Photocatalytic Degradation of 2,4-dichlorophenol using BiVO₄ Powder Prepared by the Sol-gel Method

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Bismuth vanadate (BiVO₄) powder was prepared by the sol-gel method using bismuth nitrate and ammonium vanadate as the starting precursors with mole ratio of 1:1 in ethanol media at 70°C for 1h and calcined at 400–600°C for 2h. The phase structure of BiVO₄ powder was characterized by X-ray diffractometer (XRD). Single phase monoclinic of BiVO₄ powder was obtained. The morphology of BiVO₄ powder was characterized by scanning electron microscope (SEM). BiVO₄ powder was irregular in shape with the particles' size range of 100–300 nm. The functional groups of BiVO₄ powder was identified by Fourier transform infrared spectrophotometer (FT-IR). The symmetric and asymmetric stretching of VO₄³⁻ was showed at 826–829 and 737–741 cm⁻¹, respectively. The surface area of BiVO₄ powder was determined by surface area analyzer (BET) and shown in the range of 2.20–2.75 m²g⁻¹. The photocatalytic degradation of 2,4-dichlorophenol was investigated by high performance liquid chromatograph (HPLC). The percentage of degradation of 2,4-dichlorophenol using BiVO₄ powder after calcination at 500°C for 2h was 55.42%.

Key words: Photocatalytic, BiVO₄, Sol-gel Method, 2,4-dichlorophenol

1. INTRODUCTION

2,4-dichlorophenol (DCP) are phenolic compounds which have been widely used as an intermediate making in pesticides, herbicides, fungicides, antiseptics, disinfectants, wood preservatives, dyes and drugs [1–3]. Chlorophenolic compounds are difficult to be biodegraded and have been considered to be harmful for human health due to their potential carcinogenic, mutagenic activity and toxicity [4–6]. An increasing discharge of these compounds from industrial activities into the environment leads to enhance water pollution. They have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA) and the European Union (EU) [7–10]. Recently, the variety of photocatalysts is employed for solving the serious environmental and pollution challenges. The use of photocatalysis technology for destruction of the organic pollutants in water is an interesting method which can replace the traditional methods. In this technique, the active species such as OH[•], O₂^{•-} and hole (h⁺) are generated by light energy and performed the degradation of organic pollutants [11–12]. The semiconductors have been found to exhibit organic substance degradation under light irradiation such as TiO₂ and ZnO have been widely studied and worked. However, these are only activated under UV light irradiation with a wide band gap of 3.23–3.37 eV. This poor solar efficiency has hindered the commercialization technology [13–15]. Therefore, the development of visible light responsive catalysts (Eg < 3.0 eV) with high efficiency and stability still offers

unexplored opportunities for total destruction of aqueous organic pollutants and has become one of the most important research directions in this field. BiVO₄ is one of the most promising semiconductors for various potential applications for solar energy conversion with visible light response which has recently been developed. The electronic structure of BiVO₄ is a direct bandgap semiconductor due to the presence of empty 3d orbital of vanadium coupled to orbitals 2p of oxygen and 6p of bismuth, resulting in a conduction band minimum at the Brillouin zone edge, favorable to low energy direct transition. It has been recognized as a strong photocatalyst for pollutant decomposing and relatively strong oxidation properties for water splitting and organic pollutant photodegradation under visible light irradiation. [16–18]. However, the photophysical and photocatalytic properties of BiVO₄ are strongly influenced by the way of preparation and its crystal structure. The monoclinic phase BiVO₄ has been reported to show higher photocatalytic activity for O₂ evolution compared with the tetragonal phases. It was reported that tetragonal BiVO₄ with a 2.9 eV band gap mainly possesses a UV absorption band, while monoclinic BiVO₄ with a 2.4 eV band gap has a characteristic visible light absorption band besides the UV band [19–20]. There are several routes for preparation of BiVO₄ [21–23].

In the study, BiVO₄ powder prepared by the sol-gel method was characterized by XRD, SEM, FT-IR and BET. The photocatalytic activity of BiVO₄ powder was investigated for degradation of 2,4-dichlorophenol under

visible light irradiation.

2. EXPERIMENTAL

2.1 Preparation of BiVO_4 powder by the sol-gel method

Bismuth vanadate (BiVO_4) powder was prepared by the sol-gel method using bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and ammonium vanadate (NH_4VO_3) were mixed together with mole ratio of 1:1. The solution was then added with $\text{C}_2\text{H}_5\text{OH}$ and heated at 70°C by stirring for 1 h. The yellow sol solution was obtained. Sol was changed to a yellow gel after addition in 1M CH_3COOH . Finally, the yellow gel was dried in oven (637G, Fisher Scientific, USA) at 100°C for 24h and calcined in furnace (AAF11/18/301, Carbolite, UK) at 400 – 600°C for 2h.

2.2 Characterization of BiVO_4 powder

The phase structure of BiVO_4 powder was characterized by X-ray diffractometer (XRD, X'Pert Pro MPD, Panalytical, Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda=1.546 \text{ \AA}$). The detection range was 10 – 60° with a step of 0.10° ($2\theta/\text{s}$), and the diffraction pattern was compared with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No. 14–0688. The morphology of BiVO_4 powder was characterized by scanning electron microscope (SEM, JSM-5410LV, JEOL, Japan) with the tungsten filament K type, accelerate voltage of 15.0 kV . The specific surface area of BiVO_4 powder was determined by Brunauer, Emmett and Teller analyzer (BET, Autosorb 1 MP, Quantachrome, USA.). The functional groups of BiVO_4 powder were identified by Fourier transform infrared spectrophotometer (FTIR, Spectrum RX I, Perkin Elmer, England).

2.3 Photocatalytic degradation of 2,4-dichlorophenol using BiVO_4 powder

The photocatalytic property of BiVO_4 powder prepared by sol-gel method has been studied for degradation of 2,4-dichlorophenol under visible irradiation. The experiment consisted of 0.1000 g of BiVO_4 powder added in 100 mL of an initial concentration of 5.0 mg/L 2,4-dichlorophenol solution, the suspensions were magnetically stirred and stored in the dark for 24h, in order to achieve the maximum adsorption of the 2,4-dichlorophenol onto the BiVO_4 surface. Solution was irradiated with a 8 Watt fluorescent lamp (Philips, Thailand) for 180 min. A 5 mL of 2,4-dichlorophenol solution was drawn every 30 min and filtered for analysis through $0.45 \mu\text{m}$ millipore syringe filter to remove BiVO_4 powder. The residual concentration of 2,4-dichlorophenol was analyzed by the high performance liquid chromatograph (HPLC, HP1100, Agilent, USA) which is equipped with a reversed column (Zorbax C18, $4.6 \times 100 \text{ mm}$) and DAD detector.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of BiVO_4 powder

The crystal structure of BiVO_4 powder prepared by the sol-gel method at different calcination temperature at 400 – 600°C for 2h was investigated by XRD, as shown in Fig. 1. All peaks show a pure monoclinic

single phase structure and no peaks of any other phases or impurities compared with the JCPDS file No.14–0688 [24]. The main peaks can be indexed as (110), (011), (121), (040), (200), (002), (211), (132), (240), (042), (202) and (161) planes of monoclinic BiVO_4 . The full width at half maximum value of (011) and (121) diffraction peak decreased and peak intensity increased, suggesting that the sizes of crystallite grow with increasing the temperature. According to the line width analysis of the (121) diffraction peak based on Scherrer formula, the crystalline size of BiVO_4 powder after calcined at 400 – 600°C for 2h was 2.08, 2.12 and 2.32 nm , respectively. It indicates that the crystalline of BiVO_4 powder improved gradually with the increase of calcination temperature [25].

Fig. 1 XRD patterns of BiVO_4 powder prepared by the sol-gel method after calcination at (a) 400°C , (b) 500°C and (c) 600°C for 2h.

Fig. 2 SEM micrographs of BiVO_4 prepared by the sol-gel method after calcination at (a) 400°C , (b) 500°C and (c) 600°C for 2h.

Fig. 2 shows the morphology of the BiVO_4 powder prepared by the sol-gel method after calcination at 400 – 600°C for 2h under SEM microscope. The SEM micrograph indicated that the particle size of BiVO_4 powder was irregular in shape. The tendency of agglomeration is more at higher temperature than at

lower temperature. The particles were found to become larger with increasing temperature. The average particles' sizes range is 100–300 nm. The average particle size was smaller than the ones previously reported [26].

The FTIR spectrum of BiVO_4 powder prepared by the sol-gel method after calcination at 400–600°C for 2h as shown in Fig. 3 was confirmed by the purity of the obtained product. A weak and intense absorption band at 474 cm^{-1} assigned to the symmetric bending of VO_4^{3-} was also visible range correspond with the previously reported [27]. The absorption band at 700–900 cm^{-1} was characteristic of the asymmetric stretching and symmetric stretching vibration of the V–O bond. The spectrum of BiVO_4 powder after calcined at 400°C for 2h was characterized by a broad and strong absorption band at 741 cm^{-1} assigned to the asymmetric stretching of VO_4^{3-} . The absorption band at 741 cm^{-1} observed and compared with BiVO_4 powder calcined at 500°C and 600°C for 2h shifted to 738 cm^{-1} and 737 cm^{-1} , respectively. The absorption band at 829 cm^{-1} assigned to the symmetric stretching of VO_4^{3-} observed and compared with BiVO_4 powder calcined at 500°C and 600°C for 2h shifted to 828 cm^{-1} and 826 cm^{-1} , attributable to the change in particle size and hence the metal ion oxygen bond distances when increasing calcination temperature [22,27]. In this study, it indicates that all BiVO_4 powder exhibited the monoclinic structure, although their particle morphologies increased then increasing calcination of temperature from 400 to 600°C.

Fig 3. FTIR spectrum of BiVO_4 powder prepared by the sol-gel method after calcination at (a) 400°C, (b) 500°C and (c) 600°C for 2h.

Table I The specific surface area of BiVO_4 powder prepared by the sol-gel method after calcination at 400°C, 500°C and 600°C for 2h

Temperature of calcination	BET Surface area (m^2g^{-1})
400	2.38
500	2.75
600	2.20

The specific surface area of BiVO_4 powder prepared by the sol-gel method after calcination at 400°C, 500°C

and 600°C for 2h as shown in Table I. The BET results of this research indicated that BiVO_4 calcined at 500°C for 2h was the highest surface area. Therefore, the BiVO_4 calcined at 500°C for 2h was selected for studying photocatalytic activity.

3.2 Photocatalytic degradation of 2,4-dichlorophenol using BiVO_4 powder

The photodegradation efficiencies of 2,4-dichlorophenol using BiVO_4 powder prepared by the sol-gel method after calcination at 500°C for 2h under visible light irradiation as shown in Fig. 4. After 180 min of light irradiation time, the concentration of 2,4-dichlorophenol solution was determined by HPLC. The percentage degradation of photocatalytic activation was calculated by the following equation:

$$D = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where, D is the degradation percentage, C_0 is the initial 2,4-dichlorophenol concentration and C_t is the 2,4-dichlorophenol concentration at time, t. All C_0 and C_t values were determined by the maximum absorption at the wavelength of 230 nm. The progress of the photocatalytic degradation of 2,4-dichlorophenol under visible light was monitored by HPLC. The results indicated that if only the irradiation was employed, the degradation of 2,4-dichlorophenol showed non-significant as shown in Fig 4. The degradation rate of 2,4-dichlorophenol under visible light increased from 9.87% to 10.23%. However, the degradation rate increased significantly when a small amount of BiVO_4 powder was added in the solution and was exposed to the visible light illumination. The degradation rate increased from 20.53% to 55.42% after 180 min irradiation.

Fig. 4 The degradation of 2,4-dichlorophenol with (a) control (◆) (b) under visible light (■) (c) non visible light with BiVO_4 powder (▲) and (d) under visible light with BiVO_4 powder (●)

However, the efficiency degradation in this study showed lower photocatalytic efficiency than the previously reported. It has been reported that 2,4-dichlorophenol degradation at the percentage over 90% under visible light irradiation (150 Watt) in 5 h [28].

In this study, the irradiation was used a low-energy light source (8 Watt) in order to reduce the cost of light source. In fact, the efficiency of photocatalytic process increase with increasing of irradiation intensity [29].

4. CONCLUSIONS

Bismuth vanadate (BiVO₄) powder was successfully prepared by the sol-gel method with bismuth nitrate and ammonium vanadate as precursors. The BiVO₄ powder was studied after calcined at 400–600°C for 2h. The result of XRD, SEM and FTIR indicated that the structural and morphological studies confirmed the formation of a pure monoclinic phase with average particles' size range of 100–300 nm. BiVO₄ powder after calcined at 500°C for 2h was the highest surface area and can be used as a photocatalyst for the degradation of 2,4-dichlorophenol under visible light.

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6. REFERENCES

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