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# Visible Light Induced Enhanced Photocatalytic Degradation of Industrial Effluents (Rhodamine B) Using BiVO<sub>4</sub> Nanoparticles

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**Abstract.** This study investigates the photodegradation of the organic dye Rhodamine B (RhB) under visible light irradiation by BiVO<sub>4</sub> photocatalysts synthesized hydrothermal method. A RhB solution (100 mL, 15 ppm) was degraded in 20 min using the BiVO<sub>4</sub> photocatalysts with visible light irradiation. The effect of temperatures calcination on visible-light photocatalytic activity and light absorption performance of BiVO<sub>4</sub> was discussed in details. The results showed that BiVO<sub>4</sub> sample calcined at 450 °C exhibited the highest photocatalytic performance on the degradation of a Rhodamine B solution. The RhB degradation by the BiVO<sub>4</sub> catalyst is 62.38% after 200 min of simulated solar irradiation.

## 1. Introduction

The prevalence of wastewater generated from industries and household activities poses a serious problems to the modern society. Among common contaminants in water, organic dyes, especially Rhodamine B, have caused increasing concern [1-5]. Characteristically, the dye is easily dissolvable in water and is commonly utilized in textile, food, and pharmaceutical industry [6-8]. In addition, Rhodamine B is water tracer fluorescent and has been known to cause allergies to the skin, eyes, and respiratory system. Such adverse effects have underlain studies exploring the degradation mechanism of RhB [9,10] and raised dye control as an important issue to be tackled with globally. In the literature, previous studies have mostly dealt with degradation mechanism under visible illumination, suggesting photocatalytic oxidation an efficient technology to remove organic pollutants.

Heterogeneous photocatalysis using semiconductors is one of the most promising techniques for environmental remediation. Photocatalytic degradation has various advantages including simplicity, efficiency, low cost and low secondary pollution [11-14]. Under proper irradiation, semiconductors



could act as a photocatalyst for the degradation of pollutants. Among semiconductors, bismuth vanadate ( $\text{BiVO}_4$ ) prevails as a potent photocatalyst owing to its capability to be activated under solar radiation [15-17]. The catalyst is also nontoxic, inexpensive, chemically stable and highly resistant to photocorrosion. The most photoactive structure is the monoclinic scheelite-like crystalline structure with a band gap of 2.4 eV. As a result,  $\text{BiVO}_4$  has already been studied for the photo-oxidative degradation of many organic compounds such as phenol, organic dyes and metal organic compounds. The aim of this study is to examine the photocatalytic activity of the prepared  $\text{BiVO}_4$  materials against the degradation of Rhodamine B dye under visible light irradiation. Different samples of  $\text{BiVO}_4$  materials were synthesized by hydrothermal method at different temperature ranging from 350 °C to 600 °C.

## 2. Materials and Method

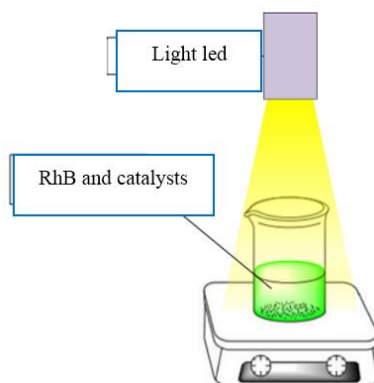
### 2.1. Materials

$\text{NH}_4\text{VO}_3$  ( $\geq 98\%$ , Sigma-Aldrich),  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  ( $\geq 98.0\%$ , Sigma-Aldrich),  $\text{HNO}_3$  (65-68%),  $\text{NH}_4\text{OH}$  (25-28%, Xilong), Rhodamine B (RhB, Jihuada), and distilled water (from Lasany's two-storey water machine). The  $\text{BiVO}_4$  was synthesized by hydrothermal method: First, a mixture containing 4 mmol of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 20 mL of 4M  $\text{HNO}_3$  solution was prepared. Second, the mixture was introduced into a stoichiometric of  $\text{NH}_4\text{VO}_3$  in 40 mL of hot water, followed by one hour of stirring to obtain a stable and homogeneous solution. The pH of the mixture is adjusted with  $\text{NH}_4\text{OH}$  or  $\text{HNO}_3$  solution. The mixture was autoclaved and heated at 160 °C for 24 hour under pressure. The produced precipitate then was filtered, washed with distilled water and dried overnight at 110 °C and then calcined in air at different temperature (350 °C, 400 °C, 450 °C, 500 °C and 600 °C) for 2 hours.

### 2.2. Photocatalytic test

The  $\text{BiVO}_4$  photocatalyst was tested for photocatalytic performance against RhB (Sigma-Aldrich) under visible light irradiation. Rhodamine B (RhB) is commonly used in colored papers, temporary hair dyes, fabric dyes and many other applications. However, RhB is toxic and is responsible for diseases such as vomiting, cyanosis, affecting the nervous system of humans. In this study, the light source used is compact Philip 60W (LED light, cree L6, 60W).

The evaluation process of  $\text{BiVO}_4$  photocatalytic through the following steps : First, 0.1 g of synthesized  $\text{BiVO}_4$  was introduced into 100 mL of RhB solution. The suspension was then magnetically stirred in the dark for 1h to reach the adsorption-desorption equilibrium. Following that, the suspension was exposed to irradiation in 2 hours. Periodically, 3 mL of aliquot was taken and centrifuged at 7000 rpm/min to remove the particles. The concentration were analyzed by UV-Visible Spectrophotometer. The diagram illustrating the experiments is shown in Figure 1.

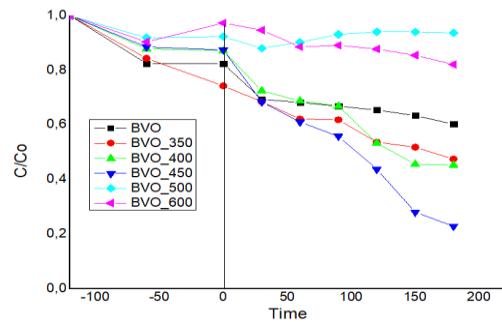


**Figure 1.** Process diagram of visible light induced enhanced photocatalytic degradation of Rhodamine B using  $\text{BiVO}_4$  nanoparticles

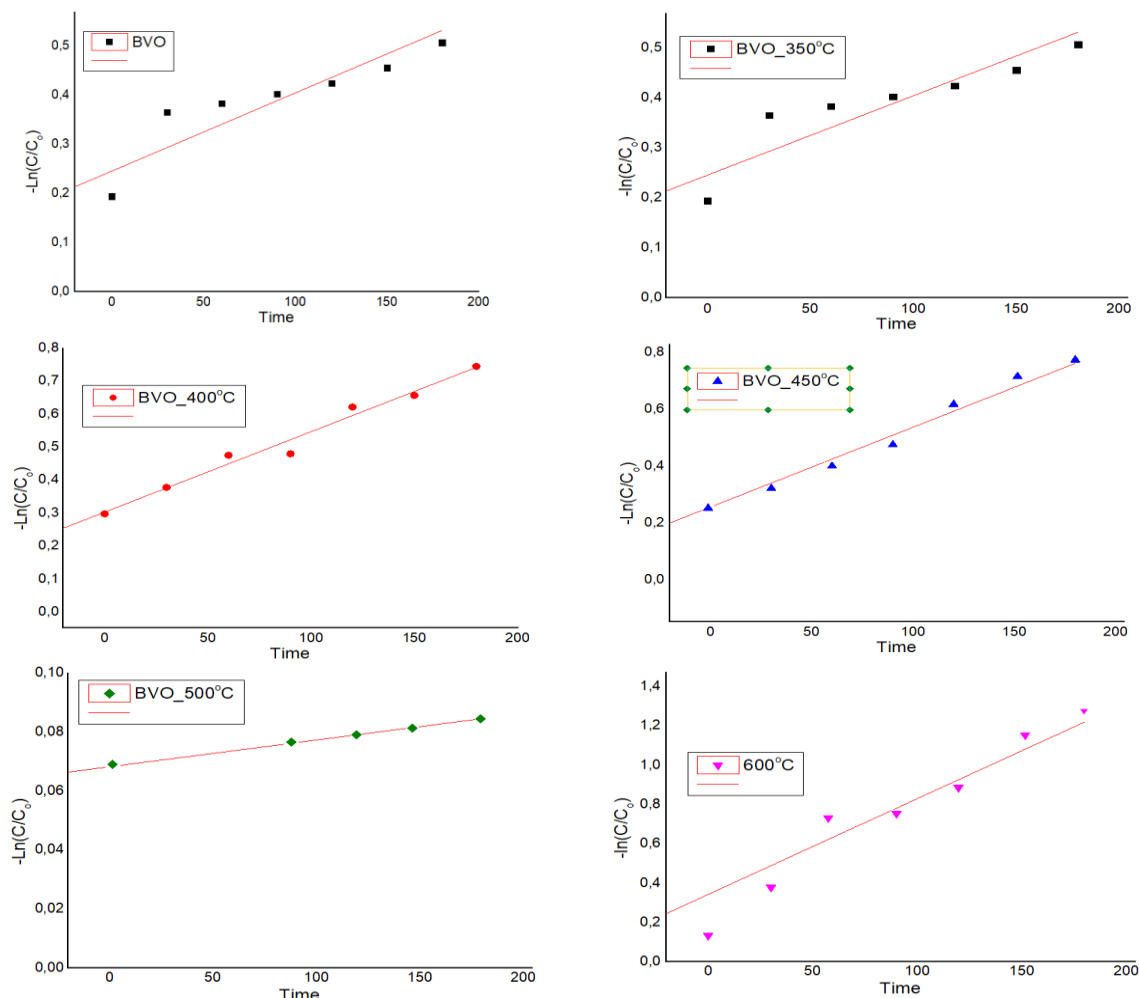
## 3. Results and Discussion

According to the UV-vis diffuse reflectance spectrum produced by UV-vis DRS, the band gap of the  $\text{BiVO}_4$  catalyst was estimated to be approximately 2.42 eV. The activity of photocatalytic materials are evaluated based on decomposition reaction of organic pigments RhB using visible light. Figure 2 shows the photocatalytic decomposition of RhB on  $\text{BiVO}_4$  samples synthesized by hydrothermal

method. BVO\_450 sample catalyst exhibited the highest activity in the photocatalytic decomposition of RhB under visible light. Figure 3 shows the result of constant optical decomposition rate ( $k$ ) RhB on the catalyst sample determined from the first-order kinetic model:  $-\ln(C/C_0) = kt$ . As shown in Figure 2, when the RhB solution was illuminated for 120 minutes without a catalyst, about 8% RhB was decomposed. Also according to Figure 3, the peak absorption intensity of 664 nm of RhB solution under photocatalytic treatment of synthetic  $\text{BiVO}_4$  materials at different calcination temperatures showed a significant decrease. Notably, the as-synthesized samples calcined at 450 °C (Figure 2) is the highest processing efficiency, 62.38% of RhB in solution was decomposed (Table 1).



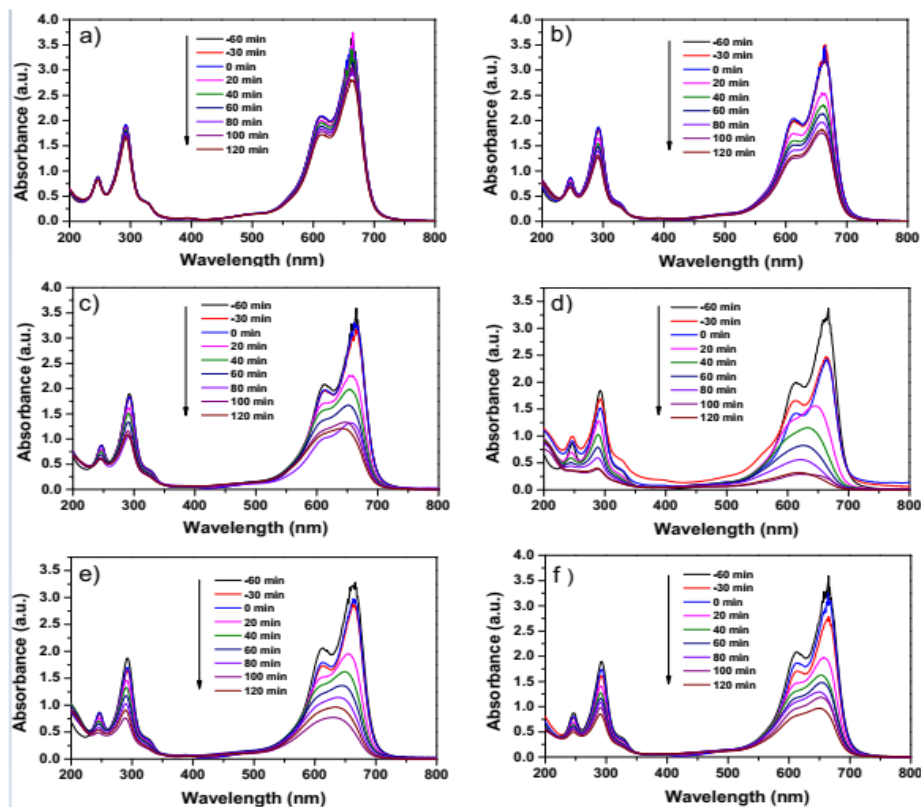
**Figure 2.** Photolysis of RhB on  $\text{BiVO}_4$  samples at different calcination temperatures.



**Figure 3.**  $-\ln(C/C_0)$  over time of photo-catalytic decomposition of RhB on  $\text{BiVO}_4$  samples synthesized by hydrothermal method.

**Table 1.** Optical and catalytic performance results of samples kinetics  $\text{BiVO}_4$

Name sample	Calcination temperature (°C)	Degradation rate constants K (min)	R <sup>2</sup>	Efficiency H%
BVO	350	0.00244	0.9173	52,52
	400	0.00281	0.9242	54,7
	450	0.00487	0.9497	62,38
	500	0.0023	0.9317	45,31
	600	0.0142	0.922	43,22



**Figure 4.** UV-vis change of RhB on BiVO<sub>4</sub> samples at different calcination temperatures: a) BVO, b) BVO\_350 °C, c) BVO\_400 °C, d) BVO\_450 °C, e) BVO\_500 °C, f) BVO\_600 °C

Figure 4 presents the change of absorption peak intensity on the absorption spectrum of the RhB solution over time with BiVO<sub>4</sub> calcined at different temperatures. Photocatalytic activity in visible light region indicates absorbance of visible light. Visually, absorption curve presents in the range of 550–800 nm for most catalyst samples and the intensity of characteristic absorption peak at 652 nm diminished rapidly with time and had gradually hypsochromic shifts of absorption bands from 652 nm to 735 nm, which is commensurate with other reported results [18]. Except for Figure 4a, where weak absorption in the region of 550–800 nm of pure BiVO<sub>4</sub> is presented, all remaining BiVO<sub>4</sub> samples showed enhanced absorption in this region upon calcination at different temperatures in range of 350 °C to 600 °C. In particular, Figure 4d showed strongest absorption in the visible-light regions with the intensity of characteristic absorption peak at 664 nm. On the contrary Figure 4a and b showed weakest absorptions in the visible-light regions with the intensity of absorption peak at 652 nm and 653 nm. In addition, the peak was slightly shifted to longer wavelength, possibly due to an increase of BiVO<sub>4</sub> particle size. This result shows that the sample of BiVO<sub>4</sub> prepared at calcination temperatures of 450 °C has a larger surface area than all other, thus enhancing the absorption of pigments on the surface of the material and thereby increasing the activity photochemistry, which is consistent with those reported in literature.

#### 4. Conclusion

The photocatalytic activity of BiVO<sub>4</sub> was tested for the photodegradation of rhodamine B under visible light irradiation. The as-synthesized samples calcined at 450 °C gave the highest processing efficiency with 62.38% of RhB in solution was decomposed. This result opens the possibility of wide application of BiVO<sub>4</sub> material specially applied as catalyst for environmental treatment, especially when it comes to removing RhB dye from wastewater by degradation.

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