High degradation of BiVO$_4$ nanoparticle for organic dyes under visible light irradiation mediated by $S_2O_8$

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Abstract. In this study, we have successfully synthesized BiVO$_4$ materials by hydrothermal method. The degradation of methylene blue (MB) under LED visible light mediated by $S_2O_8$/BiVO$_4$/Vis system. The obtained BiVO$_4$ catalyst was characterized by X-ray diffraction (XRD), Raman, scanning electron microscope (SEM), and UV-visible diffuse reflectance spectrum (UV-vis DRS). We investigated the effect of $S_2O_8$ concentrate, pH value and initial concentration on the removal rate of MB. The results of XRD spectra showed that the BiVO$_4$ fragment has a crystalline structure in moneblinite monoclinic phase alone. The degradation of MB concentration under visible light mediated $S_2O_8$ / BiVO$_4$ / Vis was 78% after 100 minutes of irradiation. The band gap (Eg) of BiVO$_4$ was estimated to be 2.39 eV. Therein, the presence of Na$_2$SO$_4$ anions decrease concentration of MB with compared to the original using $S_2O_8$ / BiVO$_4$ system alone.

I. Introduction
The wastewater from industrial production processes when discharged into canals and rivers pollutes water environment water and soil. Therein, organic dyes in textile and industrial effluents have become the major environmental contaminants. In particular, Methylene Blue (MB) is available in organic dyes, it is very toxic to humans and causes cancer when exposed regularly. Furthermore, many dyes are highly water-soluble, and some traditional treatment methods, such as activated carbon adsorption, flocculation, and biological treatment, do not work efficiently [1,2].

The photocatalytic technology is one of the mostly effective pollution control procedure. The multifarious kinds of effective and low cost photocatalysts for the degradation of organic pollutants have been study as TiO$_2$, but it is has a large bandgap $\geq 3.2$ eV and only active under UV light. In
recent years, researchers notice has been paid to the use of photocatalysts under visible such as CdS, Cu2O, Fe3O4, WO3, and BiVO4 [3–5]. Therein, bismuth vanadate (BiVO4) is paid attention by researchers because bandgap energy is 2.4 eV for photocatalytic activity under visible light. It has a number of specific applications such as: photocatalyst for the cleavage of water [6] and the oxidative degradation of rhodamine B (RhB) [7,8], methyl orange [9], methylene blue (MB) [10], copper acetylacetonate [11], 4-alkylphenols [12], and phenol [7,13] with photocatalysts using under visible light.

There are three crystal structures of BiVO4 consist: tetragonal scheelite phase (t-s), tetragonal zircon phase (t-z) and monoclinic scheelite phase (m-s) [14]. BiVO4 in form m-s crystal for exhibits a higher photocatalytic activity than its tetragonal zircon and tetragonal scheelite peers, its photocatalytic activity under visible-light irradiation owing to the lone pair deformity of Bi 6s orbital in BiVO4 semiconductor [15]. BiVO4 synthesized by various methods such as [16], Microwaves [17], Solvothermal [18], Sol-gel [19] and co-precipitation method [20]. Persulfate ion (S2O82−) is not a photocatalyst. However, it is an attractive candidate to photochemically decompose MB because each persulfate ion (S2O82−) can be activated to produce two SO42− as depicted by Eq1 and the created SO42− can act as a potent oxidant in solution [21]:

$$S_2O_8^{2−} + hv \rightarrow SO_4^{−} + SO_4^{2−}$$

(1)

In this paper, we report the the synthesized of BiVO4 by hydrothermal method. The photocatalytic degradation of methylene blue (MB) over S2O8/BiVO4 system was under visible light irradiation. To improve the photocatalytic degradation of MB, a more stable Na2S2O8 was added into BiVO4/Vis process. We studied the effect of Na2S2O8 concentrate, pH, and catalyst dosage on the degradation evaluate of MB in conspicuous.

2. Material and methods

2.1. Material

Bismuth(III) nitrate pentahydrate (Bi(NO3)3.5H2O, ≥ 98.0%), ammonium metavanadate (NH4VO3, ≥ 98%) and Sodium persulfate (Na2S2O8, ≥ 98.0%) were purchased from Sigma-Aldrich. Methylene Blue (C16H18ClN3S2H2O), nitric acid (HNO3, 65-68%), Sodium chloride (NaCl, ≥ 99.5%), Sodium sulfate anhydrous (Na2SO4, ≥ 99.0%), Sodium hydrogen carbonate (NaHCO3, ≥ 99.5%), Sodium Carbonate (Na2CO3, ≥ 99.5%), NaOH and HCl were obtained from Xilong Chemical Co., Ltd. (China). All reagents were used as received without further purification.

2.2. Synthesis of BiVO4

Typically, four mmol of Bi(NO3)3 was added to 40 mL HNO3 0.1 M under vigorous stirring to get a colorless solution (denoted as solution A). Four mmol of NH4VO3 was dissolved in 40 mL H2O to get a clear yellow solution (denoted solution B). Then, a yellow precipitate was formed immediately when the solution B was added to solution A. After stirring 1 h, the pH of the mixed solution was adjusted 5.0 using 1 M NaOH solution. The obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 24 h. After cooling naturally, the yellow precipitate was washed with water by centrifugation at 6500 rpm for 10 min five times and dried at 110 °C for 24 h followed by calcining at 400 °C for 3 h.

2.3. Characterization

The XRD of BiVO4 nanoparticles was carried out on a Bruker D8 Advance powder diffractometer with a Cu-Kα excitation source and a scan rate of 0.02 °/s from 10° to 70°. Raman spectra were taken on a Raman spectrometer (Horiba Jobin Yvon) using a red laser (633 nm) as the excitation source.
SEM was recorded on a Jeol instrument (JSM 7401F, Japan. UV-visible diffuse reflectance spectrum (UV-vis DRS) was recorded on a Shimadzu UV-vis spectrophotometer.

2.4. Photocatalysts Test
The photocatalytic activity tests were conducted in a 250 ml double layer interbed interlayer glass photocatalytic reactor under visible light irradiation using six white LED lamp (Cree L6, 10W, 1040 lm) at room temperature. The beaker was filled with a mixture of MB (100 mL), BiVO₄ sample (50 mg), and Na₂S₂O₈. 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 to ensure adsorption-desorption equilibrium between MB and the surface of BiVO₄ before lighting on. During light irradiation, five ml of aliquots were withdrawn and immediately centrifuged to separate photocatalyst particles every 5 min. MB concentration was analyzed by a UV-visible spectrophotometer (Model Evolution 60S, Thermo Fisher Scientific) with the absorption intensity at its maximum absorbance wavelength of λ = 664 nm.

To investigate effects of Na₂S₂O₈ concentration, pH, and MB concentration on photocatalytic activity of BiVO₄, the Na₂S₂O₈ concentration was increased from 0 to 10⁻³ mol/L, and pH was increased from 3 to 9, whereas different amount of BiVO₄ from 25 to 150 mg.

3. Results and Discussion

3.3. Structural analysis
Figure 1(a) shows the morphology of BiVO₄ studied by scanning electron microscopy (SEM). The SEM analysis indicated that BiVO₄ consists of fiber particles and overlap. The crystalline phase of the BiVO₄ were identified by XRD technique. Figure 1(b) shows the XRD patterns of the BiVO₄ synthesized using of 1 M NaOH to adjust the pH=5 value. Compared with the standard XRD pattern of BiVO₄ (JCPDS card no. 14-0688). It can be seen that BiVO₄ sample has monoclinic structure with characteristic diffraction peaks at 18.6, 18.9, 28.7, 30.5, 34.1, and 34.9°. Moreover, characteristic peaks of bismuth oxide and vanadate oxide or impurities were not find in the XRD spectrum of BiVO₄. The main peaks can be indexed as (11 0), (011), (121), (0 40), (2 00) and (0 02) planes of monoclinic BiVO₄. The results show that, synthesized BiVO₄ by Hydrothermal method show the crystal has a monoclinic scheelite structure of BiVO₄.

Figure 1(c) shows Raman spectra of BiVO₄ synthesized by Hydrothermal method. As shown in figure 1(c), the strongest band at 805 cm⁻¹ is attributed to the symmetrical bending vibrations (υₛ) mode of V-O bond, while the peaks at 615 cm⁻¹ and 684 cm⁻¹ are due to the asymmetric vibration (δₘₐ) mode of V-O bond. The Raman peak at 301 cm⁻¹ and 342 cm⁻¹ are assigned to the asymmetric bending vibrations (υₘₐ) of the VO₄³⁻ group. we calculate the V–O bond length of BiVO₄ (R, Å) by using the empirical expression: \( v = 21349e^{-19176/R} \) [22]. The photoabsorption property of a semiconductor was acknowledged as the key in determining factor its photocatalytic activity [23]. The UV–vis diffuse reflectance spectrum of the synthesized BiVO₄ by Hydrothermal method is shown in Figure 1(d). The Result in figure 1 (d) shows that, BiVO4 sample show the photoabsorption natures from the Ultraviolet light area to visible-light area till 550 nm. The band gap (Eg) of BiVO₄ was estimated to be 2.39 eV, indicating that the BiVO₄ sample had a band gap suitable for photocatalytic degradation of organic contaminants under visible-light irradiation [7].
Figure 1. Structure of BiVO₄ synthesized by hydrothermal method: SEM images (a), Wide angle XRD pattern of pure and pH=5 value of BiVO₄ (b), Raman spectra (c) and UV-vis diffuse reflectance spectra (d).

3.2. Photocatalytic activity

Figure 2 shows the decline in MB concentration of factors such as Na₂S₂O₈, pH, concentration and catalyst. The degradation of MB and BiVO₄ with irradiation only Light was not improved, indicates that Na₂S₂O₈ is capable of rise the likelihood of MB degradation by visible light irradiation as show in fig. 2(a). The photodegradation of MB with single BiVO₄ is 51.41% after 100 min of irradiation, whereas the degradation rate with the Na₂S₂O₈/BiVO₄/Vis system at Na₂S₂O₈=10⁻⁵ M increases 69.18% after 100 min of irradiation. The concentration of Na₂S₂O₈ higher lead to higher adsorption. The achievable photocatalytic achievable for BiVO₄ with the attendance of S₂O₈ under visible light irradiation was described as underneath:

\[
\text{BiVO}_4 + \text{hv} \rightarrow h_{\text{vb}}^+ + e_{\text{cb}}^- \quad (2)
\]

\[
\text{S}_2\text{O}_8^{2-} + e_{\text{cb}}^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (3)
\]

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{SO}_4^{2-} + \text{H}^+ \quad (4)
\]

The HO° radical was recognized as a powerful oxidizer, and so the creation rate of HO° radicals has a good connection with the photocatalytic activity [17,24]. The influence of the initial pH value on the photodegradation of MB in the S₉O₈/BiVO₄ system by under visible light is shown in figure 2(b). In which, the dosage of BiVO₄ and Na₂S₂O₈ were fixed at 0.05 g and 10⁻⁵ M. The results indicate that the decomposition rate decreases when the pH value is equal to 7. However, at higher or lower pH
value lead to lower performance of \( \text{S}_2\text{O}_8/\text{BiVO}_4 \) system under visible light, because it is due to the special nature of \( \text{Na}_2\text{S}_2\text{O}_8 \).

Figure 2(c) shows the photodegradation efficiencies of MB with the pH=7 value, concentration of MB and \( \text{Na}_2\text{S}_2\text{O}_2 \) were fixed at 15 ppm and \( 10^{-5} \text{ M} \), different amount of BiVO\(_4\) (25 mg to 150 mg) under visible-light irradiation. The results showed that only the BiVO\(_4\) content added to the solution with 50 mg reduced the MB concentration better than different survey condition. Though, but the higher the BiVO\(_4\) content was lead to adsorption and poor decomposition efficiency. The study of the effects by anions on the photocatalytic degradation of MB was significant because anions were rather common in natural water and wastewater. The effects of the presence of various anions such as chloride, sulfate anhydrous, hydrogen carbonate and carbonate were studied using 3 mM solutions of their sodium salts and an initial concentration of 15 ppm of MB with a 50 mg of BiVO\(_4\) and \( 10^{-5} \text{ M} \) of \( \text{Na}_2\text{S}_2\text{O}_8 \) as show in figure 2(d). The results show that, the attendance of \( \text{Na}_2\text{SO}_4 \) significant difference is noticed in the MB photodegradation degree and \( \text{NaCl}, \text{Na}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \) could inhibit the photodegradation significantly.

![Figure 2](image)

**Figure 2.** Photocatalytic degradation of MB: effect of concentration of \( \text{Na}_2\text{S}_2\text{O}_8 \) (a), the initial pH value (b), catalyst of BiVO\(_4\) (c), and anions (d).

The UV-vis spectral changes of MB by under visible light with pH=7 value, concentration of MB and \( \text{Na}_2\text{S}_2\text{O}_2 \) were fixed at 15 ppm and \( 10^{-5} \text{ M} \) as show in figure 3(a). The major absorption band centered at 664 nm of MB has been used to monitor the photocatalytic degradation of MB. The results
show that, temporal evolution of the spectral changes during the photodegradation of MB. The degradation of MB was observed more clearly when comparing figure 3(a) and figure 3(b), show that presence of Na$_2$SO$_4$ degrades concentration with compared to the original.

Figure 3. UV-vis spectral changes of MB as a function of irradiation time over BiVO$_4$: the absence of Na$_2$SO$_4$ (a) and the presence of Na$_2$SO$_4$ (b).

4. Conclusions
In this work, we successfully synthesized BiVO$_4$ by hydrothermal method with pH=5 value. the crystal of BiVO$_4$ has a monoclinic scheelite structure of BiVO$_4$. The S$_2$O$_8$/BiVO$_4$ system had much higher photocatalytic activities in the MB degradation under visible light irradiation compared with the pure BiVO$_4$ photocatalyst. The best condition for decomposition of MB concentration at solution value ph = 7, the amount of catalyst is 50 mg, Na$_2$S$_2$O$_8$ concentration is 10$^{-5}$ M, with efficiency of decomposition MB is 70% after 100 min under visible light irradiation. The results of Anion survey showed that Na$_2$SO$_4$ significant difference is noticed in the MB photodegradation degree.

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