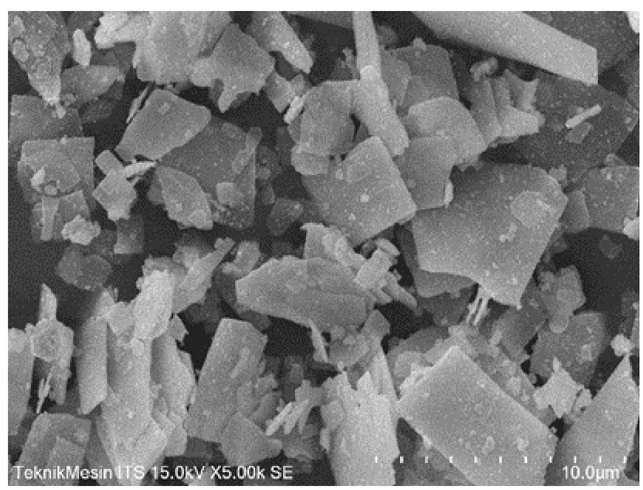

Figure 2 SEM Results of $CaBi_4Ti_4O_{15}$

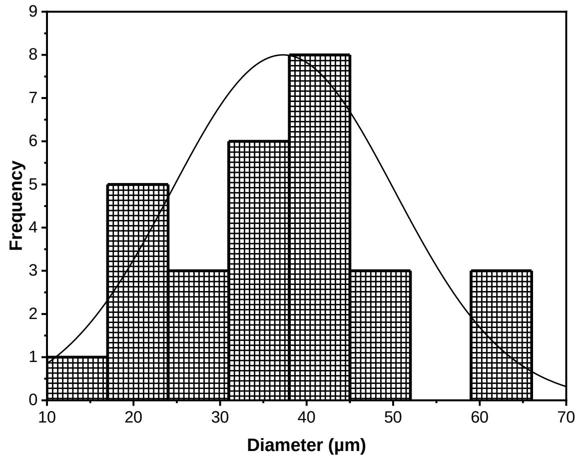

Figure 3 Distribution of $CaBi_4Ti_4O_{15}$ particles

The reflectance spectra of the $CaBi_4Ti_4O_{15}$ compound was shown in Figure 4 and then processed using the Kubelka-Munk equation to calculate the band gap energy. Figure 5 showed that the results of the Kubelka-Munk calculation (band gap energy value) is 3.48 eV.

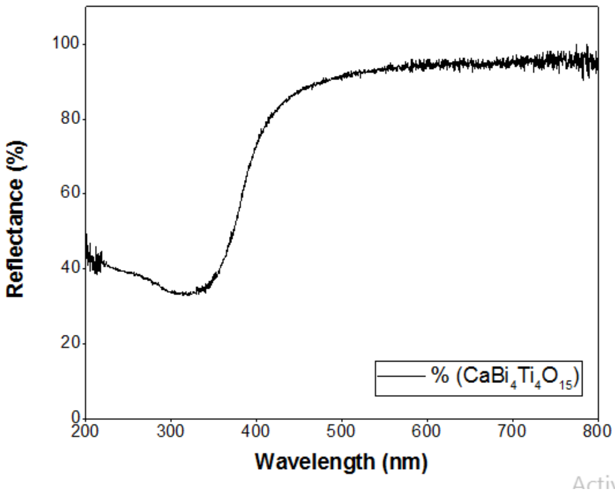

Figure 4 Reflectance spectra of the compound $CaBi_4Ti_4O_{15}$

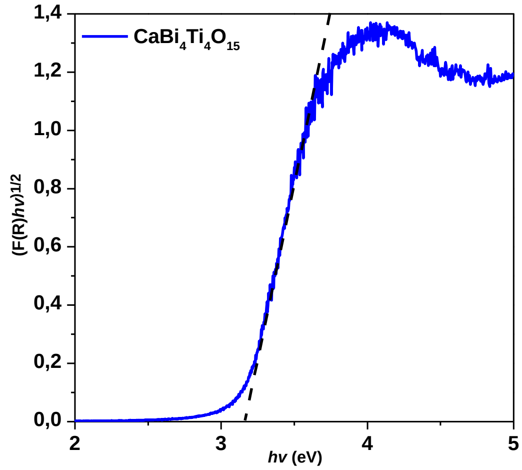

Figure 5 Tauc plot of $CaBi_4Ti_4O_{15}$ compound

Photocatalytic Activity Test of $CaBi_4Ti_4O_{15}$ Using Ciprofloxacin

B. Adsorption Test of $CaBi_4Ti_4O_{15}$ Compounds Against Ciprofloxacin

Figure 6 showed that the $CaBi_4Ti_4O_{15}$ compound has the ability to adsorb ciprofloxacin compounds. The adsorption ability of CBT is consistent with previous reports. The adsorption properties of Aurivillius compounds have been documented by several studies. Al-Abror et al. (2022) reported that the absorbance of the Aurivillius compound $SrBi_4Ti_4O_{15}$ slightly decreases as the concentration of methylene blue decreases. This suggests that $SrBi_4Ti_4O_{15}$ is capable of absorbing methylene blue.

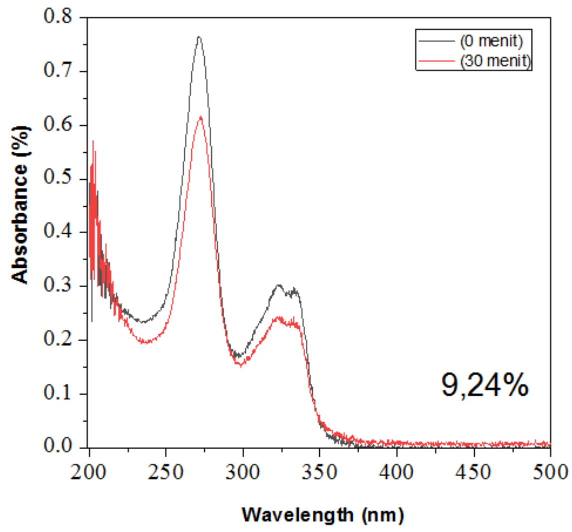

Figure 6 Results of the adsorption test of the $CaBi_4Ti_4O_{15}$ compound

C. Adsorption-Photocatalyst Test of $CaBi_4Ti_4O_{15}$ Compounds Against Ciprofloxacin Using UV Lamps

Figure 7 shows a decrease in absorbance of approximately 35%, indicating a reduction in ciprofloxacin concentration by the same percentage. When compared to the adsorption capability (Figure 6), which is 9.24%, it becomes evident that the photocatalytic mechanism contributes more significantly than adsorption. The presence of the photocatalytic mechanism results in a substantial reduction in ciprofloxacin concentration.

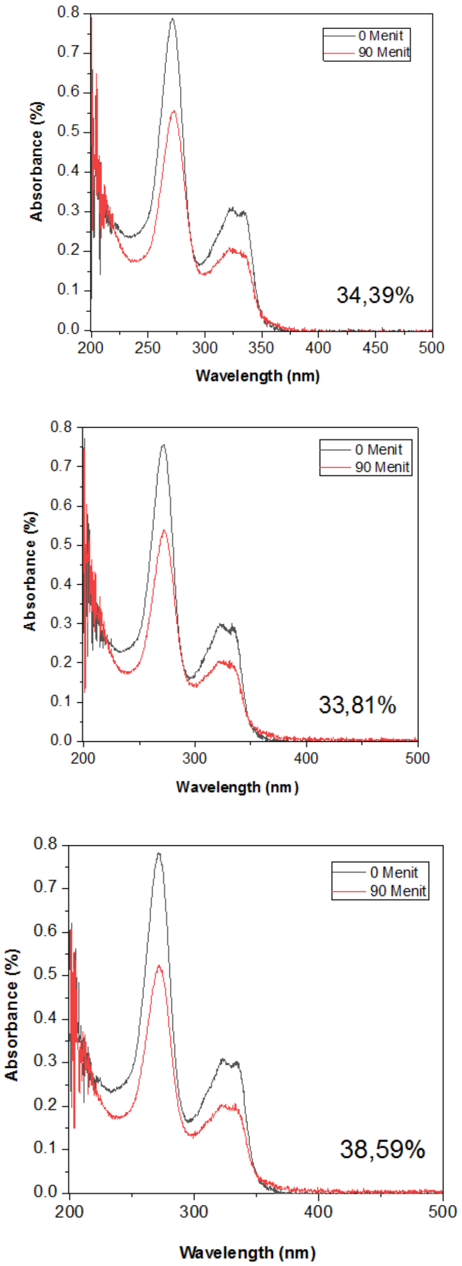

Figure 7 Results of the degradation test of the $CaBi_4Ti_4O_{15}$ compound

IV. CONCLUSION

The $CaBi_4Ti_4O_{15}$ compound was successfully synthesized using the NaCl/KCl by molten salt method The SEM image sohewed that the $CaBi_4Ti_4O_{15}$ morphology is plate-like. The results of the kubelka-munk calculation showed that the band gap energy value of $CaBi_4Ti_4O_{15}$ is 3.148 eV. The results of the adsorption-photocatalyst test showed that $CaBi_4Ti_4O_{15}$ can decreases ciprofloxacin concentration at around 35%.

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