Degradation of ciprofloxacin antibiotic under visible light by BIVO$_4$ photocatalyst

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Abstract. In this paper, we have successfully synthesized BiVO$_4$ by co-precipitation method. Results of BiVO$_4$ are synthesized under the support of urea, forming a single-line scheelite structure of BiVO$_4$. The synthesized sample were characterized by X-ray diffraction, scanning electron microscopy, raman and UV-visible diffuse reflectance spectra. In this work, the degradation of Ciprofloxacin (CFX) irradiated under visible light (Lamp LED 60W) by BiVO$_4$. The results of SEM images of BiVO$_4$ show that the crystal structure is granular, nanoparticle size and uneven. The Eg value of BiVO$_4$ is 2.312 Ev. The decrease in CFX concentration at pH=3, concentration of 10 ppm and catalyst dosage of 100 mg is the most optimal condition with photodegradation efficiencies of CFX is 75% after 180 min of irradiation. Material obtained in study can be applied in the decomposition of other antibiotics.

I. Introduction
Pollutants such as suspended solids, heavy metals, antibiotics and other substances greatly affect human health and aquatic organisms. The extensive use of antibiotics make it easily spread into aquatic environment via domestic wastewater and industrial wastewater, which have caused serious environment pollution [1–4]. Therein, Ciprofloxacin (C$_{17}$H$_{18}$FN$_3$O$_3$) is widely administered as both human and veterinary medicine, and currently holds the fourth position in the European antibiotic market [5–7]. In fact, a recent study conducted in Europe reported that, the ciprofloxacin represents 73% of the total consumption, with a daily dose between 0.39 – 1.8 per 1000 inhabitants [8]. Ciprofloxacin (CFX) exists in different water such as wastewater, surface water, ground water and even in drinking water [9–11]. Just the same as many other pharmaceutical chemicals, CFX cannot be removed efficiently by biodegradable process [12,13].
The presence of these antibiotics may cause severe threats to the environment. The removal of antibiotics up to an allowable permissible limit from the wastewater is essential before discharge into the drainage system. Many techniques have been developed to eliminate antibiotic substrates from water, such as electrolysis, membrane filtration, coagulation and advanced oxidation processes (AOPs) [14–18]. The Photocatalytic catalysts have received much attention from researchers because of its potential applications in materials technology as well as in environmental treatment. Among the semiconductors, the most prominent is TiO$_2$ because it has some advantages such as low cost, nontoxic, thermal stability and other advantages. However, this material has a huge disadvantage of using UV rays in the reaction process.

At the present time, photocatalysts under visible light is the most important direction for this field, because the utilization of visible light, which accounts for more than half of the solar spectrum and use from sustainable energy source. The Scientists have successfully studied materials using visible light such as CdS, Cu$_2$O, Fe$_2$O$_3$,WO$_3$ [19–21]. However, most of the photocatalysts developed thus far have wide bandgaps, and can therefore utilize only a very small portion of sunlight, and Chemical durability. Among various semiconductor photocatalysts, Bismuth vanadate (BiVO$_4$) has attracted great attentions of researchers owing to its nontoxic, with visible light response ability and chemical durability. BiVO$_4$ has three crystalline phases: monoclinic scheelite (m-s), tetragonal zircon (s-t) and tetragonal scheelte structure (z-t) [22]. According to previous research reports, BiVO$_4$ in single form m-s have the best photochemical catalyst activity of its three crystal structures [23,24].

In this study, We report herein the successful synthesis of BiVO$_4$ by co-precipitation method. The factor affecting photodegradation efficiencies of CFX is discussed by the comparison of pH value, CFX concentration and catalyst dosage.

2. Material and methods

2.1. Material

Bismuth(III) nitrate pentahydrate (Bi(NO$_3$)$_3$.5H$_2$O, ≥ 98.0%), ammonium metavanadate (NH$_4$VO$_3$, ≥ 98%) and Ciprofloxacin (C$_{17}$H$_{18}$FN$_3$O$_7$, ≥ 98%) were purchased from Sigma-Aldrich. Urea (CON$_2$H$_4$, 99%), and nitric acid (HNO$_3$, 65-68%) were purchased from Xilong Chemical Co., Ltd. (China). All reagents were used as received without further purification.

2.2. Synthesis of BiVO$_4$ by co-precipitation method

The BiVO$_4$ sample was synthesized according in presence of urea. Firstly, 20.0 mmol of Bi(NO$_3$)$_3$.5H$_2$O was dissolved in 200 mL of HNO$_3$ (2M) for about 30 min under stirred to give solution A. Then, 20.0 mmol of NH$_4$VO$_3$ was dissolved in 200 mL of water to give solution B and was stirred for about 120 min at 65 ºC until a uniform transparent yellow solution. The solution B was drop by drop into solution A, a dark yellow solution was obtained. A certain amount of urea were added to the mixture to obtain the molar ratio of Bi:V:urea = 1:1:28. The obtained mixture is stirred vigorously for 30 min then heated at 80 ºC and for overnight. Finally, the obtained powder was calcined at 350 ºC for 3 h with a heating rate of 5 ºC/min from room temperature to the annealing temperature.

2.3. Characterization

The phase structures of BiVO$_4$ were characterized by the powder X-ray diffraction (XRD) patterns on a D8 Advance Bruker powder diffractometer with a Cu Kα excitation source at a scan rate of 0.030 º/s in the 2-theta range of 5-80º. Raman spectra were recorded by operating a micro Raman spectrometer (HORIBA Jobin Yvon) in a wavelength range of 100 to 1000 cm$^{-1}$ with a laser beam of 633 nm. The morphology of the as-prepared BiVO$_4$ were visualized by scanning electron microscope (SEM, JEOL JSM 7401F) with an accelerating voltage of 3 kV. The UV–Visible diffuse reflectance spectrum (UV–Vis DRS) of the composite was recorded on a Shimazu UV-2450 using BaSO$_4$ as the standard.
2.4. Photocatalysts Test

The photocatalytic activity of products were prepared experimentally during the decomposition of Ciprofloxacin antibiotic (CFX) and all experiments are using a Lam LED (60W, Vietnam) as the visible-light resource. The experiments conditions will find the best photocatalytic activity ability through: pH, CFX concentration and catalyst dosage. Firstly, the beaker was filled with a mixture of CFX concentration at 10 mg/L (100ml), BiVO₄ (100 mg) and pH value. The pH value of the mixed solution was adjusted using 1 M NaOH or 1 M HCl solution, and then the suspension was magnetically stirred in the dark for 60 minutes. After during light on irradiation, four ml of solutions were withdrawn and catalyst dosage on immediately centrifuged every 20 min. To investigate effects of CFX concentration, ph and catalyst dosage on photocatalytic activity of BiVO₄, the pH was increased from 3 to 9 and CFX concentration was increased from 10 to 30 mg/L, We was catalyst dosage of BiVO₄ from 30 to 150 mg. The concentration of CFX in the solution after time was analyzed by a thermo evolution 60S UV-Visible Spectrophotometer with wavelength were recorded is 278 nm.

3. Results and discussion

3.1 Structural analysis

The Crystal morphology of BiVO₄ is synthesized under the support of urea as observed through the SEM image in figure 1. The BiVO₄ has formed a granular crystal structure, size nanoparticles and uneven.

![Image of SEM image of BiVO₄, image at 5µm (a) and image at 1µm (b).](image-url)

The crystal structure of BiVO₄ were studied by XRD as illustrated in figure 1. BiVO₄ sample with characteristic peaks with 20 at 15.3, 18.8, 19.1, 29.1 and 30.6° are similar to the standard card of BiVO₄ (JCPDS card no. 14-00688) as show in fig.1a. The main peaks can be indexed as (11 0), (011), (121), (0 40), (2 00) and (0 02) planes of monoclinic BiVO₄. The result of BiVO₄ is synthesized by co-precipitation method under the support of monoclinic scheelite structure of BiVO₄ alone. Fig 1B, Raman result of BiVO₄ sample has characteristic vibration mode in the monoclinic crystal phase, such as symmetrical stretching vibration (δₛ) and asymmetric vibration (δₘₐₓ) mode of V-O bond; symmetrical bending vibrations (υₛ) and asymmetric bending vibrations (υₘₐₓ) of the VO₄³⁻ group; and external modes in BiVO₄ [25]. The V-O bond lengths at wavenumber corresponding symmetrical stretching vibration of V-O bond of all samples can be calculated via the empirical expression: \[ ν = 21349e^{-19176/R} \] [26] and were listed in table 1. The V-O bond lengths of all samples matched with the V-O bond length of BiVO₄ with pure monoclinic scheelite crystal phase [14].
Figure 2. XRD pattern (a) and Raman spectra (b) of BiVO₄.

Table 1. Sample properties.

| Samples | lattice parameters (Å)ᵃ | Volume (Å³) | crystallite size (nm) | V-O length (Å) |
|---------|-------------------------|-------------|----------------------|----------------|
| BiVO₄   | 5.165 11.645 5.074      | 305.224     | 48.594               | 1.709          |

ᵃData obtained by XRD data; ᵇData obtained by Raman data.

The BiVO₄ sample show absorption in the visible light (Fig. 3a). The bandgap energy of sample can be estimated from the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (Fig. 3b) and band gap energy of BiVO₄ was estimated to be 2.312 eV. The band gap energy dependence of optical transition strengths can be expressed which is given by (Eq1) [27], where $\alpha$ is the measured optical absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the transition energy, and A is a proportionality constant.

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$ (1)

The results show that the BiVO₄ sample had a band gap energy appropriate for photocatalytic degradation of organic contaminants under visible-light irradiation.

Figure 3. UV-Vis DRS spectra (a) and $(\alpha h\nu)^2$–$h\nu$ curves of BiVO₄ (b).
3.2 Photocatalytic activity

Figure 4 shows the decline in CFX concentration of factors such as pH value, concentration CFX and catalyst of BiVO$_4$ under visible light. CFX concentration decline is expressed as $C / C_0$: where $C_0$ represents the initial concentration of CFX and $C$ is the CFX concentration at the time of sampling. Therein, negative values (-) represent reactions in dark and positive (+) is a irradiation under visible light. The effect of pH values on the photodegradation degree of CFX concentration as show in figure 4(a). The results showed that in high photocatalyst activity at pH=3 than other pH values. However, when the solution pH was increased 5 to 9, the lower conversions were observed.

The photocatalyst activity by concentration 10 ppm better photocatalytic ability than other concentrations as shown in figure 4 (b). The result showed that, at high CFX concentrations with decomposition is poorly and vice versa at the low concentration was more easily decomposed. When was compare the catalyst dosage during photocatalyst activity by pH=3 value and concentration of 10 ppm shown in figure 3 (c). The survey results show that the catalyst dosage of 100 mg gives the best efficiencies, but the reduction of catalyst dosage will reduce photocatalytic activity.

In addition, the decrease in CFX concentration at pH=3, concentration of 10 ppm and catalyst dosage of 100 mg was observed through the maximum absorption peak of CFX at 278 nm decreases as show in figure 4 (d). Finally, the photodegradation efficiencies of CFX is 75% after 180 min of irradiation.

![Figure 4](image-url)

Figure 4. Photocatalytic degradation of CFX by BiVO$_4$: the initial pH (a), the initial concentration (b), catalyst dosage of BiVO$_4$ and UV-Vis absorption spectra of CFX (10ppm) from catalyst suspension during illumination using BiVO$_4$ (100mg) and pH=3 (d).
4. Conclusions

We have successfully synthesized BiVO₄ photocatalyst through co-precipitation method. The result of BiVO₄ are synthesized with the combination of urea to form a single monoclinic scheelite structure and Eg value of the BiVO₄ is 2.312 eV. SEM image results of BiVO₄ has a granular crystal structure and uneven particle size. The catalytic activity of BiVO₄ reduces the concentration of CFX at the conditions: pH = 3 value, concentration of 10 ppm, and 100 mg catalyst volume. It achieved an optical decomposition performance of CFX of 75% after 270 minutes of irradiation. Through the above results, we will study more about the amount of urea in BiVO₄ synthesis method, and increase the irradiation time to achieve better optical decomposition effect.

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