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# Influence of NH<sub>4</sub>OH Concentration in Synthesis of Bismuth Oxide to Physicochemical Properties and Photocatalytic Activity in Methyl Orange Degradation

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**Abstract.** Synthesis of bismuth oxide was undertaken by precipitation method using NH<sub>4</sub>OH precipitating agent with various concentrations. The purpose of this study was to determine the effect of NH<sub>4</sub>OH concentration on the physicochemical characteristics and photocatalytic activity of bismuth oxides produced. Bismuth oxide synthesis was conducted by varying the concentration of NH<sub>4</sub>OH which was 1.5 M and 2.5 M. Synthesis was carried out through a reaction between HNO<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O then added NH<sub>4</sub>OH with various concentrations. The resulting precipitate was then filtered and dried in an oven at 110 °C for 24 hours. After that, the oven product was calcined at 600 °C for 1 hour. The XRD results showed that bismuth oxide produced from precipitating agents with a concentration of 1.5 M and 2.5 M resulted in the same crystal structure mixture, namely  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>. Then the results of DRS-UV showed that products synthesized using 1.5 and 2.5 M NH<sub>4</sub>OH have band gap of 2.65 eV and 2.67 eV, respectively. Bismuth oxides synthesized with NH<sub>4</sub>OH 1.5 M and 2.5 M has degradation rate constants of methyl orange of  $4.46 \times 10^{-2}$  and  $2.37 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$  respectively with percent degradation for 120 minutes at 82.98% and 37.23%, consecutively.

## INTRODUCTION

Bismuth oxide is a pale yellow solid, which has a melting point of 825 °C [1] and is known to have six forms of polymorphs, namely  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (monoclinic),  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> (tetragonal),  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> (body centered cubic),  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> (face centered cubic),  $\epsilon$ -Bi<sub>2</sub>O<sub>3</sub> (orthorhombic) and  $\omega$ -Bi<sub>2</sub>O<sub>3</sub> (triclinic) [2, 3]. Bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) has optical and electrical properties, such as a refractive index, electrical conductivity, and good dielectric permittivity and has a band gap energy of 2-3.96 eV [2]. Therefore, Bi<sub>2</sub>O<sub>3</sub> can be applied in various fields, such as solid oxide fuel cells [4], and photocatalysts [5, 6].

Bismuth oxide synthesis can be undertaken by several methods, including the solution combustion method [7, 8], hydrothermal method [9], sol gel method [1], and precipitation method [10, 11]. Synthesis using precipitation method has advantages compared to other methods, including easy control of chemical composition, low process temperature, and low cost. One of the factors that plays a role in the deposition process is the use of precipitating agent [12]. This factor affect the physicochemical properties of the products such as crystal structure, morphology, and band gap and photocatalytic activity. Some substances commonly used as precipitating agents are hydroxides, carbonates, sulfates and oxalates [13].

Previously we have synthesized bismuth oxide using precipitating agents of NaOH and NH<sub>4</sub>OH with bismuth oxynitrat (Bi<sub>5</sub>O(OH)<sub>9</sub>(NO<sub>3</sub>)<sub>4</sub>) as a precursor. The results showed NH<sub>4</sub>OH precipitating agent produced bismuth oxide with better photocatalytic activity than NaOH [11]. In addition, this research reported products synthesized using NH<sub>4</sub>OH and NaOH contained  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and a mixture of  $\alpha$ - and  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>, consecutively. Ramli et al. [14] reported a study on the effect of the concentration of NaOH precipitating agent in the synthesis of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. The results indicated that variations in the concentration of NaOH as precipitating agent influenced the formation of crystal nucleation or crystal growth. While research on the effect of variations of NH<sub>4</sub>OH concentration in bismuth

oxide synthesis has never been undertaken till recently. Therefore, this research studies the effect of  $\text{NH}_4\text{OH}$  concentration variation on physicochemical character and photocatalytic activity of resulting products.

## **EXPERIMENT**

### **Material**

The materials used in this study were bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , (Sigma Al-drich), nitric acid ( $\text{HNO}_3$ ) 65% (Merck), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) (Merck), distilled water, and metyl orange (Merck).

### **Bismuth Oxide Synthesis**

5 ml of 65%  $\text{HNO}_3$  was poured into a glass beaker and then added 2.5 gram of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ . The mixture was stirred using the stirrer until the solution became homogeneous. The process continued with the addition of  $\text{NH}_4\text{OH}$  precipitating agent to form precipitate with a pH of 9-10. Then proceed the stirring process for 1 hour at a speed of 667 rpm [15]. The variation of  $\text{NH}_4\text{OH}$  precipitating agent used was 1.5 M, and 2.5 M. The precipitate formed was then filtered and dried at 110 °C for 24 hours in an oven. After that, calcined at 600 °C for 1 hour. After calcination, a pale yellow powder was formed which was then used for further characterization. This procedure followed the procedure reported by Iyyapushpam et al. [16] with a slight modification, namely the variation in the concentration of  $\text{NH}_4\text{OH}$ .

### **Characterization**

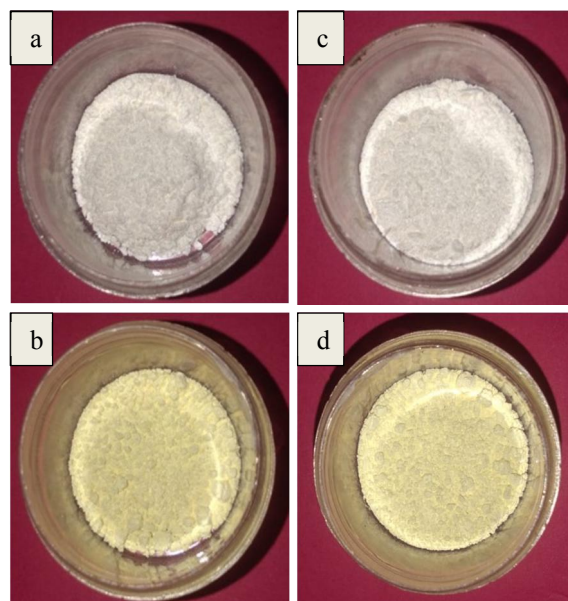
The resulting products were characterized using FTIR, XRD, and DRS-UV. FTIR analysis was applied to determine the functional groups that exist in the products. XRD analysis was undertaken to identify the crystal structure of the resulting products and DRS-UV analysis was performed to determine the band gap of the synthesized material.

### **Photocatalytic Activity Test**

Photocatalytic activity of the resulting products was tested using the previously reported procedure by Astuti et al. [11]. 0.1 gram of bismuth oxide was added to 50 mL of 5 ppm methyl orange (MO). Then it was stirred at medium speed (667 rpm). The variation of time taken was 2 hours without light to find out whether there was an adsorption process or not, 30, 45, 60, 75, 90, and 120 minutes with UV light A. The suspension after the photocatalysis process was then centrifuged at 6000 rpm for 5 minutes to separate the photocatalyst (resulting products) from MO solution. The supernatant concentration was then measured using a UV-Vis spectrophotometer at 463 nm.

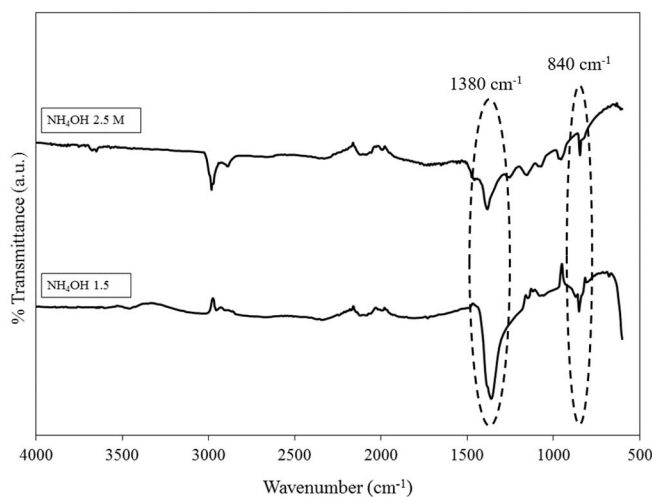
## **RESULT AND DISCUSSION**

Bismuth oxide synthesis by precipitation method using various  $\text{NH}_4\text{OH}$  concentrations in the first step, namely, drying in an oven at 110 °C for 24 hours, the resulting products showed white powder in colour which might be the formation of  $\text{Bi}(\text{OH})_3$  [17] as shown in Fig. 1(a) and Fig. 1(c) for 1.5 M and 2.5 M  $\text{NH}_4\text{OH}$ , respectively. After calcination at 600 °C for 1 hour, the white powder changed color to yellow as seen in Fig. 1(b) and Fig. 1(d). It is assumed that the color change from white to yellow indicated that bismuth oxide was formed.



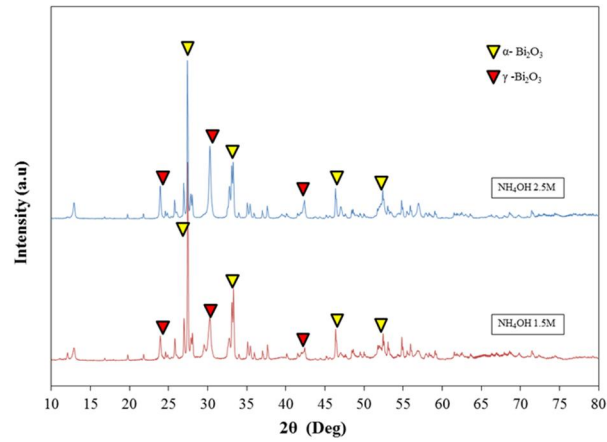
**FIGURE 1.** Resulting products after heating for 24 hours at 110 °C in an oven and calcination at 600 °C for 1 hour using  $\text{NH}_4\text{OH}$  1.5 M (a), (b), and  $\text{NH}_4\text{OH}$  2.5 M (c), (d), respectively.

FTIR spectra presented in Fig. 2 indicate the presence of Bi-O-Bi vibrations as observed at vibration mode around  $840\text{ cm}^{-1}$  (Bartonickova et al., 2007); while at vibration mode around  $1380\text{ cm}^{-1}$  indicated the stretching vibration of Bi-O [18] although in this absorption band some references mention the existence of  $\text{NO}_3^-$  [15].

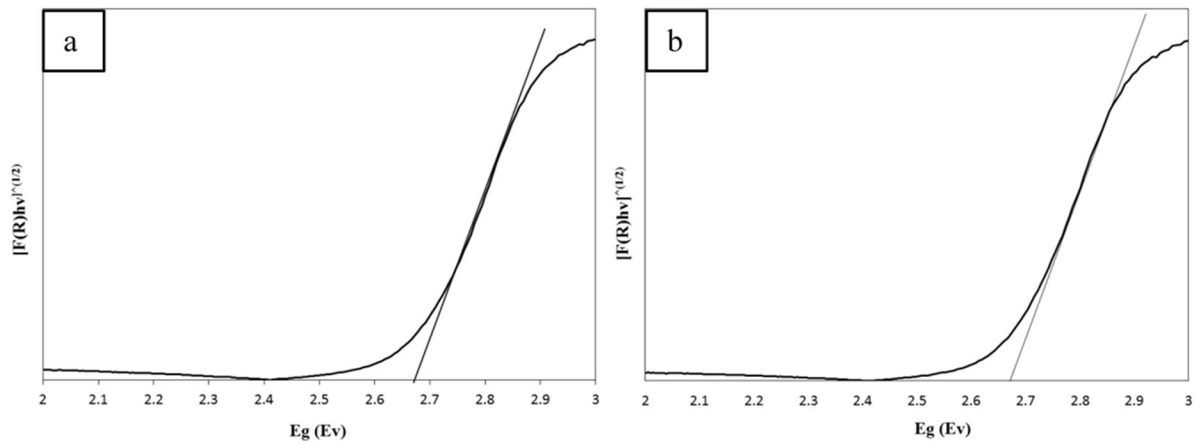


**FIGURE 2.** FTIR spectra of resulting products using various concentrations of  $\text{NH}_4\text{OH}$

Fig. 3 shows the diffractograms of the resulting products synthesized by  $\text{NH}_4\text{OH}$  precipitating agent with a concentration of 1.5 and 2.5M. Both resulting products contain a mixture of the same crystal structure, namely, monoclinic structure ( $\alpha\text{-Bi}_2\text{O}_3$ ) and tetragonal ( $\gamma\text{-Bi}_2\text{O}_3$ ) according to JSPS database no. 41-1449 for  $\alpha\text{-Bi}_2\text{O}_3$  and 45-1344 for  $\gamma\text{-Bi}_2\text{O}_3$ .

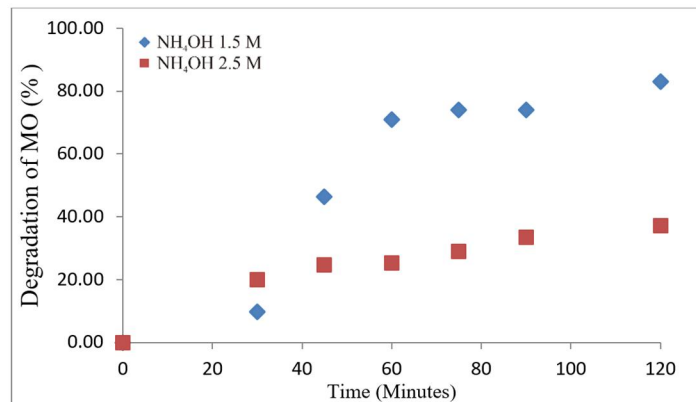


**FIGURE 3.** Diffractograms of resulting products synthesized by  $\text{NH}_4\text{OH}$  with concentrations of 1.5 and 2.5 M



**FIGURE 4.** DRS-UV spectra of resulting products synthesized using  $\text{NH}_4\text{OH}$  with concentration of (a) 1.5 M and (b) 2.5M

The results of DRS-UV analysis of the two products show that the synthesized products with  $\text{NH}_4\text{OH}$  1.5 and 2.5 M have a band gap of 2.65 and 2.67 eV, respectively as shown in Fig. 4(a) and Fig. 4(b).



**FIGURE 5.** Photocatalytic activity of resulting products on MO degradation

Photocatalytic activity of bismuth oxide particles synthesized with variations in concentration of  $\text{NH}_4\text{OH}$  1.5 M and 2.5 M precipitating agents was evaluated by studying the degradation of 5 ppm methyl orange solution under UV light A. Fig. 5 shows photocatalytic activity of bismuth oxide synthesized using different concentration of  $\text{NH}_4\text{OH}$ . The photodegradation of methyl orange by resulting products was undertaken in variations of times, i.e. 30, 45, 60, 75, 90, and 120 minutes. Methyl orange (MO) degradation by bismuth oxide synthesized using  $\text{NH}_4\text{OH}$  1.5 M is higher than that of bismuth oxide synthesized using  $\text{NH}_4\text{OH}$  2.5 M. Therefore, it can be concluded that bismuth oxide synthesized using  $\text{NH}_4\text{OH}$  1.5 M gives better photocatalytic activity compared to  $\text{NH}_4\text{OH}$  2.5 M with percent degradation of 82.98% and 37.23%, respectively for 120 minutes of irradiation.

Kinetic evaluation shows that the rate of MO degradation by synthesized products follows the second-order kinetics model with the equation (1).

$$\frac{1}{ct} = kt + \frac{1}{co} \quad (1)$$

where  $C_0$  is the initial concentration of MO solution,  $C_t$  is the concentration of methyl orange at different times of (t) irradiation, k is the constant rate of MO degradation, and t is the radiation time. Fig. 6 shows a linear plot of  $1/C_t$  vs t. The results of the calculation show that the product synthesized with 1.5 M  $\text{NH}_4\text{OH}$  has a degradation rate constant of  $4.64 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$ ; while with 2.5 M  $\text{NH}_4\text{OH}$  the product has a degradation rate constant of  $2.37 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$ .

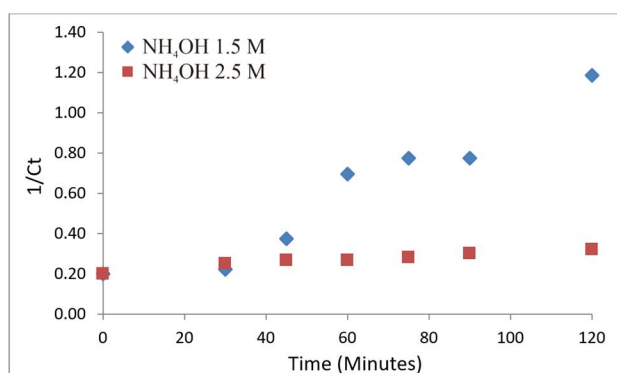


FIGURE 6. First order kinetics of MO degradation rate

## CONCLUSION

The use of variation of weak base concentration ( $\text{NH}_4\text{OH}$ ) as a precipitating agent in the synthesis of bismuth oxide generated the same crystal structure, namely,  $\alpha\text{-Bi}_2\text{O}_3$  and  $\gamma\text{-Bi}_2\text{O}_3$ . The band gap of bismuth oxide produced using 1.5 M  $\text{NH}_4\text{OH}$  is almost the same as that of using 2.5 M  $\text{NH}_4\text{OH}$ . In addition, the photocatalytic activity of  $\text{Bi}_2\text{O}_3$  synthesized using 1.5 M  $\text{NH}_4\text{OH}$  showed better activity in the degradation of methyl orange than  $\text{Bi}_2\text{O}_3$  synthesized using 2.5 M  $\text{NH}_4\text{OH}$  with a degradation rate constant of  $4.46 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$  and  $2.37 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$ , consecutively.

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