SYNERGYSTIC ADSORPTION-PHOTOCATALYSIS EFFECT OF $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ FOR CIPROFLOXACIN REMOVAL

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ABSTRACT

The triple-layer Aurivillius compound $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ has been reported to exhibit both adsorption and photocatalytic properties and, therefore, can be used to remove organic waste such as antibiotic residues. In this study, the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound was synthesized using the molten salt method. The diffractogram showed $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound was successfully synthesized with no impurity phases detected. Scanning electron microscopy (SEM) images revealed that the compound has a plate-like/sheet-agglomerated particle morphology, with sizes ranging from 2 to 6 μm. Band gap energy calculations showed that the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound has a band gap of 2.74 eV (453 nm). Adsorption tests demonstrated that the compound could adsorb 54.47± 0.56% of ciprofloxacin. Adsorption-degradation tests over 30, 60, 90, and 120 minutes reduced ciprofloxacin c oncentration by 59.84±0.54, 64.05±0.056, 70.04±0.091, and 62.55±0.052%, respectively. It indicates that the adsorption mechanism is more dominant than the photocatalytic mechanism. This may be due to the large number of ciprofloxacin molecules adhering to the BIT surface, making it difficult for light to penetrate, thereby preventing the photocatalytic mechanism from operating at its maximum efficiency.

Keywords: $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$; ciprofloxacin; adsorption-photocatalyst

Introduction

Overusing ciprofloxacin can lead to environmental pollution, which may threaten ecosystems.[1,2] Ciprofloxacin pollution has drawn considerable attention from many parties due to its persistent nature and resistance to degradation, causing serious environmental problems.[3] Various efforts have been made to reduce environmental pollution resulting from ciprofloxacin use. Several methods for ciprofloxacin waste treatment that have been reported include photolysis, photocatalysis, sonocatalysis, and adsorption.[4-6] One promising method is photocatalytic technology.[3] Photocatalysis has gained much attention because it is low-cost, efficient, eco-friendly, and capable of degrading antibiotics under environmental conditions and sunlight exposure.[7]

One class of compounds reported to possess photocatalytic capabilities is the Aurivillius family of compounds.[8] Aurivillius compounds have higher photocatalytic activity than other compounds due to their ferroelectric materials properties, which can inhibit the electron-hole recombination rate (e^-/h^+) and more readily transfer electrons from the valence band to the conduction band.[9] $Bi_4Ti_3O_{12}$ is one of the three-layer Aurivillius compound families with the potential as a photocatalyst with a band gap energy of 2.95 eV.[10] One strategy to enhance photocatalytic activity is to doped the $Bi_4Ti_3O_{12}$ compound with metal elements like Fe. Liu et al.[11] reported that the photocatalytic activity of Fe-doped $Bi_4Ti_3O_{12}$ is higher than that of $Bi_4Ti_3O_{12}$. In this study, Fe-doped $Bi_4Ti_3O_{12}$ ($Bi_4Ti_{2.9}Fe_{0.1}O_{12}$) compounds were synthesized to reduce the band gap energy, thus expected to have good photocatalytic activity.

The photocatalytic activity mechanism involves the molecules' adsorption onto the surface of the catalytic material.[12] It indicates that the adsorption properties of the

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photocatalytic material influence its activity. Several researchers have reported the adsorption properties of Aurivillius compounds. Al-Abror reported that the $SrBi_4Ti_4O_{15}$ compound was able to adsorb methylene blue by 8.7%,[13] while Ziyaadini reported that adsorption is a physical method that offers superior characteristics compared to other technologies due to its low cost, simple design, wide accessibility, and its ability to achieve dye removal with high purity even at high concentrations.[14]

Morphology and particle size of photocatalyst materials influence photocatalytic activity.[15] Many researchers reported that $Bi_4Ti_3O_{12}$ has a small plate-like morphology with a large surface area. In addition, smaller platelets can shorten the migration distance of electron-hole pairs to reactive sites. The internal electric field promotes efficient separation of photon-induced charge carriers and effectively suppresses recombination rates, significantly enhancing photocatalytic activity.[16] Chen has reported that $Bi_4Ti_3O_{12}$ with a nanosheet/nano plate-like morphology exhibits good photocatalytic activity.[17] In addition, one of the synthesis methods that has been reported to produce plate-like/sheet $Bi_4Ti_3O_{12}$ compounds successfully is the molten salt method.[18-19] It indicates that the molten salt method has the potential to be used to obtain plate-like $Bi_4Ti_3O_{12}$ morphology with good photocatalytic activity.

Photocatalytic activity involves two processes: adsorption and degradation reactions on the surface of the photocatalyst material. Therefore, particle size also affects photocatalytic activity[12]. Bashofi has reported the adsorption properties of the $Bi_4Ti_3O_{12}$ compound, which can absorb the rhodamine B dye.[20] The adsorption ability of $Bi_4Ti_3O_{12}$ provides an opportunity to enhance its photocatalytic activity. However, studies on the adsorption-photocatalysis of Bi4Ti3O12 for the antibiotic compound, especially ciprofloxacin, are still limited. Therefore, the study of the adsorption-photocatalytic properties of $Bi_4Ti_3O_{12}$ becomes urgent to conduct.

Therefore, in this research, we synthesized Fe-doped $Bi_4Ti_3O_{12}$ (Bi4Ti2.9Fe0.1O12) using the molten salt method (using mixed salt NaCl-KCl), and then studied its adsorption-photocatalysis properties for ciprofloxacin removal.

Methods

Material

The materials used in this study include Bi_2O_3 (Himedia, 99.9%), TiO_2 (Himedia, 99.9%), NaCl (Merck, 99.5% powder), KCl (Merck, 99.5% powder), α-Fe_2O_3 (Himedia, 99.9%), $AgNO_3$ (Merck, 2.5% solution), acetone, distilled water, and ciprofloxacin solution.

Synthesis of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$

The $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound was synthesized using the molten salt method with a NaCl-KCl mixture in a 1:1 molar ratio at temperatures of 750 and 820°C. The molar ratio of the product ($Bi_4Ti_{2.9}Fe_{0.1}O_{12}$) to the salt (NaCl-KCl) was set at 1:7. The masses of the precursors (Bi_2O_3, TiO_2, and Fe_2O_3) and salts (NaCl and KCl) were calculated stoichiometrically to 3 grams of the target compound.

The synthesis was conducted by homogenizing the precursors (Bi_2O_3, TiO_2, and Fe_2O_3) and salts (NaCl and KCl) in a molar ratio using an agate mortar for 1 hour. Subsequently, and then the mixture was heated at temperatures of 750 and 820°C for 6 hours. The product was removed from the furnace and placed on filter paper. The sample was then washed several times with hot distilled water to remove the alkali salts and analyzed using $AgNO_3$ to detect the presence of salts in the filtrate. Finally, the sample was dried in an oven at 90°C until completely dry.[17]

Characterization

The phases of the sample compound were identified using (a) *X*-ray diffraction (XRD) (Rigaku Miniflex diffractometer) with measurement range at 2θ (°) = 3-90, (b) the elemental composition of the sample was identified through *X*-ray fluorescence (XRF)

(PANalytical Minimal 4). (c) The particle morphology was analyzed using Scanning electron microscopy (SEM) (Hitachi Flexsem 1000) and used at a magnification of 20,000x. (d) The band gap energy was determined from the data obtained from Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) (Thermo Scientific Evolution 220 spectrometer) measured over a wavelength range of 200-800 nm and then calculated using the Kubelka-Munk equation.

Adsorption Test

A 100 mL solution containing 8 ppm ciprofloxacin was combined with 100 mg of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ in a beaker, which was subsequently placed inside the photoreactor without lamp exposure (dark condition) for 120 minutes. Once the tests were completed, the solution was filtered to remove the catalyst, and the filtrate was analyzed using UV-Vis spectroscopy to measure the remaining concentration of ciprofloxacin.

Adsorption-Photocatalyst Test

The Adsorption-Photocatalyst test was conducted by a homemade photoreactor with a size of 40×40×40 cm. The light source in this reactor consisted of five commercial UV lamps (LED UV spotlight bulbs with 80 LEDs, 220 V, E27), with a distance of 10 cm between the light source and the ciprofloxacin solution.

100 ml of 8 ppm ciprofloxacin solution was mixed with 100 mg of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ and then placed in the photocatalytic reactor, where commercial UV lamps exposed it for 30, 60, 90, and 120 minutes. Afterward, the mixture was filtered to separate the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound, and the absorbance of the ciprofloxacin solution was measured using UV-Vis spectroscopy

Result and Discussion

The diffractogram of the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound is shown in Figure 1, and it can be seen that the sample diffractogram matched the standard data from the Inorganic Crystal Structure Database (ICSD) No. 87808, with no additional peaks detected, confirming that the formed sample is pure $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ It indicated that $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ was successfully synthesized without impurities compound. The result of the XRF analysis is summarized in Table 1, and the detected elements are Bi, Ti, and Fe.

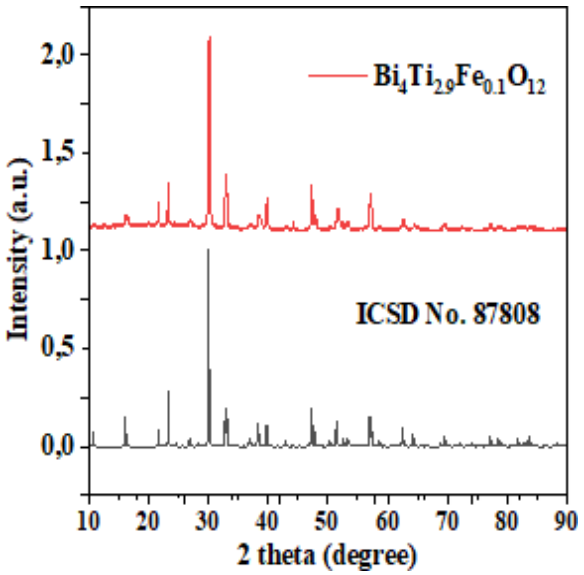

Figure 1. The diffractogram of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$

The micrograph of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ was shown in Figure 2(a) and showed that the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound has a plate-like/sheet morphology and forms agglomerates. The plate-like/sheet morphology particle is characteristic of Aurivillius compound morphology, which has been extensively reported in previous studies.[16–19] This morphology is also consistent with reports from other research that synthesized the compound using the molten salt method[16–19]. In addition, this result is also similar to previous studies that used the same type of salt mixture (NaCl/KCl)[18]. The particle size distribution is shown in Figure 2b, and it can be seen that the particle size distribution of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ is in the range of 2-18 μm, with mostly sizes at 2-6 μm.

The UV-Vis DRS spectrum of the sample is shown in Figure 3a, and it was processed by the Kubelka-Munk equation to calculate the band gap energy value (the Tauc plot was shown in Figure 3b). The resulting Tauc plot is shown in Figure 3. Kubelka-Munk

calculations result that the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound has a band gap energy of 2.74 eV (453 nm). This result is similar to previous research[21]. It indicated that $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ can operate in the visible light region ($\lambda \geqslant$ 420 nm), therefore giving an advantage for photocatalytic applications due to its coverage of a broader wavelength spectrum. The reduction in band gap energy is caused by the emergence of new electronic transitions in the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound. The electronic transition in $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ involves Fe-3*d* orbitals, altering the electronic transition from the Bi-6*s* + O-2*p* (valence band) orbitals to the Ti^{4+}-3*d* (conduction band) orbitals, to that from the Bi-6*s* + O-2*p* (valence band) orbitals to the Fe^{3+}-3*d* orbitals[11].

The adsorption test of ciprofloxacin by $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ was conducted three times, each for 120 minutes, as shown in Figure 4 and the results were summarized in Table 2. It demonstrates that there was a reduction in the ciprofloxacin concentration after interacting with $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$. The decrease in ciprofloxacin concentration indicates that $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ can also act as an adsorbent. It also indicated that the $Bi_4Ti_3O_{12}$ compound still retains its adsorption properties even when doped with Fe metal.

Ciprofloxacin was degraded three times with the same testing time variations of 30, 60, 90, and 120 minutes, as shown in Figure 5 and the results were summarized in Table 3. It can be seen that the longer the exposure to light caused the ciprofloxacin concentration decreases bigger. The biggest decrease in ciprofloxacin concentration was actually observed at minute 90. The decrease in concentration at minute 120 (the longest time) was smaller compared to minute 90. It indicated that the decrease in concentration during the adsorption-photocatalytic activity test of the compound $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ is still unstable. The instability is observed in the degradation under UV light and several factors, such as the reaction conditions, reactant concentration, and the physicochemical properties of ciprofloxacin itself[21]. In addition, the measurement of photocatalytic activity is also influenced by several factors, including (a) light intensity, (b) the homogeneity of catalyst dispersion in the test solution, and (c) environmental factors such as temperature and pH[22].

Table 1. The results of XRF characterization

Elements	%Mass	%Theoretical Mass
Bi	87.9	71.40
Ti	9.61	11.80
Fe	0.547	0.48

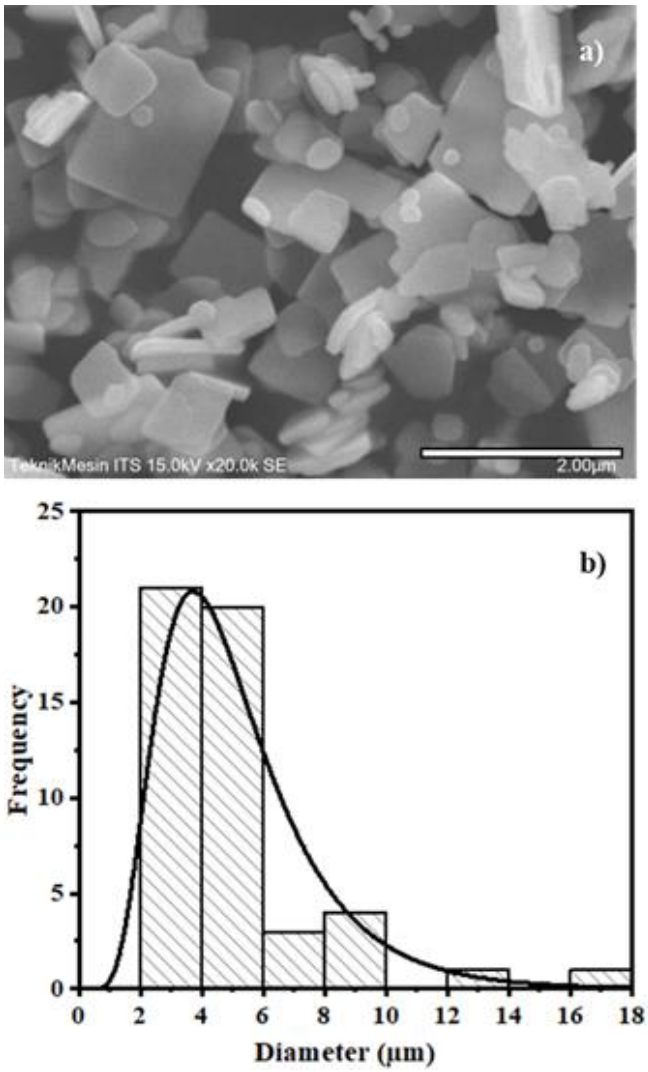

Figure 2. (a) Micrograph of $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound and (b) Particle size distribution

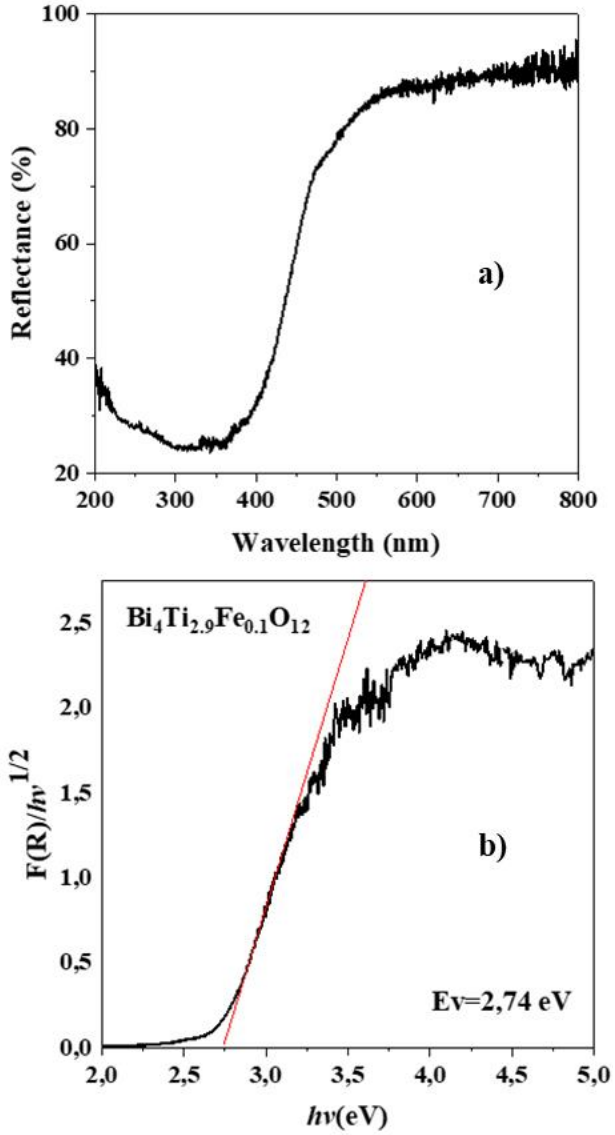

Figure 3. (a) DRS spectrum % reflectance b) Tauc plot $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$

Table 2. The result of adsorption test

Experiment	Concentration decreases (%)	Average
1	48.88	
2	53.73	54,47±0.56%
3	60.80	

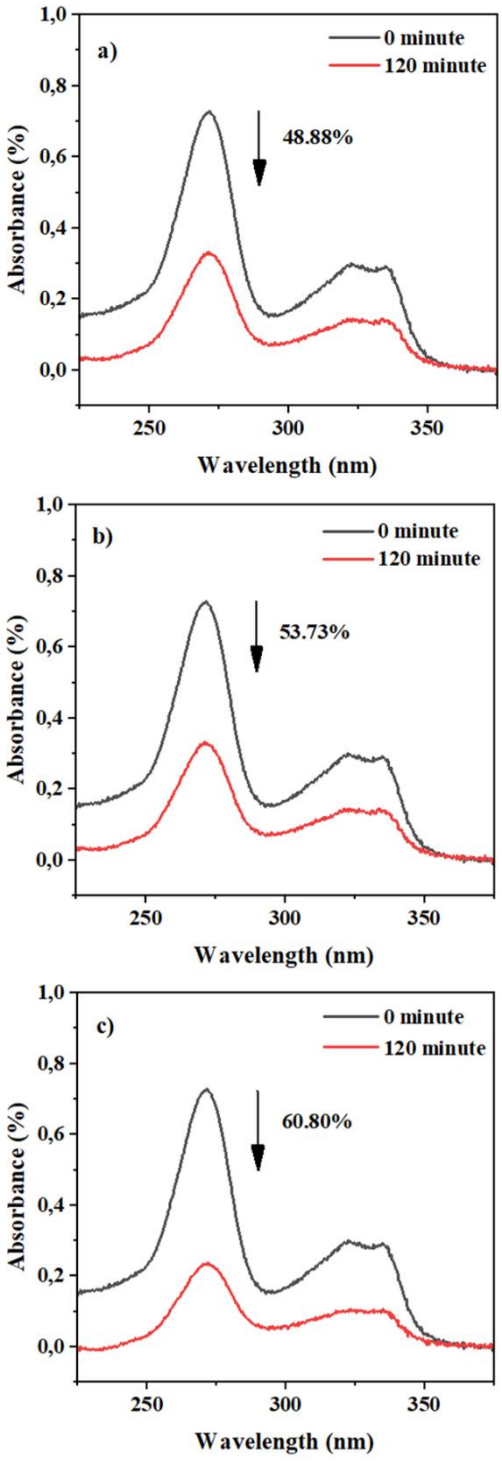

Figure 4. Adsorption test of ciprofloxacin by $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$. Experiment: (a) 1, (b) 2, and (c) 3

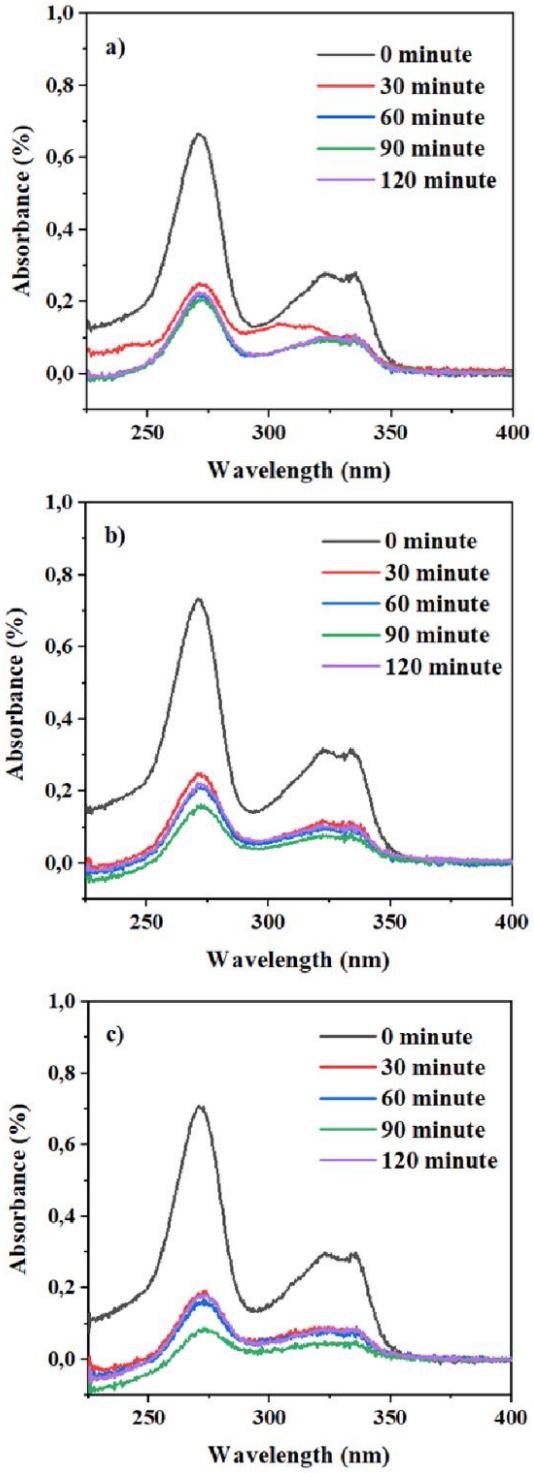

Figure 5. Adsorption-degradation test. Experiment: (a) 1, (b) 2, and (c) 3

The comparison between adsorption testing and adsorption-photocatalysis shows that the adsorption mechanism plays a larger role. It may be due to the strong adsorption properties of the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ compound. Jannus et al.[23] suggested that if a photocatalyst material has a high adsorption capacity, it can cause a large amount of dye compounds to adhere to its surface, which can block light exposure and hinder the photocatalytic process from reaching its maximum efficiency. Thus, it is possible that the surface of the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ catalyst is covered by an amount of ciprofloxacin, preventing light from penetrating the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ surface. This will result in a lower contribution of the photocatalyst.

Table 3. The result of Adsorption-Photocatalysis test

Time (minutes)	Experiment	Concentration decreases (%)	Average
30	1	54.46	59.84±0.54%
	2	59.70	
	3	65.35	
60	1	58.22	64.05±0.056%
	2	64.44	
	3	69.50	
90	1	60.71%	70.04±0.091%
	2	70.50%	
	3	78.92%	
120	1	57.40%	62.55±0.052%
	2	62.47%	
	3	67.77%	

The mechanism of ciprofloxacin degradation by the photocatalytic material $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ occurs when UV light is exposed to the compound $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$, leading to an electronic transition that involves the transfer of electrons from the valence band to the conduction band. This transfer generates h^+ in the conduction band and e^- in the valence band. Subsequently, h^+ reacts with OH^-/H_2O to form hydroxyl radicals ($OH^\cdot$). Meanwhile, e^- reacts with O_2 to form $O^\cdot$ radicals. Then, the radicals will react with ciprofloxacin and cause ciprofloxacin degradation. The degradation

products consist of smaller organic molecules until H_2O and CO_2 are eventually formed.[24] However, in this study, the identification of degradation product molecules was not carried out. The general mechanism of ciprofloxacin degradation by $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ can be illustrated in Figure 6.

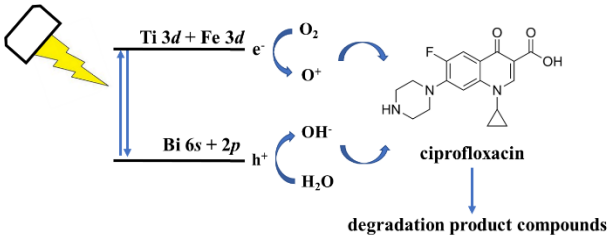

Figure 6. The mechanism of ciprofloxacin degradation by $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$

Conclusion

The compound $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ with plate-like/sheet morphology has been successfully obtained through the molten salt method (mixed NaCl-KCl). The reflectance spectrum calculations for $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ indicate that the band gap energy of the sample is 2.74 eV (453 nm). Adsorption and adsorption-photocatalyst tests showed that the $Bi_4Ti_{2.9}Fe_{0.1}O_{12}$ can decrease the ciprofloxacin concentration. The comparison between adsorption and adsorption-photocatalytic tests on ciprofloxacin compounds showed that the adsorption mechanism contributes more dominantly.

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