

**Synthesis of Photocatalytic  
Bismuth Vanadate (V) for  
Degradation of Organic Dyes**

**EA002**

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## **Abstract**

Bismuth vanadate ( $\text{BiVO}_4$ ) is a promising material for photocatalytic water oxidation. In this study,  $\text{BiVO}_4$  was synthesised using a facile precipitation reaction between bismuth nitrate and ammonium vanadate. Synthesised  $\text{BiVO}_4$  was characterised using X-Ray Diffraction and Scanning Electron Microscopy. Photocatalytic activity of  $\text{BiVO}_4$  was confirmed through a comparison between kinetics set-ups in both dark and light conditions, and a mass spectrometry analysis of degradation residues obtained under both conditions. A mechanism for the degradation of methylene blue dye via N-demethylation was proposed based on the mass spectra of degradation residues. When compared to conventional photocatalysts like zinc oxide ( $\text{ZnO}$ ) and titanium dioxide ( $\text{TiO}_2$ ) in dye removal, both non-calcined  $\text{BiVO}_4$  and  $\text{BiVO}_4$  calcined at  $350^\circ\text{C}$  showed comparable results under ultraviolet light.  $\text{BiVO}_4$  was also determined to have a lower band gap than both  $\text{ZnO}$  and  $\text{TiO}_2$  and is able to harness energy from visible light spectra to degrade dyes. Under visible light irradiation, both non-calcined  $\text{BiVO}_4$  and  $\text{BiVO}_4$  calcined at  $350^\circ\text{C}$  outperformed both  $\text{ZnO}$  and  $\text{TiO}_2$ , removing over 95% of both dyes.

## SSEF Report

### 1. Background and Purpose of Research

With a rapid growth of industries, water pollution becomes an important issue. Dyes and pigments are widely used in the textile, food, plastic cosmetics and paper industries. It is estimated that over 70,000 tonnes of synthetic dyes are produced annually worldwide (Zollinger, 2003). In the textile industry, up to 200,000 tonnes of these dyes are lost to effluents every year during the various operations, due to the inefficiency of the dyeing process (Ogugbue & Sawidis, 2011).

The high solubility of dyes in water results in their wide dissemination into the environment, thus making them detrimental to crops, aquatic life and human health (Zhao et al., 2011). Some dyes are highly toxic and mutagenic, and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation (Chequer et al., 2013). For removal of dyes from industrial wastewater, adsorption has shown to be one of the most effective methods and activated carbon is the preferred adsorbent because of its efficiency, capacity and scalability for commercial usage (Mattson & Mark, 1971). However, adsorption using activated carbon does not degrade the dye and regeneration of dye is difficult (Singh, Sinha, Tondon & Ghosh, 2003). Therefore, a high cost is incurred due to the necessity of disposal and incineration (Schrank, dos Santos, Souza & Souza, 2007).

In recent years, photocatalytic degradation has attracted increasing attention as a cleaner and greener technology for removing toxic organic and inorganic pollutants from wastewater (Parsons, 2004). In particular, semiconductor photocatalysts, such as titanium dioxide ( $\text{TiO}_2$ ), have shown to be an eco-friendly option in degrading organic pollutants and dyes in industrial wastewaters (Fisher & Egerton, 2001).  $\text{TiO}_2$ , under ultraviolet (UV) light, is able to photocatalyse the decomposition of organic pollutants by light-induced electron/hole pairs and highly oxidising OH radicals (Pan et al., 2014). Hence, photocatalysts are able to be employed for the photomineralisation of a large number of dyes such as methylene blue and azo dyes, where the dyes are completely mineralised into simple products such as water and carbon dioxide without generating harmful by-products (Gerischer, 1993). However, photocatalyst such as  $\text{TiO}_2$  is only responsive to UV light which merely accounts for 3% of the energy of the sunlight arriving on the earth's surface (Umabala, Suresh & Prasada, 2016), reducing its effectiveness in a large-scale setting. Therefore, there is a need to develop a facile method for synthesis of a visible-light-driven photocatalyst.

Bismuth vanadate ( $\text{BiVO}_4$ ) is a promising photocatalyst to be used for water purification. Monoclinic  $\text{BiVO}_4$  with a moderate band gap (2.4 eV) exhibits the best photodegradation for pollutants like organic dyes and phenolic compounds under visible light irradiation.  $\text{BiVO}_4$  has been shown to photocatalytically degrade several organic pollutants including 4-nitrophenols, acetophenone and rhodamine-B (Umabala, Suresh & Prasada, 2016). Hence, this study aims to synthesise bismuth vanadate via a simple and facile precipitation method and to investigate its

effectiveness in degrading methylene blue and brilliant green dyes. Methylene blue is a common dye mostly used by industries involved in textile, paper, rubber, plastics, and leather (Mohammed et al., 2014). Brilliant green is extensively being used in textile industry for dyeing nylon, wool, cotton, silk as well as for colouring of oils, fats, waxes, plastics and varnishes. Both dyes are toxic to both humans and animals. Unlike most studies which only focus on degradation of dyes in the presence of visible light, this study compared the removal of dye with and without the presence of visible light through kinetic studies to better understand the mechanism by which bismuth vanadate removes dyes. Finally the performance of bismuth vanadate was compared with conventional photocatalysts TiO<sub>2</sub> and ZnO.

## Hypothesis

Under visible and ultraviolet light irradiation, BiVO<sub>4</sub> is effective in degrading methylene blue and brilliant green dyes, and is comparable with conventional ZnO and TiO<sub>2</sub> photocatalysts.

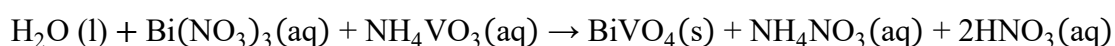
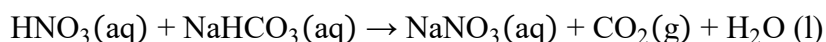
## 2. Materials and Methods

### 2.1 Materials

Bismuth nitrate, ammonium vanadate, brilliant green, titanium dioxide and zinc oxide were purchased from Sigma Aldrich. Methylene blue was procured from Unichem while sodium bicarbonate was procured from GEC Chemicals.

### 2.2 Synthesis of bismuth vanadate (BiVO<sub>4</sub>)

2 mmol of bismuth nitrate and ammonium vanadate were each dissolved in a mixture of 30ml of deionised water and 5ml of concentrated nitric acid. The 2 solutions were then stirred and mixed together before 15g of sodium bicarbonate was added in excess to neutralise the nitric acid and to precipitate BiVO<sub>4</sub>. The neutralisation and precipitation chemical equations are shown below respectively:



The suspension was then heated and stirred at 80°C for 4 hours. After which, the suspension was filtered and washed to neutral to obtain BiVO<sub>4</sub> as the residue. Samples of BiVO<sub>4</sub> were calcined at 350°C in the furnace.

### 2.3 Evaluating effectiveness of BiVO<sub>4</sub> in dye degradation

0.1g of BiVO<sub>4</sub> was dispersed in 25ml of 25 mg/l of dye solution and stirred for 24 hours under visible light by exposing the suspension to 14 W fluorescent tube and in darkness. After which, the final dye concentration was measured using a UV-Vis Spectrophotometer. Methylene blue was analysed at 664 nm while brilliant green was analysed at 623 nm. A control with no BiVO<sub>4</sub> was included in the set up. The experiments were repeated with conventional photocatalysts, ZnO and

TiO<sub>2</sub>, under visible light and UV irradiation (365 nm). The percentage removal of dye was determined using the following formula:

$$Q_d = \frac{C_b - C_a}{C_b} \times 100\%$$

where

$Q_d$  is the percentage of dye removed/%

$C_a$  is the final concentration of dye in mg/l

$C_b$  is the initial concentration of dye in mg/l

## 2.4 Investigating the photocatalytic properties of BiVO<sub>4</sub>

After the degradation experiments were conducted as described in section 2.3, the degradation residues under visible light and dark conditions were analysed by mass spectrometry to compare the degradation products in both samples. A kinetic study was also conducted over a period of 75 minutes with 15-minute intervals to compare the initial rate of dye removal under light and dark conditions.

## 3. Results and discussion

### 3.1 Characterisation of BiVO<sub>4</sub>

#### 3.1.1 By X Ray Diffraction (XRD)

Figure 1 reveals two theta peaks at 19.2°, 29.1°, 35.4° and 47.4°, which are characteristic of monoclinic bismuth vanadate (Samsudin, Sufian, Bashiri, Mohamed & Ramli, 2017), confirming the successful synthesis of BiVO<sub>4</sub>. Similar results were obtained for the calcined BiVO<sub>4</sub>.

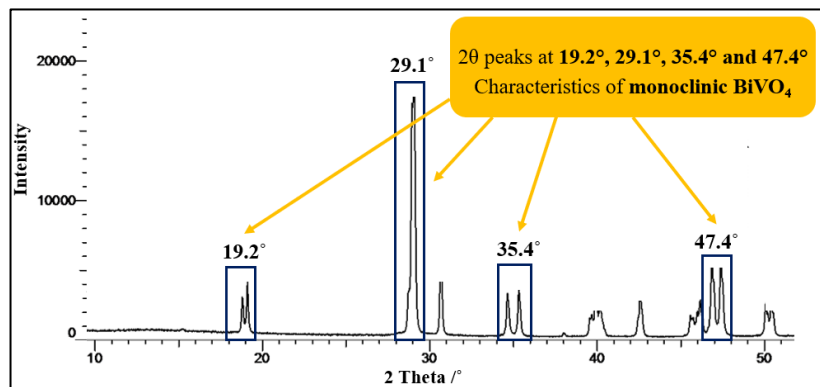


Figure 1: XRD pattern of non-calcined BiVO<sub>4</sub>

#### 3.1.2 By Scanning Electron Microscopy (SEM)

The SEM images of non-calcined and calcined BiVO<sub>4</sub> synthesized are shown in figure 2 where particles with sizes of less than 1 μm are being observed. Slight agglomeration occurred during calcination, resulting in the particle size of calcined BiVO<sub>4</sub> being larger than that of non-calcined BiVO<sub>4</sub>.

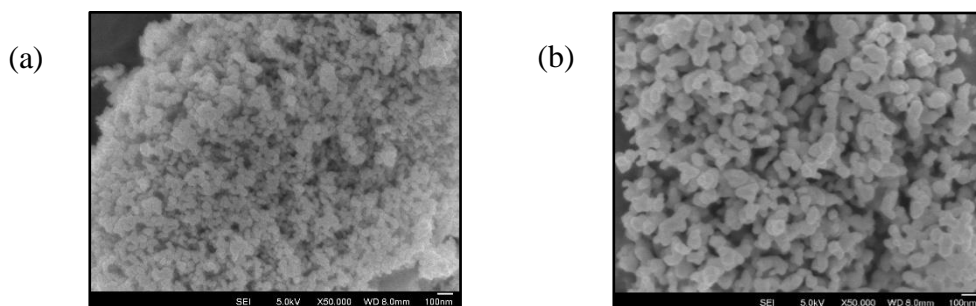


Figure 2: SEM image of (a) non-calcined BiVO<sub>4</sub> (b) calcined BiVO<sub>4</sub>

### 3.2 Removal of dyes by BiVO<sub>4</sub> in dark and light conditions

To investigate the photocatalytic activity of BiVO<sub>4</sub>, dye degradation experiments were conducted under visible light and in darkness (figure 3). Interestingly, in darkness where there is no light, BiVO<sub>4</sub> is also able to remove dye, likely due to adsorption, as the VO<sub>4</sub><sup>3-</sup> could bind to methylene blue and brilliant green, both of which are cationic dyes, through electrostatic attraction. In darkness, non-calcined BiVO<sub>4</sub> is more effective than calcined BiVO<sub>4</sub> in removing the dyes while under visible light, calcined BiVO<sub>4</sub> is more effective than non-calcined BiVO<sub>4</sub>, suggesting that calcined BiVO<sub>4</sub> has greater photocatalytic activity. To investigate if photodegradation had indeed occurred, mass spectrometry analysis was conducted on the degradation residue after the experiments in light and dark conditions.

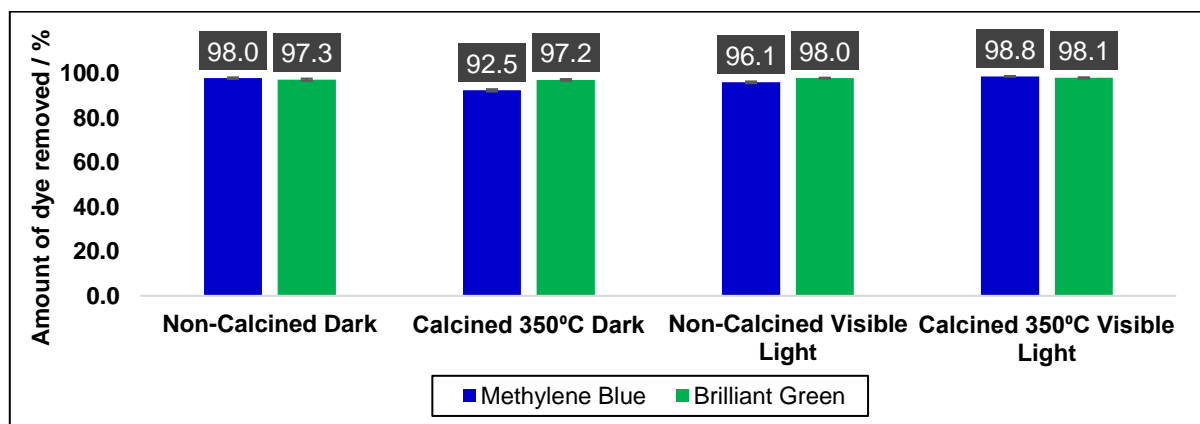


Figure 3: Comparison between amount of dye removed by calcined and non-calcined BiVO<sub>4</sub> in light and dark conditions. N = 5

The mass spectra of degradation residues of methylene blue in visible light and dark conditions are presented in figures 4 and 5 respectively. The intensity of methylene blue at peak 284 is lower in light than in dark condition, suggesting that it had been photodegraded. New peaks that correspond to degradation products in light condition at 242 and 256 were also observed, implying that photodegradation has taken place in light condition. Similar results were reported by Rauf, et al., (2010). Structures of degradation products were identified and shown in figure 6.

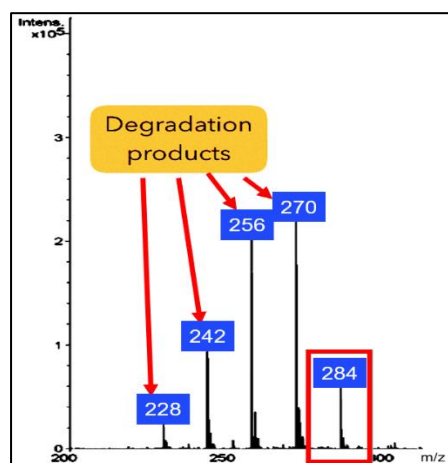


Figure 4: Mass spectrum of degradation residue (calcined BiVO<sub>4</sub>) in light condition

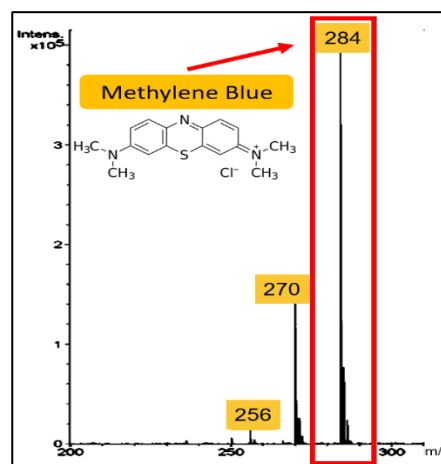


Figure 5: Mass spectrum of degradation residue (calcined BiVO<sub>4</sub>) in dark condition

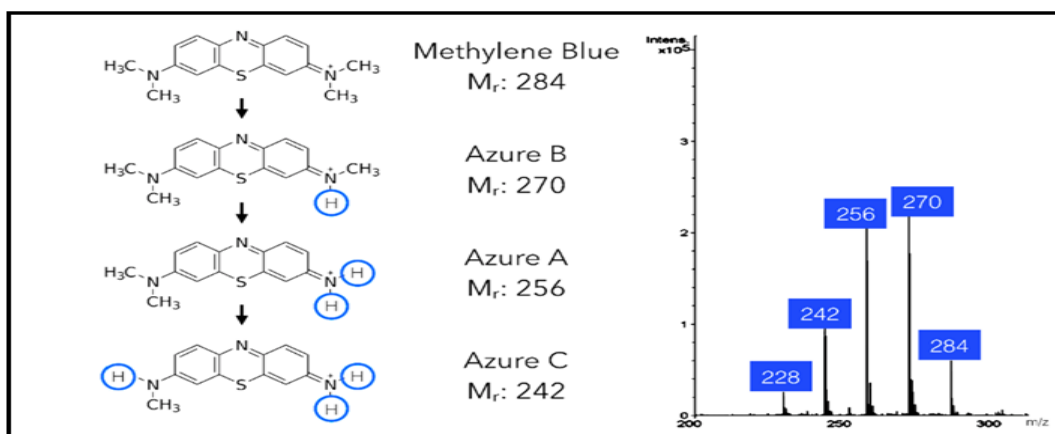


Figure 6: Structure of degradation products under light condition

The mechanism of photodegradation of methylene blue was proposed as shown in Figure 7. When exposed to light, negative-electron ( $e^-$ ) and positive-hole ( $h^+$ ) pair are created in  $\text{BiVO}_4$  (Appendix A, Pg 10). The positive-hole breaks apart water molecules, producing hydroxyl radical ( $\cdot\text{OH}$ ) while the negative-electrons react with water and oxygen to form a hydroperoxyl radical ( $\text{HO}_2\cdot$ ). These radicals attack one of the methyl groups on methylene blue via N-demethylation to form Azure B ( $M_r = 270$ ) and oxygen gas. This process is then repeated to form other degradation products.

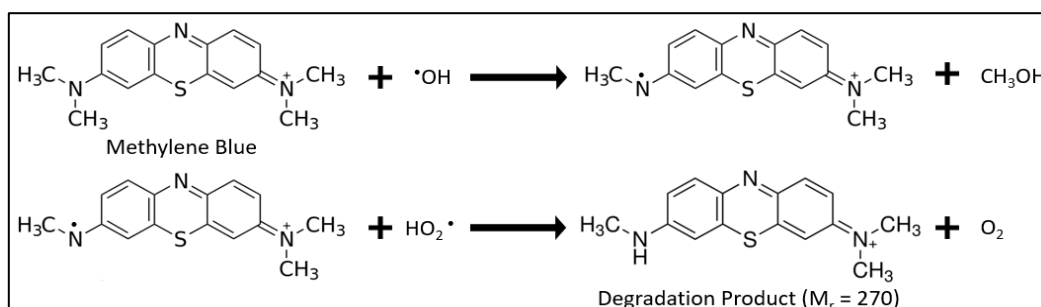
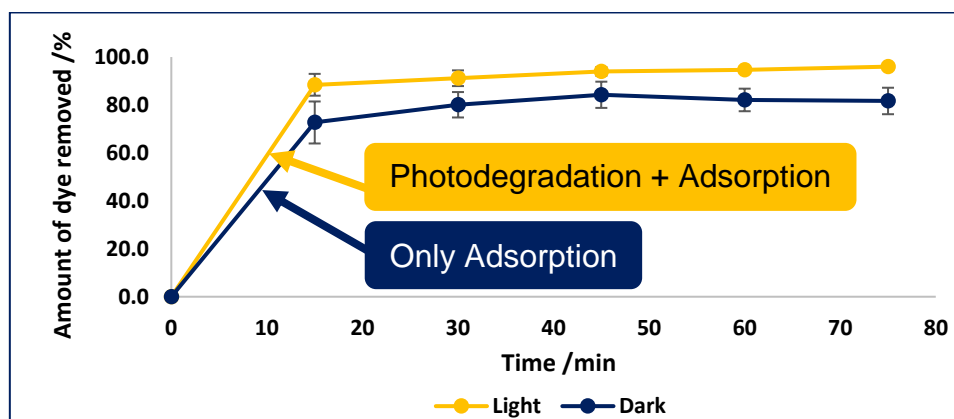


Figure 7: Proposed mechanism of photodegradation of methylene blue

In addition to the mass spectra analysis, kinetics studies were conducted for  $\text{BiVO}_4$  in light and dark conditions for 75 minutes. As seen from Figure 8, the initial rate of dye removal by  $\text{BiVO}_4$  is higher in light than in dark conditions, suggesting that the dyes are removed by photodegradation in addition to adsorption, which agrees with the mass spectra results.

Figure 8: Percentage of methylene blue dye removed by calcined  $\text{BiVO}_4$  in light and dark conditions.  $N=3$

### 3.3 Comparison between $\text{BiVO}_4$ and conventional photocatalysts under UV and visible light

Comparing  $\text{BiVO}_4$  with conventional photocatalysts ( $\text{ZnO}$  and  $\text{TiO}_2$ ) under UV light, both non-calcined and calcined  $\text{BiVO}_4$  were slightly less effective than  $\text{ZnO}$  but significantly more effective than  $\text{TiO}_2$  (Figure 9).

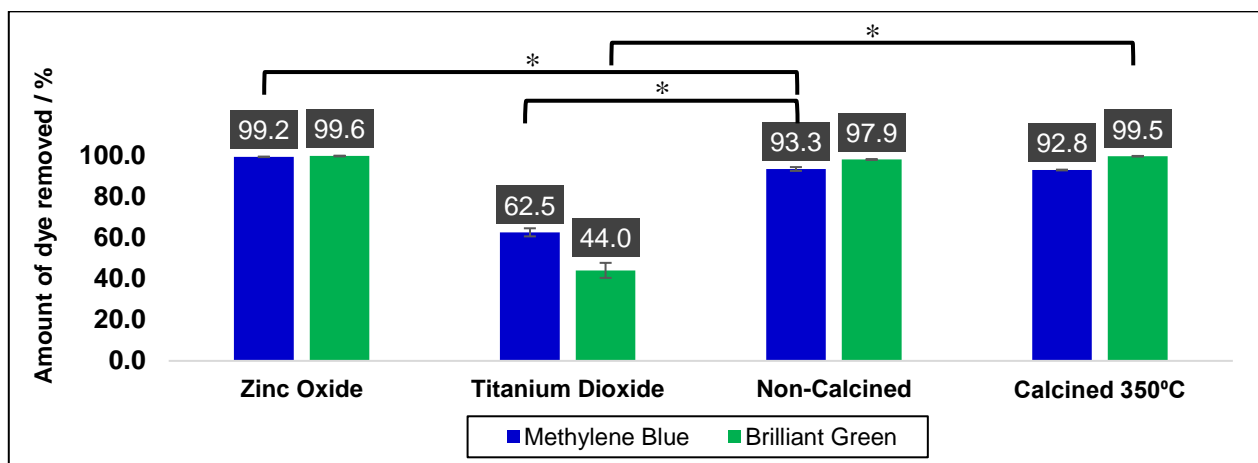


Figure 9: Comparison between percentages of dye removed by different photocatalysts in UV. N=5, \* represents statistical significance based on Mann Whitney U Test at a significance level of 0.05

On the other hand, non-calcined and calcined  $\text{BiVO}_4$  were more effective in removing dyes than both  $\text{ZnO}$  and  $\text{TiO}_2$  under visible light (Figure 10).  $\text{BiVO}_4$  was able to absorb light from both the UV and visible light spectra while conventional photocatalysts could only function effectively in the presence of UV due to their high band gaps. The band gap of  $\text{BiVO}_4$  was determined to be 2.50 eV, which was lower than that of  $\text{ZnO}$  and  $\text{TiO}_2$  which have a band gap of 3.2 eV (Dodd et al., 2009).

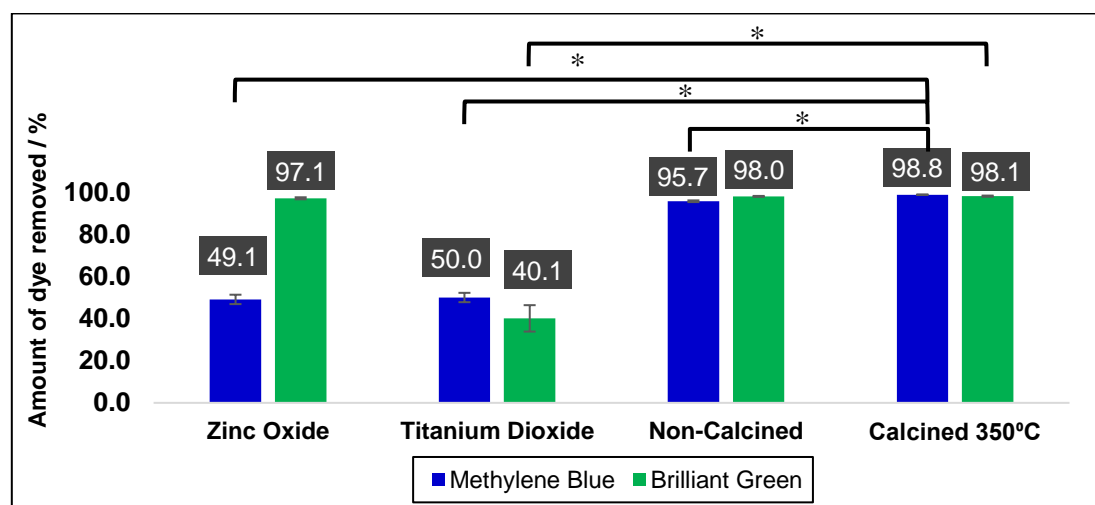


Figure 10: Comparison between percentages of dye removed by different photocatalysts in visible light. N=5, \* represents statistical significance based on Mann Whitney U Test at a significance level of 0.05

Band gap plays an important role in the photocatalytic activity of photocatalysts. As photon energy of visible light ranges from 1.7 to 3.0 eV,  $\text{ZnO}$  and  $\text{TiO}_2$  with band gaps higher than 3.0 eV are unable to harness visible light for photodegradation. In contrast, non-calcined  $\text{BiVO}_4$  and calcined  $\text{BiVO}_4$  have a lower band gap of 2.85 eV and 2.50 eV respectively and were able to absorb visible light to degrade dyes. The band gap of  $\text{BiVO}_4$  was calculated by first determining its adsorption edge



wavelength from its UV-Vis spectrum before substituting it into the Planck-Einstein relation (Figure 11).

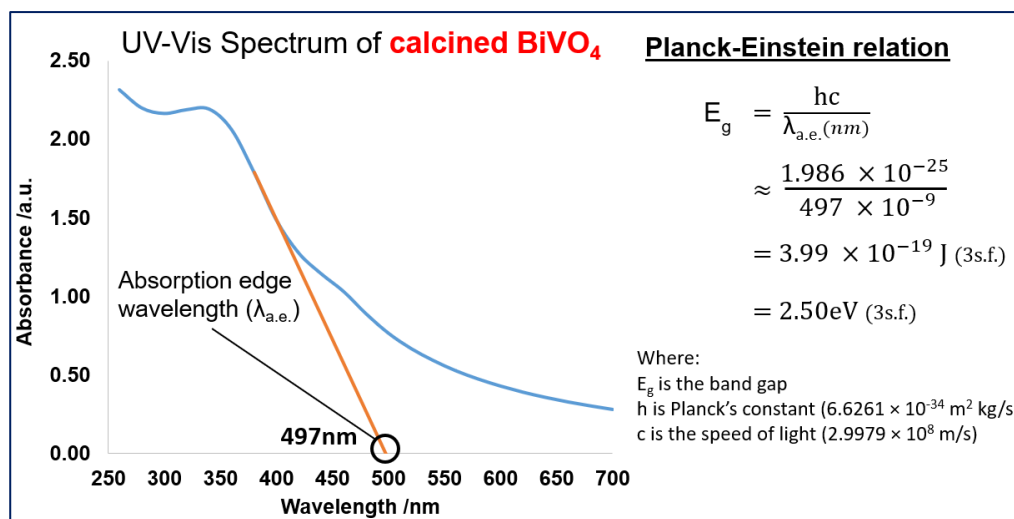


Figure 11: Calculation of optimal band gap ( $E_g$ ) from UV-Vis Spectrum of BiVO<sub>4</sub>

#### 4. Conclusion

BiVO<sub>4</sub> was synthesised through a precipitation reaction between NH<sub>4</sub>VO<sub>3</sub> and Bi(NO<sub>3</sub>)<sub>3</sub>. BiVO<sub>4</sub> has been shown to remove dyes through photodegradation in addition to adsorption under visible light. Methylene blue was degraded via N-demethylation. BiVO<sub>4</sub>, with a lower band gap than ZnO and TiO<sub>2</sub>, was able to effectively degrade dyes under both UV and visible light whereas ZnO and TiO<sub>2</sub> could only effectively degrade dyes under UV light. Hence, BiVO<sub>4</sub> is a promising and potentially cost effective photocatalyst as it could degrade dyes effectively when exposed to visible light.

In the future, BiVO<sub>4</sub> could be coated onto stainless steel meshes as a practical way to remove dyes from wastewater in industries. The proposed prototype, which involves the use of BiVO<sub>4</sub> coated steel mesh, is shown in Figure 12. Other future plans include evaluating the ability of BiVO<sub>4</sub> in degrading other organic pollutants such as pesticides and doping it with transition metals to further lower its band gap.

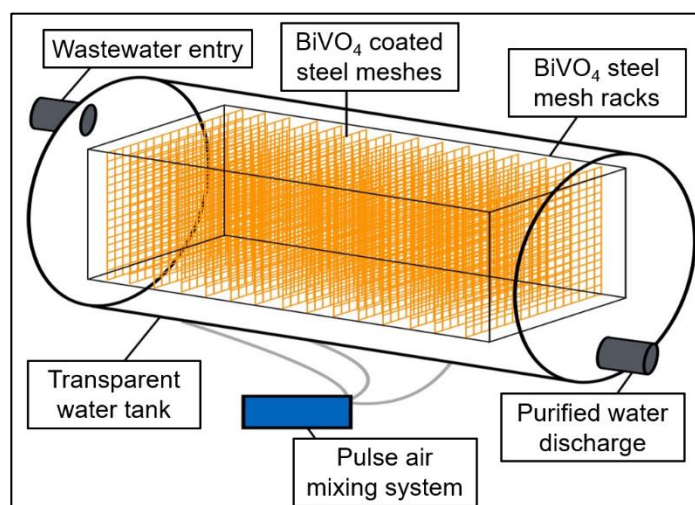


Figure 12: Proposal of how BiVO<sub>4</sub> coated steel meshes can be used to remove dyes in large scale

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**Appendix A: Proposed mechanism of how bismuth vanadate acts as a photocatalyst to degrade methylene blue**

