Photocatalytic activity for degradation of sulfamethoxazole by BiVO$_4$ using visible light

L X Nong$^1$, V H Nguyen$^{*}$, L G Bach$^1$, T V Tran$^1$, T D Nguyen$^{1,2}$

$^1$ NTT Institute of High Technology, Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4, Ho Chi Minh City, Vietnam

$^*$nguyenduytrinh86@gmail.com, ndtrinh@ntt.edu.vn

Abstract. In this study, BiVO$_4$ photocatalysts have been successfully synthesized by hydrothermal method and were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), UV-Vis diffusion reflectance spectra (UV-Vis DRS), and Raman spectroscopy. From XRD, Raman, and UV-Vis DRS results, the as-synthesized BiVO$_4$ showed monoclinic scheelite structure and narrow band gap energy ($E_g = 2.35$ eV). The morphology of as-prepared powder showed a small crystallite size with different shapes. The photocatalytic performances of the as-prepared sample were evaluated by the degradation of sulfamethoxazole under visible light. Also, H$_2$O$_2$ was added to enhance the photocatalytic activity of BiVO$_4$. It has been noticed that 70% photodegradation of antibiotic occurs on the catalyst surface with visible light irradiation. Besides, the effects of pH and organic salts are also discussed in this study.

1. Introduction
In the past decades, the healthcare industry has used many different antibiotics to counteract different types of bacteria. However, antibiotics are discharged into the environment and cause a serious impact on public health. Sulfamethoxazole (SMX) is commonly used in medicine. It is one of the widely used antibiotics of the Sulfonamides group. It is used in preventing infections such as urinary tract infections, bronchitis, and prostatitis [1]. Incomplete handling of this antibiotic may form resistant bacteria when released into the environment [2]. For this reason, advanced oxidation reactions have the potential to help break down SMX effectively.

Advanced oxidation processes are considered as an effective method in wastewater treatment. Over the years, many studies have been conducted to find the catalyst with high activity, such as TiO$_2$, ZnO, CdS, ZnS and WO$_3$. For example, TiO$_2$ is recognized as one of the common catalysts and widely used in the treatment of dyes, antibiotics, and toxic organic substances [3–5]. However, these catalysts absorb ultra-violet light with low application potential and do not occupy much in sunlight [6]. Among which BiVO$_4$ is a well-known photocatalyst with narrow band gap (2.4 eV) and outstanding photocatalytic performance under visible light irradiation [7–9]. However, the low efficiency of BiVO$_4$ in separating photogenerated electron-hole pairs leads to low photocatalytic efficiency [10], [11]. Therefore, hydrogen peroxide (H$_2$O$_2$) has been used to improve the sunlight-driven photodegradation of antibiotic substances. H$_2$O$_2$ is widely used in photocatalyst reactions to provide
hydroxy radicals when conducting advanced oxidation reactions, such as TiO$_2$/H$_2$O$_2$, ZnO/H$_2$O$_2$, photo-Fenton processes [12–14].

In this work, BiVO$_4$ crystal was synthesized by hydrothermal method using Bi(NO$_3$)$_3$ and NH$_4$VO$_3$ as precursors. The as-synthesized catalyst was characterized by XRD, SEM and UV-vis DRS. The photocatalytic active of as-synthesized BiVO$_4$ was studied by photodegradation of SMX under visible light irradiation. Also, the factors such as inorganic salts, pH, SMX concentration and H$_2$O$_2$ concentration, which affect the photocatalytic activity, were also investigated in details.

2. Experimental

2.1. Material
All reagents were used as received without further purification. Bismuth(III) nitrate pentahydrate (Bi(NO$_3$)$_3$, 98%), Ammonium metavanadate (NH$_4$VO$_3$, 99%) and SMX (SMX, 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium sulfate anhydrous (Na$_2$SO$_4$, 99%), tri-Sodium phosphate dodecahydrate (Na$_3$PO$_4$, 98%), Sodium chloride (NaCl, 99,5%) and Ammonia (NH$_3$, 25%-28%) were obtained from Guangdong Guanghua Sci-Tech Co., Ltd (Guangdong, China). Sodium hydrogen carbonate (NaHCO$_3$, 99,5%), Sodium hydroxide (NaOH, 96%), Nitric acid (HNO$_3$, 65% -68%) and Hydrochloric acid (HCl, 36%-38%) were acquired from Xilong Chemical Co., Ltd. (Guangzhou, China).

2.2. Synthesis of BiVO$_4$ photocatalyst
The BiVO$_4$ powder was synthesized by hydrothermal method. Four mmol of Bi(NO$_3$)$_3$.5H$_2$O were dissolved in 20 mL HNO$_3$ 2M under stirring to form solution A. Subsequently, four mmol NH$_4$VO$_3$ were dissolved in 40 mL deionized water under stirring to form solution B. Then, solution B was added dropwise into solution B to the solution was dropped slowly to Bi(NO$_3$)$_3$.5H$_2$O solution. The pH of the solution was adjusted to 3 by using ammonia solution. The mixture was stirred for 30 min and transferred into a 100 mL Teflon-lined stainless steel autoclave and heat treated at 160 °C for 24 h. The yellow precipitate was centrifuged, washed three times with deionized water and then dried at 90 °C for 12 h. Finally, the powder was calcined in air at 450 °C for 2 h.

2.3. Characterizations
X-ray powder diffraction (XRD) patterns were carried out using Advance Bruker powder diffractometer with a Cu–Kα excitation source and a scan rate of 0.02°/s from 20° to 90°. The scanning electron microscope (SEM) of the as-prepared sample was observed with an S4800, Japan with an accelerating voltage source of 10 kV and the magnification of 7000. Raman spectra were detected by the HORIBA Jobin Yvon spectrometer with a laser beam of 633 nm, UV-vis diffuse reflectance spectra (DRS) was measured by the Shimazu UV-2450, Japan in the range 200–900 cm$^{-1}$.

2.4. Photocatalytic test
The photocatalytic activity of the as-prepared sample was monitored by the photodegradation of SMX (SMX) under visible light irradiation. A 60-W LED was used as the visible-light source. Experiments were conducted as follows: 100 mg of photocatalyst was added into 100 mL of 20 mg/L SMX solution. Before irradiation, the solution was stirred for 1 hour in darkness in order to reach the absorption-desorption equilibrium. After a specified time, 4 ml of the solution was withdrawn and immediately centrifuged to remove photocatalyst practical for 10 min. The concentration of SMX was evaluated by using a UV-visible spectrophotometer (Model Evolution 60S, Thermo Fisher Scientific, USA) at a maximum absorbance wavelength at 266 nm. Besides, to investigate the effect of parameters such as antibiotic concentration (10- 50 mg/L), initial solution pH (3, 5, 6.5, 9), H$_2$O$_2$ concentration (10$^{-3}$, 8.10$^{-3}$, 10$^{-3}$, and 10$^{-6}$ M) and inorganic salts (NaCl, Na$_2$SO$_4$, Na$_3$PO$_4$, and NaHCO$_3$) on the ability to degradation antibiotic.
3. Results and discussion

3.1. Characterization of BiVO₄

Figure 1 (a) shows XRD patterns of the as-prepared sample. It can be seen that the sample was well crystallized, and all the diffraction peaks of BiVO₄ could be well indexed to the monoclinic scheelite BiVO₄ (JCPDS 14-0688). Characteristic peaks at 18.5; 29; 30.6; 35 and 46° of 2θ is observed for the as-prepared sample. The lattice constant of the as-prepared sample was calculated by Unit Cell software from the XRD pattern. In addition, the results of lattice parameters and crystal size of prepared BiVO₄ catalyst is given in Table 1. It shows a little change in lattice parameters of BiVO₄ (a = 5.195, b = 11.701, c = 5.092, β = 90.38) and the crystal size of m-BiVO₄ was estimated to be about 35.54 nm.

The UV-Vis DRS spectra of an as-prepared sample is plotted in Figure 1 (b). The band gap absorption edge of the m-BiVO₄ was about 527.6 nm. The bandgap energy was estimated to be 2.35 eV and was calculated according to the equation:

$$\alpha hν = A(hν - E_g)^{1/2}$$  \hspace{1cm} (1)

where $\alpha$, $h$, $ν$, $A$ and $E_g$ stand for the absorption coefficient, Planck’s constant, the light frequency, a constant and the bandgap energy, respectively, and C demonstrates a constant. It can be concluded that the BiVO₄ in this research has a narrow bandgap and absorb visible light very well.

The Raman spectrum of BiVO₄ synthesized by the hydrothermal process is displayed in Figure 1 (c). It showed all typical vibrational bands of monoclinic BiVO₄ including the symmetric V–O stretching mode around 825, 710 and 640 cm⁻¹; the asymmetric and symmetric deformation modes of the VO₄³⁻ tetrahedron around 366 and 324 cm⁻¹; the external modes around 210 cm⁻¹ [15]. From the above results, it was confirmed that BiVO₄ was successfully synthesized by hydrothermal method.

Figure 1. (a) XRD patterns of BiVO₄, (b) UV-vis diffuse absorption spectra of BiVO₄, (c) Raman spectra of BiVO₄

The morphology structure of the as-prepared BiVO₄ sample was characterized by SEM. As shown in Figure 2, the shape of BiVO₄ particle was a rod and spherical like with particle sizes in the range of 2.5-0.1 μm.
Figure 2. SEM images of the as-prepared sample.

Table 1. Calculated lattice constants and band gap energy of BiVO₄.

| Sample  | a (Å)  | b (Å)  | c (Å)  | β      | Volume (nm³) | Crystallite size (nm) |
|---------|--------|--------|--------|--------|--------------|-----------------------|
| BVO_3   | 5.18864| 5.09155| 11.6818| 89.82813| 308.61       | 36.54                 |

3.2. Photocatalytic activity

Photocatalytic activity of samples was observed by the degradation of SMX with a major absorption band at 266 nm. Figure 3 shows the UV-vis absorption spectra of the aqueous solution containing 20 ppm SMX. Clearly, with the increase in degradation time, the intensity of the peak around 266 nm decreased. As shown in Figure 4 (a), the SMX conversions were 70.42%, 68.35% 53.75%, 49.88% and 38.67% when SMX concentrations were respectively 10 ppm, 20ppm, 30ppm, 40ppm and 50 ppm. The above results showed that the higher the SMX concentration, the lower the reaction efficiency.

Figure 3. UV-vis absorption spectra of the SMX solution in the presence of BiVO₄.
Figure 4 (b) displays the photocatalytic activity of BiVO₄ for the degradation of SMX with the absence or presence of a small amount of H₂O₂ under visible light illumination. Also, the direct photolysis of SMX was investigated in the presence of H₂O₂ without a catalyst. The results show that SMX photolysis was negligible under the conditions conducted in this study. With the addition of a small amount of H₂O₂, the BiVO₄ sample enhanced significantly in photodegradation performance. Therefore, the appearance of H₂O₂ increases the ability of the catalyst to break down antibiotic. Closer inspection of the table shows an increase in the amount of H₂O₂ added to the reaction solution encourage an increase in the SMX conversion. To conclude, with an appropriate amount of H₂O₂ it is possible to enhance the photocatalytic degradation performance.

Figure 4 (c) shows the photodegradation of SMX under visible light at different pH levels. The results indicate that the degradation of antibiotic increases as the pH of the reaction solution decreases. It can be seen that the degradation of SMX at pH 9 in the presence of the as-prepared sample is only about 27.1%. Meanwhile, at pH 6.5, 5 and 3 the SMX degradation capacities are 68.3%, 72.4% and 91.6%. This outcome is because H₂O₂ decomposes into water and oxygen when increasing the pH level. Hence, it can be confirmed that pH has a significant influence on the ability to degradation of SMX.

Figure 4. (a) Photocatalytic activity of BiVO₄ at different SMX concentrations, (b) Photocatalytic activity of BiVO₄ at different pH, (c) Photocatalytic activity of BiVO₄ at different H₂O₂ concentrations, (d) Photocatalytic activity of BiVO₄ in the presence of inorganic salts.
Figure 4 (d) shows the inhibition of inorganic salts present in the photodegradation of SMX. As can be seen, sodium hydrogen carbonate inhibits the photocatalyst activity of BiVO₄. Moreover, a small amount of sodium phosphate and sodium sulfate added to the reaction solution led to a decrease in SMX conversion. As can be seen, the appearance of sodium chloride does not affect the photocatalysts activity of BiVO₄. This result can be explained by the scavenging of OH• radicals by ions [16].

4. Reference

In summary, BiVO₄ has been successfully synthesized with monoclinic structure by hydrothermal method. The results show that the presence of H₂O₂ helps the photodegradation of the catalyst more effectively. Besides, some factors in reaction solutions such as pH, inorganic salts, SMX concentrations and H₂O₂ concentrations which affect the photocatalyst activity of the material to decompose antibiotic. This study displays the possibility of applying BiVO₄ in the treatment of some common antibiotics and helps protect public health.

Acknowledgement

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.05-2018.336.

Reference

[1] Nasuhoglu D, Yargeau V and Berk D 2011 J. Hazard. Mater. 186 67–75
[2] Gunduz S and Uluða˘g Altun H 2018. Glob. Heal. Res. policy 3 10
[3] Muruganandham M and Swaminathan M 2006 Pigment. 68 133–42
[4] Kusvuran E, Samil A, Atanur O M and Erbatur O 2005 Appl. Catal. B Environ. 58 211–6
[5] Tassalit D, Laoufi A N and Bentahar F 2011 Sci. Adv. Mater. 3 944–8
[6] Xiang Z, Wang Y, Zhang D and Ju P 2016 J. Ind. Eng. Chem. 40 83–92
[7] Zou Z, Ye J, Sayama K and Arakawa H 2001 Nature 414 625–7
[8] Akihiko K, Keiko O and Kato H 1999 J. Am. Chem. Soc. 121 11459-11467
[9] Wang B, Guo L and He T 2016 RSC Adv. 6 30115–24
[10] Lim A R, Choh S H and Jang M S 1995 J. Phys. Condens. Matter 7 7309–23
[11] Sun Y, Wu C, Long R, Cui Y, Zhang S and Xie Y 2009 Chem. Commun. 4542
[12] Salem I A 2000 Monatshefte fuer Chemie/Chemical Mon. 131 1139–50
[13] Li X, Chen C and Zhao J 2001 Langmuir 17 4118–22
[14] Méndez-Arriaga F, Esplugas S and Giménez J 2010 Water Res. 44 589–95
[15] Thalluri S M, Martinez Suarez C, Hussain M, Hernandez S, Virga A, Saracco G and Russo N 2013 Ind. Eng. Chem. Res. 52 17414–8
[16] Guillard C, Lachheb H, Houas A, Ksibi M, Elaloui E and Herrmann J-M 2003 J. Photochem. Photobiol. A Chem. 158 27–36