Visible-Light-Responsive Photocatalytic Degradation of Sulfamethoxazole in Aqueous Suspension of Bismuth Vanadate

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Abstract

This study is the evaluation of Visible-light-responsive photocatalyst as a suitable process to degrade an antibiotic, the Sulfamethoxazole. Recently, the presence of drugs in the aquatic environment and thus its adverse potential effects have become of increasing concern. Sulfamethoxazole (SMZ) are important bacteriostatic agents, commonly used in human and veterinary medicine. SMZ are released into the environment via industrial effluents, household and hospital wastewaters. Although the concentration of SMZ is usually low, its long life-time in the environment can results in its accumulation in food chains. In this way, SMZ in aqueous solution was treated by using bismuth vanadate ($BiVO_4$) in suspension as catalyst, and Visible-light-responsive. Bismuth vanadate ($BiVO_4$) powder have been synthesized at by using Microwave Hydrothermal Methods. In the preparation procedure, $Bi(NO_3)_3 \cdot 5H_2O$ and NH_4VO_3 is dissolved in HNO_3, NaOH aqueous solution is added to adjust the pH value at 7. The products are characterized by X-ray diffractrommeter (XRD), the field emission scanning electron microscopy with energy dispersive X-ray spectrometer (FE-SEM/EDS), and UV–vis diffusion reflectance spectrum (DRS), attentuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Here, we demonstrate that the obtained powders materials consisted of monoclinic and tetragonal structure of $BiVO_4$, and with an optical band gap of 1.7-2.0 eV. Under the studied conditions, the SMZ concentration was measured by using HPLC-PDA, and to reveal the SMZ is degraded completely. In order to obtain a better understanding on the mechanistic details of the bismuth vanadate-assisted photodegradation of the SMZ under visible irradiation, the intermediates of the process are separated, identified and characterized by HPLC-PDA-ESI-MS technique in the study.

Keywords: Bismuth vanadate, Sulfamethoxazole (SMZ), Microwave hydrothermal,Visible-light-responsive photocatalyst.

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1 Introduction

Recently, the presence of drugs in the aquatic environment and thus its adverse potential effects have become of increasing concern [1]. Sulfamethoxazole (SMZ) are important bacteriostatic agents, commonly used in human and veterinary medicine [2]. SMZ are released into the environment via industrial effluents, household, hospital wastewaters, and the removal of SMZ during sewage treatment by biodegradation is incomplete, thus trace SMZ has been found in municipal sewage treatment plant effluents from different countries [3]. Although the concentration of SMZ is usually low, its long life-time in the environment can results in its accumulation in food chains[4]. The release of SMZ wastewater effluents has caused pollution and many human diseases. For the past decades, the most useful photocatalyst is titania (TiO_2) due to its behaviors that are non-toxic, inexpensive, highly oxidative and chemically stable. However due to its large band gap energy (3.2 eV), TiO_2 only respond to UV light irradiation which occupies only 4 % of the whole solar energy. Since 43% of solar light is visible-light, therefore it is necessary to develop photocatalyst which can work in visible light range [5] .Bismuth vanadate ($BiVO_4$) has recently attracted considerable attention not only for its interesting technological properties but also for its strong photocatalytic effect on water splitting and organic pollutant decomposing under visible light irradiation. There are three crystalline phases (the monoclinic wolframite-type, the tetragonal scheelite-type and the tetragonal zircon-type) reported for synthetic BiVO4, and according which its photocatalytic properties are strongly related to its crystal phase [6] .This study is the evaluation of Visible-light-responsive photocatalyst as a suitable process to degrade an antibiotic, the SMZ, and that in aqueous solution was treated by using $BiVO_4$ in suspension as catalyst, and Visible-light-responsive. SMZ physico-chemical properties are as follows: molecular weight = 278 g mol^{-1}, [7,8,9,10,11] solubility in water = 1500 mg L^{-1} [7], $pK_{bH+(1)}$ =2.7 and $pK_{bH+(2)}$ =7.4 [7], log Kow = 0.89 [8]and Henry's constant = 3.05×10^{-13} atm m^3 mol^{-1} [9,10,11]. The $BiVO_4$ powder have been synthesized at 100℃ for 30, 60, and 90 minutes and 150℃ for 30, 60, and 90 minutes by using Microwave Hydrothermal Methods.

2 Experiment

2.1 Materials and Preparations

All chemicals were analytical grade and were used as received without further purification and deionized water was used for preparation of solutions. Sulfamethazine ($C_{12}H_{14}N_4O_2S$; ≥99%, SMZ) were obtained from Sigma-Aldrich, and just before experiments, weighed amounts of SMZ were added to distilled water and samples were intensively mixed, then put into dark brown laboratory bottle and were stored at 4℃ environment. In a synthesis , 0.02 mol of $Bi(NO_3)_3 \cdot 5H_2O$ (ACROS，98%) was dissolved into HNO_3 solution, (DONG SHING INDUSTRIAL Company Analytical Grade) and ammonium metavanadate (NH_4VO_3, analytical grade) from KATAYAMA CHEMICAL Company were dissolved into 8M HNO_3, and was stirred for 2 hrs. After the two solutions were mixed and was stirred for 1 hr to give a bisque solution. The pH value of the mixed solution was adjusted to 7.0 with 8M NaOH solution, Finally, the mixed This precursor solutions were set into a microwave, and were heated to 100℃, 150℃ and kept for 30, 60, 90 minutes. The samples are listed in Table 1. The precipitate formed was filtered by suction filtration, and then were dried in oven at 60℃ for 24hrs.

Table 1: Bismuth vanadate obtained under different reaction conditions.

Experimental conditions for the preparation of $BiVO_4$ powder samples

Sample	Amount of $Bi(NO_3)_3 \cdot 5H_2O$	Amount of NH_4VO_3	Synthesis Temp.(℃)	Synthesis Time(min)
MH-100-30	0.02mol	0.02mol	100℃	30min
MH-100-60	0.02mol	0.02mol	100℃	60min
MH-100-90	0.02mol	0.02mol	100℃	90min
MH-150-30	0.02mol	0.02mol	150℃	30min
MH-150-60	0.02mol	0.02mol	150℃	60min
MH-150-90	0.02mol	0.02mol	150℃	90min

2.2 Characterization

The precipitates were further characterized. Powder X-ray diffraction (XRD) was performed on a MAC Sience, MXP18 X-ray diffractometer with Cu Kα radiation, and operated at 40 kV and 80 mA. FE-SEM-EDS measurements were carried out with a field-emission microscope (JEOL JSM-7401F) at an acceleration voltage of 15 kV. UV–vis/diffuse reflectance spectroscopy (UV–vis/DRS) reading were recorded on a Cary 500. The HPLC-PDA-ESI-MS system consisted of a Waters 1525 binary pump, a 2998 photodiode array detector, and a 717 plus autosampler. Besides, a ZQ2000 micromass detector and an Atlantis TM C18 column (250 mm × 4.6 mm i.d., dp = 5 μm) were used for separation and identification. The column effluent was introduced into the ESI source of the mass spectrometer

2.3 Photocatalytic reaction

Photocatalytic activities of Bismuth vanadate were studied by the degradation of SMZ under visible light irradiation of a 20 watt lamp. An average irradiation intensity of 5.2 W/m^2 was maintained throughout the experiments and measured by the internal radiometer. Aqueous dispersions of SMZ (10 ppm) and the given amount of catalyst powder were placed in a Pyrex flask. The pH value of the dispersions was adjusted by adding either NaOH or HNO_3 solutions. Before irradiation, the dispersions were magnetically stirred in the dark for 30 min to reach an adsorption/desorption equilibrium between the SMZ and the surface of the catalyst under ambient air-equilibrated conditions. At the given irradiation time intervals for 24hrs, 5 ml aliquot was collected and was filtered by 0.2 μm filter. The filtrate was analyzed by HPLC-PDA.

3 Results and Discussion

3.1 Characterizations of as-prepared powder

3.1.1 X-ray Diffraction analysis

To investigate the phase structure of $BiVO_4$ powders prepared with different microwave heat wave temperature and heatable time, the XRD patterns of the prepared $BiVO_4$ recorded, the XRD patterns are shown in Figure 1. The $BiVO_4$ samples were heated to 100℃, 150℃ and kept for 30, 60, 90 minutes. The color of $BiVO_4$ varies from inhomogeneously yellow-brown to homogeneously lemon yellow depends on many factors including phase composition, stoichiometry, particle size and morpho logy. By means of X-ray diffraction analysis, The XRD pattern main crystal forms of BiVO4 for all samples, matched with the JCPDS data no: 83-1699; which is assigned to monoclinic $BiVO_4$ and data no:83-1812; which is assigned to tetragonal $BiVO_4$, X-ray diffraction data, Except MH-100-90 sample and MH-150-30 sample, Mostly, the crystal form of $BiVO_4$ is crystal forms of $BiVO_4$ (distorted scheelite structure).

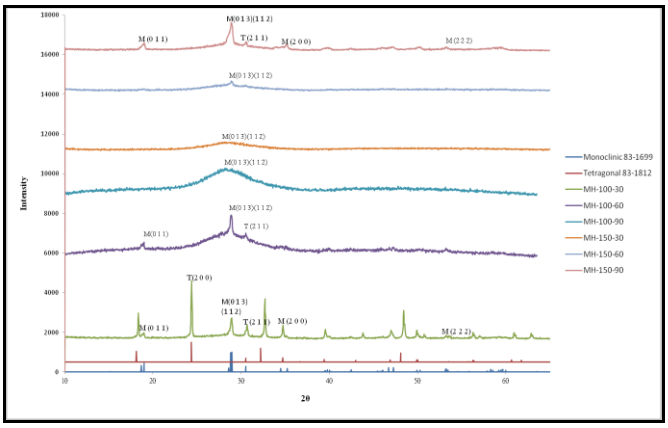
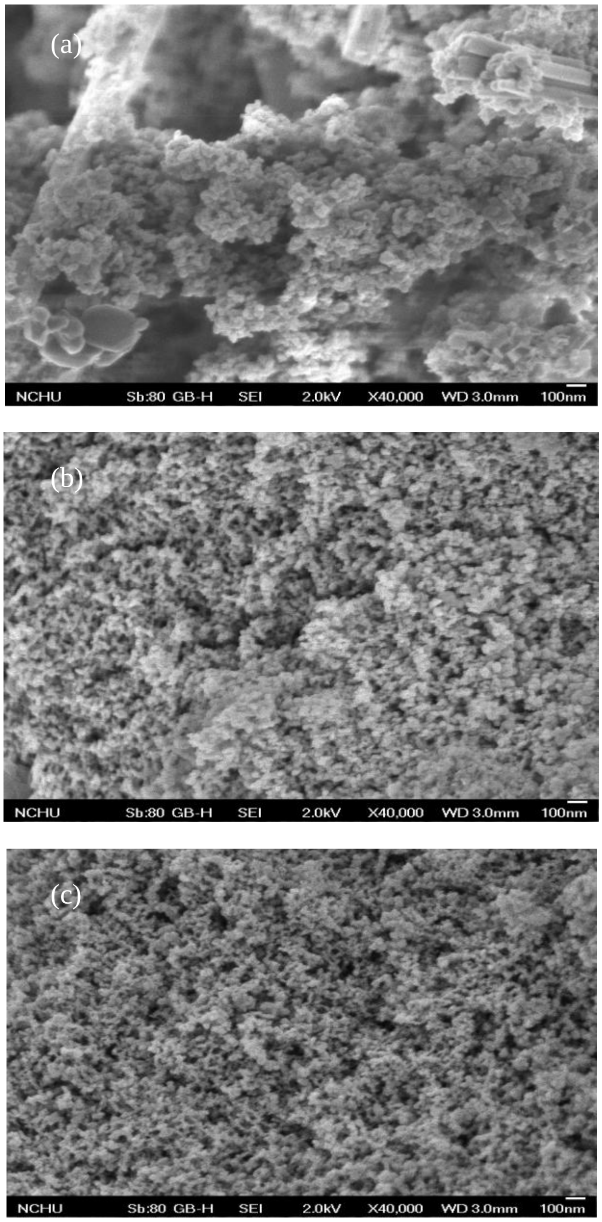


Figure 1: XRD patterns of as-prepared under different of $BiVO_4$ from different microwave hydrothermal synthesis temperature and time.

3.1.2 FE-SEM/EDS analysis

The $BiVO_4$ samples were heated to bismuth vanadate was prepared with $Bi(NO_3)_3•5H_2O$ and NH_4VO_3 by the microwave hydrothermal method at 100℃, 150℃ and kept for 30, 60, 90 minutes. The surface morphology of the photocatalysts was examined by FE-SEM/EDS (Figure.2,3), that reveal the concentrations of O,V,Bi elements of powder, the bismuth vanadate powder synthesized were composed of nano-sized particles, which were about 50 nm in size, and that particles connected to each other in shape and dense in density, figure 2(a) MH-100-30, showing fewer part of the needle bar and plate structure; figure (e) MH-150-60, showing fewer part of platy block structure.



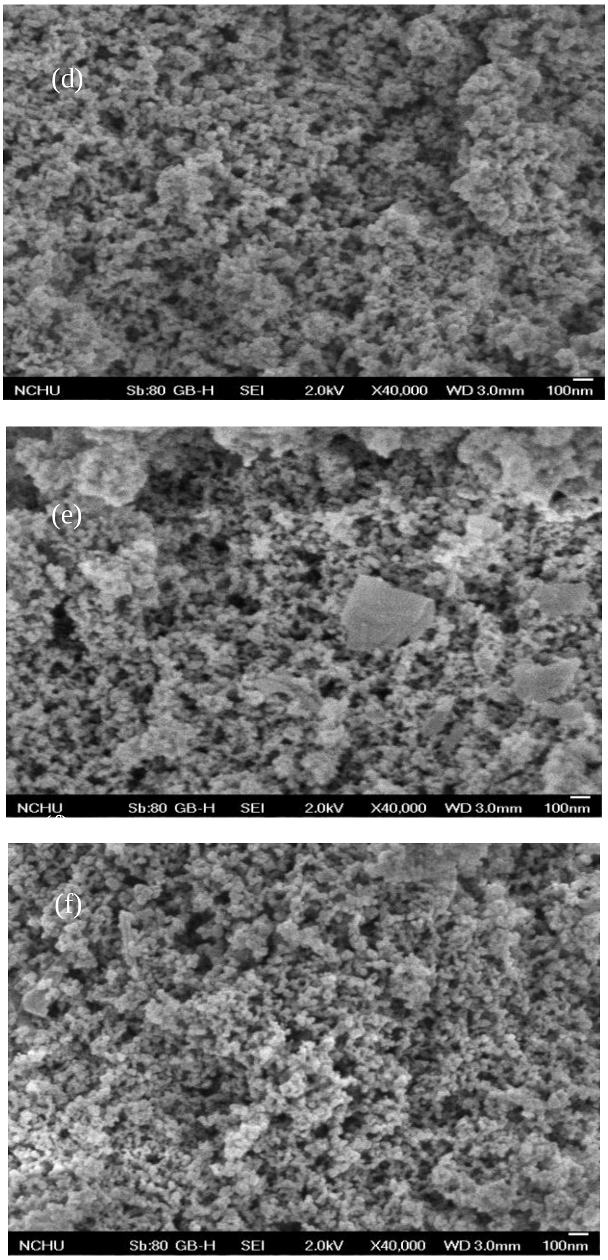
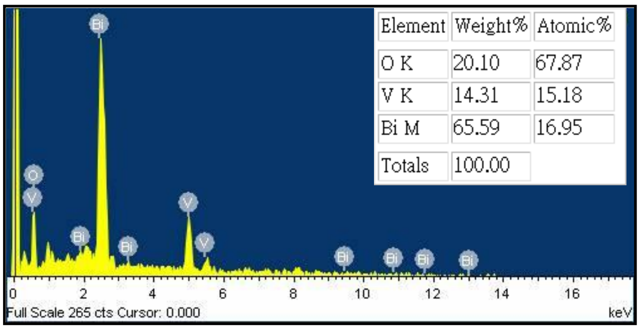


Figure 2: FE-SEM photographs of sample $BiVO_4$ from different conditions: (a)MH-100-30, (b)MH-100-60, (c)MH-100-90, (d)MH-150-30, (e)MH-150-60, (f)MH-150-90.



Element	Weight%	Atomic%
O K	20.10	67.87
V K	14.31	15.18
Bi M	65.59	16.95
Totals	100.00	

Figure 3: FE-SEM-EDS photographs of sample $BiVO_4$ at MH-100-60.

3.1.3 UV–vis–DRS analysis

The UV–vis adsorption spectra of synthesized catalysts are shown in Figure 4. UV–vis adsorption spectra of the prepared bismuth vanadate under different microwave hydrothermal method at 100℃, 150℃ and kept for 30, 60, 90 minutes are shown in the inset of Figure 4. Their corresponding band gap energies were calculated, (MH-100-30)=2.0eV, (MH-100-60)=1.83eV, (MH-100-90)=1.66eV, (MH-150-30)=1.75 eV, (MH-150-60=1.85 eV, and (MH-150-90)=1.99 eV.

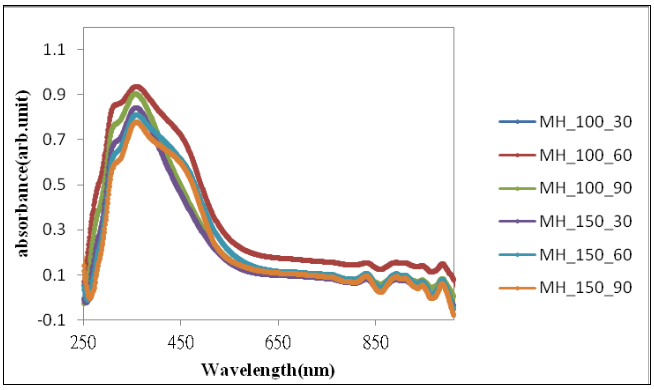


Figure 4: Diffuse reflectance spectra of BiVO4 synthesized from different synthesis temperature and time.

3.1.4 ATR-FTIR analysis

Illustrated in Figure 5, shows ATR-FTIR spectra of synthesized samples, recorded ranging from 450 to 2000 cm^{-1} at room temperature. All the samples show a characteristic broad and strong IR band near 700 cm^{-1} with shoulders at 800 to 600 cm^{-1}. One sharp CO_3^- derived band is observed at 1386 cm−1, which might be due to the adsorption of atmospheric carbon dioxide during the experiments as other report [12]. The tiny band near 1600 cm^{-1} can be assigned to the resence of residual trace water in the structure. ATR-FTIR spectra indicated that samples prepared for longer heatable time may be consisted of more antisymmetric VO_4 tetrahedral in its local structures, Bi–O stretching vibration and thus changed the electronic structures of products. [6].

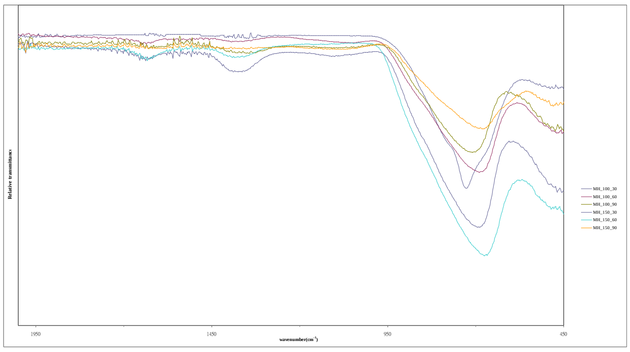
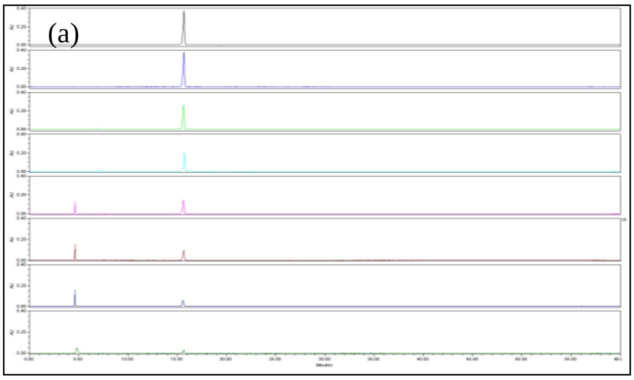


Figure 5: ATR-FTIR spectra of samples $BiVO_4$ synthesized from different synthesis temperature and time.

3.2 Photocatalytic Activity Evaluation

The photocatalytic performances of the bismuth vanadate catalysts were evaluated by degrading SMZ under visible light irradiation with 5 gL^{-1} of catalyst added. The degradation efficiencies as a function of physico-chemical properties of catalyst (illustrated in Figure 6, 7), that microwave hydrothermal method at 100℃, 150℃ and kept for 30, 60, 90 minutes. The main crystal forms of $BiVO_4$ for all samples; which is assigned to monoclinic $BiVO_4$; MH-100-60, MH-150-60, MH-150-90 and tetragonal $BiVO_4$; MH-100-30. except MH-100-90 sample MH-100-90 sample .Evaluation of photocatalytic degradation of SMZ , Under this studied conditions, the SMZ concentration was measured by using HPLC-PDA, and to reveal the SMZ is degraded completely at MH-100-60 and MH-150-90 .



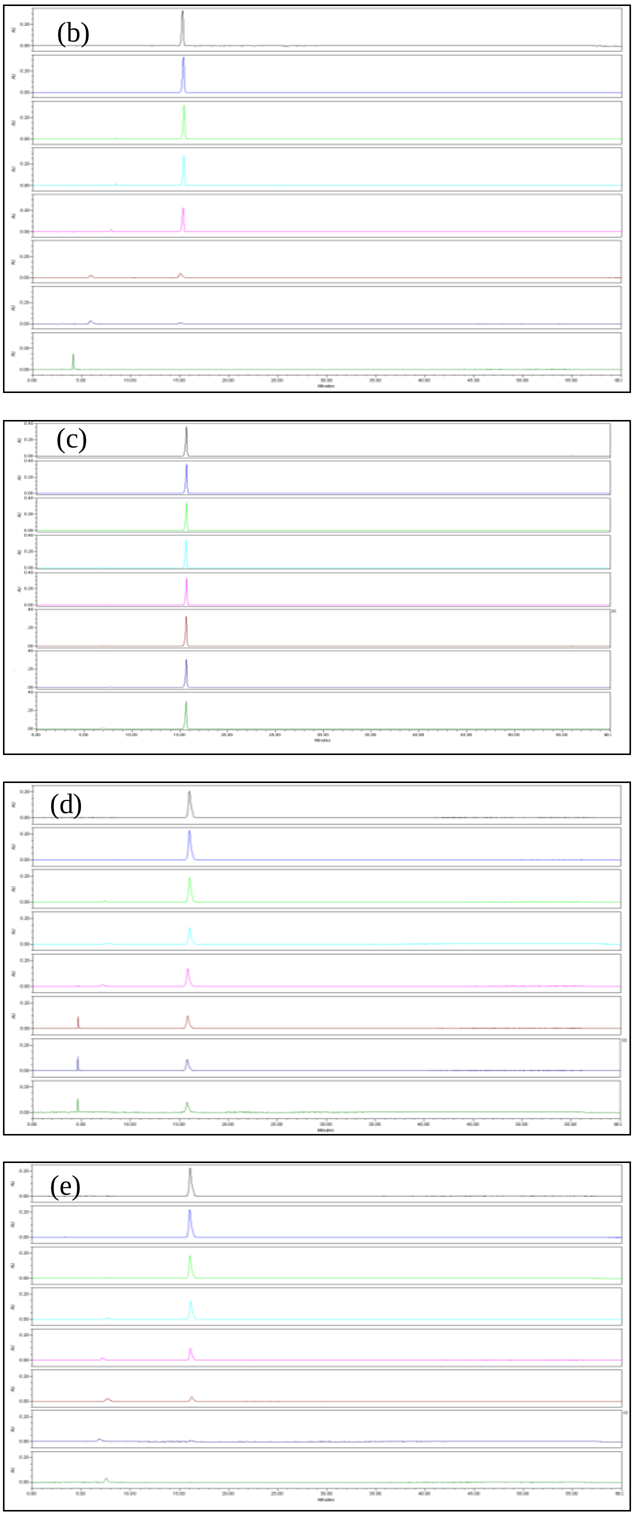


Figure 6: Chromatography of photocatalytic degradation of SMZ by HPLC-PDA, the catalyst ($BiVO_4$) synthesized from different synthesis conditions:(a)MH-100-30, (b)MH-100-60, (c)MH-100-90, (d)MH-150-30, (e)MH-150-90.

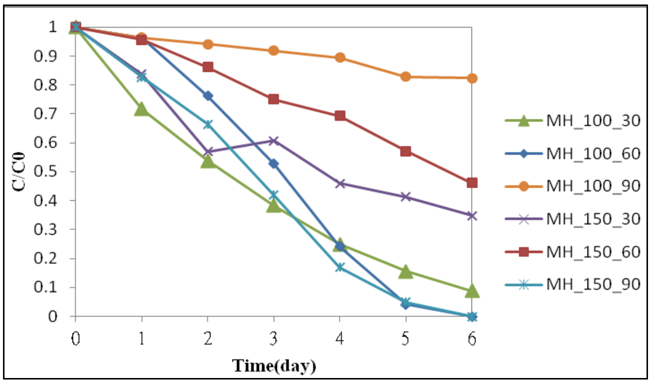


Figure 7: Evaluation of photocatalytic degradation of SMZ by HPLC-PDA: the catalyst ($BiVO_4$) synthesized from different synthesis temperature and time.

4 Conclusion

The XRD pattern main crystal forms of $BiVO_4$ for all samples; which is assigned to monoclinic $BiVO_4$ or tetragonal $BiVO_4$. In this way, these data agrees with its components (monoclinic type $BiVO_4$) and clearly demonstrate that a good visible-light-driven photocatalyst can be synthesized by this microwave hydrothermal processing. Under the studied conditions, chromatography of photocatalytic degradation of SMZ reveal the SMZ is degraded completely.

Acknowledgments

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References

[1] M. Gotic, S. Music, M. Ivandaa, M. Soufek, S. Popovic. Synthesis and characterisation of bismuth(III) vanadate, *Journal of Molecular Structure*, **744–747**, 535–540, 2005.

[2] W. T. Hughes, P. C. McNabb, T. D. Makres, S. Feldman. Efficacy of Trimethoprim and Sulfamethoxazole in the Prevention and Treatment of Pneumocystis carinii Pneumonitis, Antimicrob Agents *Chemother*, **5,** 289–293, 1974.

[3] L. Xu, G. Wang, F. Ma, Y. Zhao, N. Lu, Y. Guo, X. Yang, Photocatalytic degradation of an aqueous sulfamethoxazole over the metallicsilver and Keggin unit codoped titania nanocomposites *Applied Surface Science* **258,** 7039 – 7046, 2012.

[4] T.Y. Tzeng, C.C. Chen, S.L. Wang. Photocatalytic activity of sulfonamide antibiotic in aqueous suspension of TiO_2-P25, *2011 International Conference on Environment Science and Engineering, IPCBEE*, **8**, 270-272, 2011.

[5]L. Zhou, W. Wang, S. Liu, L. Zhang, Xu H and W. Zhu. A sonochemical route to visible-light-driven high-activity BiVO4 photocatalyst. *Journal of Molecular Catalysis A: Chemical* **252,** 120-124. 2006

[6]A. Zhang., J. Zhang. Hydrothermal processing for obtaining of $BiVO_4$ nanoparticles. *Materials Letters* **63**, 1939–1942, 2009.

[7] W. Lertpaitoonpan, S.K. Ong, T.B. Moorman, Effect of Organic Carbon and pH on Soil Sorption of Sulfamethazine *Chemosphere* **76,** 558–564. 2009

[8] J. Beausse, Selected drugs in solid matrices: a review of environmental determination, occurrence and properties of principal substances *TrAC: Trends Anal. Chem.* 23 , 753–761. 2004.

[9] C. Hansch, D. Hoekman, A. Leo, L. Zhang, P. Li, The expanding role of quantitative structure-activity relationships (QSAR) in toxicology Toxicol. Lett. 79, 45–53. 1995

[10] L. Lissemore, C. Hao, P. Yang, P.K. Sibley, S. Mabury, K.R. Solomon, An exposure assessment for selected pharmaceuticals within a watershed in Southern Ontario. Chemosphere 64 , 717–729. 2006

[11]P.S. Yap, Y.L. Cheah, M. Srinivasan, T.T. Lim Bimodal N-doped P25-TiO_2/AC composite: Preparation, characterization, physical stability, and synergistic adsorptive-solar photocatalytic removal of sulfamethazine *Applied Catalysis A: General* **427–428,** 125– 136. 2012.

[12]A. Galembeck, OL. Alves. Bismuth vanadate synthesis by metallo-organic decomposition: thermal decomposition study and particle size control *J. Mater. Sci.*, **37**, 1923–1927. 2002.