Coconut Fiber Decorated with Bismuth Vanadate for Enhanced Photocatalytic Activity

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ABSTRACT: Bismuth vanadate/coconut fiber (BiVO4/CF) composites were synthesized by coprecipitation and calcination methods. All catalysts used in this work were prepared by a simple coprecipitation method and fully characterized by means of XRD, SEM-EDS, PL, BET N2 adsorption, zeta potential, and UV–vis DRS. Degradation of indigo carmine (IC) under visible light irradiation was tracked by the UV–vis technique. It was documented that XRD patterns of BiVO4 and BiVO4/CF samples retained the monoclinic structure. From SEM, the CF sheets were visualized, covering the surface of BiVO4 particles. The specific surface area of the synthesized catalysts increased from 1.77 to 24.82 m²/g. The shift of absorption edge to a longer wavelength corresponded to a decrease in band gap energy from 2.3 to 2.2 eV. The photocatalytic degradation rate of the BiVO4/CF composite was five times higher than that of pristine BiVO4. Moreover, the photocatalyst can be separated and recycled with little change after the third times recycling. The improved activity of the composite resulted from the combination of the adsorption performance of the substrate CF and the photocatalytic activity of BiVO4. In addition, the position of the specific mechanism could occur via both the active species of superoxide radical and hydroxyl radical.

1. INTRODUCTION

The synthetic dye compounds have been used in various manufacturing industries, such as in the textile, plastics, and paper industries. Over 700,000 tons of synthetic dyes is annually produced worldwide.¹ Up to 200,000 tons of textile dye waste from the dyeing process and finishing operations is released to effluents every year.² Since the chemical structure of dye molecules is represented by a backbone of the complex aromatic molecular structures that are nonbiodegradable chemicals, they tend to accumulate in an organism and form different aromatic intermediates that are toxic and thus pose a serious threat.³⁴ Furthermore, most of them can persist in the environment and are considered to be the main source of pollution to the environment, which directly affect human health and cause ecological damage even at low concentrations.⁵⁶

Various techniques including adsorption, precipitation, crossflow microfiltration, electrodialysis, and reverse osmosis have been used to actively investigate the removal of dye from the environment.⁷⁻¹¹ However, these methods are unproductive at low-concentration contaminants. One of the most promising techniques applied for efficient degradation of antibiotics is advanced oxidation processes (AOPs) based on the use of highly oxidizing species responsible for mineralization of organic pollutants in the presence of a photocatalyst combined with photon energy.¹²¹³

The monoclinic phase of bismuth vanadate (BiVO4) with a band gap of 2.4 eV is a semiconductor often used as a heterogeneous photocatalyst for wastewater purification under visible/sunlight irradiation. This material is readily available and possesses various desirable properties, including chemical stability in acidic or alkaline conditions, low toxicity, and strong oxidation properties for water purification.¹⁴⁻¹⁶

However, some disadvantages in terms of surface properties of the BiVO4 photocatalyst and recombination of photo-generated e⁻ and h⁺ during the process limit its applications in photocatalysis.¹⁷,¹⁸ Therefore, the main challenge lies mainly on the design and development by combining the photocatalyst with other materials, which extensively increases the charge transfer and helps separate the e⁻/h⁺ pair. To prevent charge recombination, heterojunctions with other materials are one example of an effective modification strategy of the photocatalyst for potential applications in photocatalysis.¹⁹⁻²⁷

The specific surface area is another important intrinsic property of surface-adsorbed pollutant molecules. Large
specific surface areas for the adsorption are an essential step in a photocatalytic reaction because the adsorbed dye molecules from bulk aqueous solution are more likely to react with the photocatalyst and photon energy. Various modification methods have been involved in the modification of the photocatalyst to enhance not only $e^−/h^+$ recombination but also surface properties.

A heterogeneous photocatalyst in a solid form of the composite with porous carbon-based materials was reported by Xing et al. They prepared the composite material between the TiO$_2$ photocatalyst and activated carbons from bituminous coal for the degradation of rhodamine B. The nanosized TiO$_2$ particles on activated carbon could be attributed to the excellent adsorption effect in the dark and high efficiency photocatalytic degradation in the presence of UV light irradiation. They also found that the photocatalytic activity of the composite photocatalyst was dependent on the TiO$_2$ loading amount.

This result corresponds with the finding of Guo et al. The result was investigated by modifying TiO$_2$ on powdered activated carbon (TiO$_2$/PAC) for 2-methylisoborneol (2-MIB) waste treatment. The decolorizations of such a pollutant collected from a river were obtained with adsorption experiments, followed by photodegradation experiments under UV light. The PAC adsorbent does not only enhance the specific surface area of the TiO$_2$ photocatalyst but also enable the mobility of electrons/holes. Various toxic effluents (like dyes and pesticides) were investigated for the photocatalytic degradation by Sharma et al. It was observed that the mesoporous silica-supported ZnO photocatalyst performed well in adsorption capacity.

Another synthetic reactive black KN-B (RB5) dye was investigated for the decolorization by Zhang et al. Immobilizing BiVO$_4$ on activated carbon fibers (ACFs) was reported to be effective in the photocatalytic reaction rather than in single-phase BiVO$_4$. This activity increase was mostly attributed to the formation of interfacial contact between BiVO$_4$ and ACFs, thereby suppressing its charge recombination. The corresponding results were also described by Saleem et al. Their experiments were conducted using monoclinic BiVO$_4$-coated@carbon fibers for the decolorization of synthetic RhB dye under visible light irradiation. BiVO$_4$ with the presence of carbon fibers showed higher photocatalytic activity as compared to pure form. Apart from that, its photocatalytic activity on antimicrobial activity against pathogenic microbes (Escherichia coli and Staphylococcus aureus) was also investigated. Based on the literature review, the enhanced photocatalytic activity of the photocatalyst combined/supported with highly porous material compared individually with that of the single-phase photocatalyst was mechanically efficient.

Thus, this work contributed to the development of BiVO$_4$ combined with natural coconut fiber (CF). Indigo carmine (IC) dye was used as a degradable substance. IC in bulk was concentrated on the adsorbate surface extracted from CF, while BiVO$_4$ was used as a photocative phase to degrade the adsorbed IC molecules under visible light. Therefore, carbon material in CF could effectively increase the active surface area and inhibit the recombination of electrons and holes of BiVO$_4$ during photocatalysis.

2. RESULTS AND DISCUSSION

The XRD patterns of CF, pure BiVO$_4$, and the BiVO$_4$/CF composite are provided in Figure 1. The broad peaks of CF derived from banana fiber can be indexed to amorphous carbon at $2\theta = 24^\circ$, which correspond to the reflections of the (002) plane. The main peaks can be indexed as (020), (110), (011), (121), (040), (200), (002), (211), (150), (132), (240), (042), (202), (161), (251), (170), (321), and (123) crystal planes of monoclinic BiVO$_4$ (JCPDS no. 14-0668). The XRD patterns of the BiVO$_4$/CF composite demonstrate that the existence of CF does not change the crystal structure or form new crystal phases of BiVO$_4$. In addition, no characteristic signal of CF (002) appears in the XRD pattern of the composite sample. This is possibly due to the high crystallinity of the BiVO$_4$ phases, which appear as the dominant peaks in the XRD spectra of the composite sample.

The optical properties of BiVO$_4$ and the BiVO$_4$/CF composite in terms of reflectance spectra ($R$) were investigated using UV−vis diffuse reflectance spectroscopy (DRS) for solid samples, as shown in Figure 2a. These reflectance data can be converted to the absorption spectra ($\alpha(R)$) according to the Kubelka−Munk (K-M) theory. The K-M equation is given as eq 1.

$$F(R) = \frac{(1 - R)^2}{2R}$$

As shown in Figure 2b, the absorption edge of the BiVO$_4$/CF composite exhibited a little shift from 500 to 530 nm, indicating that adding CF in BiVO$_4$ can act as a photosensitizer to effectively improve the visible light response. Tauc plots presented in Figure 2c were used to determine the band gap energy ($E_g$). The band gap values estimated from the intercept of the tangents to the plots are 2.3 and 2.2 eV for BiVO$_4$ and the BiVO$_4$/CF composite, respectively.

Thus, it can be inferred that the band gap of the BiVO$_4$/CF composite became narrower, and the absorption edge was shifted to a longer wavelength by the addition of CF. This can be attributed to the chemically doped and metal ion-implanted semiconductors since the carbon additive derived from coconut fiber could introduce impurity levels within the band gap of BiVO$_4$. This is consistent with the results of Rajamanickam and Shanthi on the TiO$_2$/activated carbon
composite. They found that the composite had a higher absorption edge than the naked TiO₂ in the entire visible region.

Moreover, the photoluminescence (PL) spectra explored the efficiency of separating the photogenerated electron–hole pair of the prepared photocatalysts. Usually, the separation of photogenerated charge carriers is associated with PL signals, in which the lower the PL intensity provided, the higher the separation rate. As shown in Figure 3a, the PL emission peak intensity of BiVO₄ is higher than that of the BiVO₄/CF composite, which is attributed to the decrease in band gap energy in the BiVO₄/CF composite according to Figure 3b.

Figure 2. UV–vis DRS of BiVO₄ and the BiVO₄/CF composite. (a) Diffuse reflectance spectra, (b) absorption spectra, and (c) Tauc plot.

Figure 3. (a) Comparison of the intensity of PL and (b) proposed energy level diagram of BiVO₄ and the BiVO₄/CF composite.
This indicated that the separation and transfer of photo-generated carriers help enhance photocatalytic performance when BiVO₄ is modified with CF.

The scanning microscopy images are shown in Figure 4. The SEM images of BiVO₄ photocatalysts with different magnifications showed spherical-shaped morphology with the particle size distribution of approximately 6–8 μm. The original CF shows 2D sheet-like morphology with a smooth layer-like surface. After the calcination, the changes in surface morphology of the plate-like structure of CF have been observed. It was covered/mixed with the aggregation of a variety of BiVO₄ particles, which increased the probability of adsorbing dye molecules on a high specific surface, resulting in a high photocatalytic activity. Jafry et al. reported similar results after the introduction of silica-decorated P25 TiO₂.

In addition, EDS analysis demonstrated further that Bi, O, V, and C coexist in the BiVO₄/CF composite as the main elements, which is expected for the composite sample. This further confirmed that the BiVO₄/CF composite has been successfully synthesized in this study.

The detailed summary of the specific surface area, pore volume, and average pore size of all samples is presented in Table 1. The BiVO₄/CF composite shows a higher surface area (24.82 m²/g) compared to the pristine BiVO₄ (1.77 m²/g). The increase in the surface area of BiVO₄ in the composite is due to the large surface area of CF (391.70 m²/g) onto the surface of the BiVO₄ particles. Besides that, the large surface area and pore volume can enrich the adsorption of organic dyes during photocatalytic activity experiments. This suggested that the photocatalytic and adsorption processes are controlled by not only the external surface of the photocatalyst but also the intraparticle diffusion in the liquid-filled pores. The N₂ adsorption–desorption isotherms of CF, BiVO₄, and the BiVO₄/CF composite are presented in Figure 5. All samples presented a typical type IV isotherm characteristic with hysteresis loops at the P/P₀ range of 0–1.0, which was related to the characteristics of mesoporous materials (2–50 nm).

On the other hand, good agreement was also observed for the BJH pore size distribution curve (insets of Figure 5), and the average values of pore size are listed in Table 1. In addition, the quantity adsorbed per gram of composite was found to increase when CF was added, leading to an enhanced specific surface area compared to that in pure BiVO₄.

The effect of contact time on IC adsorption on the BiVO₄/CF composite was studied for varying adsorption times of 15, 30, 60, and 90 min. The results are illustrated in Figure 6a. It was found that the removal of IC rises rapidly along with the contact time and attains the equilibrium after 30 min. The adsorption study was continued further for 90 min, but no significant increase was observed in IC adsorption. Therefore, 30 min was selected as an equilibrium contact time for dark adsorption before light on in this research.

Figure 6b presents the photodegradations of the IC promoted by photolysis (blank) and photocatalysis with the BiVO₄ and BiVO₄/CF photocatalysts. The photocatalysis of the pristine BiVO₄ curve demonstrates its low efficiency (∼16%) for the photodegradation of IC dye, while the photocatalysis of IC reaches ∼70% over the BiVO₄/CF composite in 120 min. The values of the pseudo-first-order kinetic constants (k) are explained by the pseudo-first-order kinetic model as given in the following equation.

\[
\ln \frac{C_t}{C_0} = kt
\]

(2)

In these cases, the rate constants were 0.0014 and 0.0082 min⁻¹ for BiVO₄ and composite material, respectively. This indicated that the photodegradation kinetics of composite material were five times faster than that of the pristine one (Figure 6c).

In general, the increase in activity is due to the greater covering of the surface of the active phase BiVO₄ with CF. This would increase the adsorption of dye molecules around the catalyst surface and provide its ability to degrade. Thus, it was noted that the addition of CF in BiVO₄ promotes a considerable increase in the IC photodegradation, which serves as another significant way to improve the efficiency of photocatalysts.

Another important factor that affects the degradation rate is the interaction between the catalyst and the dye molecule. The pH of IC aqueous solution also could affect the zeta potential of the photocatalyst. As shown in the inset image (Figure 6b), the point of zero charge (pzc) of BiVO₄/CF particles is determined at pH = 11.6. Above the pzc, particles have a

Table 1. Summary Report of the Surface Properties

| sample            | BET specific surface area (m²/g) | pore volume (cm³/g) | pore size (nm) |
|-------------------|---------------------------------|--------------------|---------------|
| CF                | 391.70                          | 0.233              | 2.79          |
| BiVO₄/CF composite| 24.82                           | 0.016              | 3.11          |
| BiVO₄             | 1.77                            | 0.004              | 5.61          |
negative surface charge, whereas the surface is positively charged below this pH. In addition, it was observed that the positive charge of particles presented over a wide range of pH values is due to remaining H⁺ residues on the catalyst surface. Since the natural pH of IC is 9, the positive charge is found for BiVO₄/CF at this pH. IC dye exists in aqueous solution as negatively charged ions, which favor electrostatic interactions with the positive charge surface of BiVO₄/CF particles, leading to the strong adsorption.

To justify the photocatalytic efficiency of BiVO₄/CF composites in this study, its potential must be compared with the other activated carbon (AC)-based photocatalysts reported in the literature. Table 2 compares the maximum photocatalytic activities of various pollutants by different activated carbon (AC)-based photocatalysts. In this study, the photocatalysis of IC reached ~70% over the BiVO₄/CF composite in 120 min, whereas if BiVO₄ alone was used, ~16% degradation was achieved, which corresponds well to the reported literature. Based on the results presented in Table 2, the BiVO₄/CF composites also exhibited good photocatalytic activity when compared with other similar composite materials.

Furthermore, the photocatalytic stability of the composite was determined by three consecutive experiments under the same reaction condition. Figure 6d compares the results of photocatalytic degradation of IC at the first, second, and third runs. After three consecutive cycles, the degradation efficiency in terms of Cₜ/C₀ decreased from 70% (1st) to 60% (2nd) and 45% (3rd), which was about 25% compared to the first cycle. This behavior suggested that the catalytic capacity could be mainly affected by the leaching of CF from the composite surface, which decreased the number of active sites for adsorption. Furthermore, the used composite cannot be reused for the fourth cycle due to black CF particles being peeled off from the composite during the process of testing.

To explain the photocatalytic mechanism where photocatalytic reactions happen based on the hydroxyl radical generated via VB or CB, an active species trapping experiment using different scavengers was conducted (see Figure 7a). 5 ppm of p-benzoquinone and t-butanol was added in the photocatalytic system for superoxide radical anions (O₂⁻) and hydroxyl radicals (HO•) scavengers, respectively. The results showed that the addition of O₂⁻ and HO• scavengers inhibited the photocatalytic degradation of IC over the BiVO₄/CF composite. It can be concluded that the position of the photocatalytic mechanism could occur via both active species.

In addition, electron spin resonance (ESR) can be used to identify the production of the active oxidation species, as it was described in the literature. The schematic drawing of the proposed energy level of the BiVO₄/CF composite is shown in Figure 7b. To find out the conduction band (E_CB) and valence band (E_VB) edge positions of BiVO₄, the values can be calculated following the equations.
χ = −EC + 0.5Eg

EC = EVB − Eg

The absolute electronegativity (χ) value for BiVO4 equals to 6.04. EC refers to the energy of the free electron on the hydrogen scale (NHE, 4.5 eV), and Eg is the calculated band gap of the BiVO4/CF composite (2.2 eV). The calculated VB and CB values of BiVO4 in composites are +2.64 and +0.44 eV, respectively.

The general mechanism of the photocatalytic activity of BiVO4 occurs when BiVO4 is illuminated by light such that photon energy equals or exceeds its band gap energy.

\[
\text{BiVO}_4 + (\text{hv}) \rightarrow \text{BiVO}_4 (h^+ + e^-) \tag{3}
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HO}^- \tag{4}
\]

\[
h^+ + \text{OH}^- \rightarrow \text{HO}^- \tag{5}
\]

In the meantime, another strong oxidizing agent such as superoxide radical anions (\( \bullet\text{O}_2^- \)) is also produced at CB by the reaction between e\(^-\) and the oxygen molecules (O\(_2\)) (eq 6). On the other hand, holes (\( \bullet\text{O}_2^- \)) can subsequently react with H\(^+\) and the produced H\(_2\)O\(_2\) molecule in aqueous solution and generate HO\(^-\) in VB, as shown in eqs 7 and 8.

\[
e^- + \text{O}_2 \rightarrow \bullet\text{O}_2^- \tag{6}
\]

\[
2(\bullet\text{O}_2^-) + 2\text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \tag{7}
\]

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{HO}^- + \text{OH}^- \tag{8}
\]

These active free radicals (HO\(^-\)) photo-oxidize the absorbed dye molecules into the degradation products such as CO\(_2\), H\(_2\)O, and short-chain fragments.\(^{35}\) Besides that, CF in the BiVO4 structure can enhance the adsorption of the organic compounds, which facilitates the closeness between photocatalysts and dyes during photocatalysis experiments.

### 3. CONCLUSIONS

The photocatalysts of BiVO4 supported on coconut fiber (CF) were obtained in situ by the wet chemical process. CF exhibited an important role in the adsorption of IC dyes, while BiVO4 played a more important role in photocatalysis. The XRD diffractograms of the BiVO4/CF composite did not present the signals corresponding with CF. The presence of CF
material was confirmed by optical, morphological, and surface analysis. After visible light irradiation for 120 min, the BiVO4/CF composite presented faster kinetics than the pristine BiVO4 for IC degradation. There are three possible alternative explanations for the enhanced photocatalytic degradation of IC by the BiVO4/CF composite used in this study: enhanced adsorption characteristics, change in band gap, and/or decreased PL signals, which prolong the recombination life span. The addition of scavengers indicated that both species (hydroxyl radical and superoxide radical) are very reactive toward IC dye degradation. The effective reusability of the BiVO4/CF composite makes it a promising photocatalyst for the degradation of recalcitrant organic pollutants.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Carbonized Adsorbent from Coconut Fiber (CF). Coconut fiber (CF) was collected from Nakhon Sawan Province, Thailand. It was washed thoroughly with tap water to remove dirt on the CF surface and dried at 100 °C for 24 h. Treatment of CF was carried out using acid activation. The process was done by soaking a portion of CF (50 g) in 3 M hydrochloric acid for 24 h. The treated CF was then thermally processed in a muffle furnace at 500 °C for 6 h before storage and use.

4.2. Synthesis of Monoclinic BiVO4. For the experiment, 12 mmol of bismuth nitrate pentahydrate and ammonium vanadate was suspended in 100.0 mL of 2 M nitric acid under mechanical stirring for 30 min. Then, 6 M sodium hydroxide was added dropwise to adjust pH to 5, and then a yellow precipitate was obtained after vigorous stirring for 2 h. Afterward, the solid was removed by centrifugation (8000 rpm, 15 min) and washed several times with deionized water until a neutral pH was reached. The yellow product was further dried in an oven at 70 °C for 24 h. The monoclinic phase of BiVO4 could be obtained after calcination at 500 °C for 4 h.

4.3. Synthesis of the BiVO4/CF Composite. In the case of the BiVO4/CF composite, the as-prepared CF powder (25% w/w) was added to a beaker containing approximately 100.0 L of 6 M H2SO4 acid solution with 12 mmol of bismuth nitrate pentahydrate and ammonium vanadate under magnetic stirring for 60 min. The mixed suspension system was further adjusted to pH 5–6 with 6 M sodium hydroxide. After the reaction, the BiVO4/CF composite was separated by centrifugation, washed with DI water, heated at 70 °C for 24 h, and then calcined at 500 °C for 4 h.

4.4. Characterization. Crystallographic structures of the prepared samples were inspected by X-ray diffraction (XRD, Philips X’Pert MPD) with Cu Kα radiation (1.5418 Å). The reflectance of the samples was observed by diffuse reflectance spectroscopy (UV−vis DRS, Agilent 8453 spectrophotometer) from 280 to 800 nm with a 0.2 nm spacing. The photoluminescence (PL) emission spectra were collected on a spectrophuorometer (Horiba Fluoromax-4CP) with an excitation wavelength at 350 nm. Scanning electron micro-

| Table 2. Different AC-Based Photocatalysts Reported in the Literature |
|---------------------------------------------------------------|
| Fotocatalyst | condition | reference |
| BiVO4 (16%), BiVO4/CF composites (70%) | pollutant: indigo carmine | present study |
| | irradiation time: 120 min visible light | |
| TiO2 (~70%), TiO2/AC composite (~95.5%) | pollutant: Sunset Yellow | Rajamanickam and Shanthi49 |
| | irradiation time: 80 min UV light | |
| ZnO (k = 0.0051 min−1), ZnO@AC (k = 0.0465 min−1) | pollutant: Alizarin cyanine green dye | Muthirulan et al.17 |
| | irradiation time: 90 min UV light | |
| SnO2 (~9.8%), Co-doped SnO2 supported on AC (98%) | pollutant: rhodamine B | Kande et al.49 |
| | irradiation time: 120 min halide lamp | |
| CeO2 (69%), AC-CeO2 nanocomposite (94%) | pollutant: methylene blue | Jayakumar et al.50 |
| | irradiation time: 60 min sunlight | |

Figure 7. (a) Active species trapping experiment and (b) proposed photocatalysis mechanism of the BiVO4/CF composite for IC degradation.
copy and energy dispersive X-ray spectrometry (SEM/EDS, JSM–6335F, JEOL) were used for morphological feature and elemental analysis. The zeta potential was measured using a zetaplatzer (Nano ZS4700, Malvern). BET nitrogen adsorption and desorption analysis was applied to measure the specific surface area, pore volume, and pore size distribution based on nitrogen adsorption–desorption isotherms (Micromeritics TriStar II 3020).

4.5. Photocatalytic Activity. For the photocatalytic activity study, the suspensions of 50 mL of 3 M IC aqueous solution were mixed with 0.1 g of photocatalyst. The mixtures were mixed for 30 min without illumination to validate the adsorption–desorption equilibrium of the IC compound throughout the slurry at room temperature.

After that, the photocatalytic degradation of IC was examined under visible light irradiation with a 54 W halogen lamp. The concentration of the IC solution was evaluated and recorded as the initial IC concentration (C₀) to exclude the loss of IC due to the adsorption during mixing in the dark. At time intervals, 3 mL of suspension was drawn after light irradiation started and each was filtered through centrifugation. The time dependence of the IC concentration (C) could be calculated from the calibration curve at a fixed wavelength of 612 nm recorded by a double-beam UV–vis spectrophotometer (Shanghai Mapada Instruments Co., Ltd.).

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