A Comparison of Five Different Photocatalysts in the Degradation of Methylene Blue Dye

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Abstract: - The photocatalyst such as titanium dioxide(TiO₂), is known for its effectiveness in treating waste from industrial pollutions such as dyes, pesticides and other emerging contaminants. In decades, TiO₂ has attracted attention from worldwide researchers because it is cheap, abundant and stable. In this research, we are trying to find alternative materials that can endeavor better results or at least, identical to TiO₂ in the degradation of methylene blue(MB) dye. The photocatalysts that are in focus would be bismuth compounds which are sodium bismuthate(BiNaO₃), bismuth vanadate(BiVO₄), bismuth titanate(Bi₂O₃・2TiO₂), and bismuth oxide(Bi₂O₃). Degussa P25 TiO₂ is used as a control experiment. For the duration of complete degradation of MB, BiNaO₃ took about 2 hours, BiVO₄ 2 hours and 40 minutes, Bi₂O₃・2TiO₂ 4 hours and 40 minutes, Bi₂O₃ 5 hours, and finally P25 TiO₂ took about 6 hours and 20 minutes. The degradation rate at 120 minutes is as follows : BiNaO₃ (100%) > BiVO₄ (88%) > Bi₂O₃・2TiO₂ (58%) > Bi₂O₃ (56%) > P25 TiO₂ (47%). In conclusion, all of these bismuth compounds are possible to be used in degradation of methylene blue dye and results shows that the degradation rate are relatively faster than TiO₂ for all the bismuth compounds that were used.

Key-Words: - Bi₂O₃・2TiO₂, Bi₂O₃, BiVO₄, BiNaO₃, P25, methylene blue dye, photocatalytic degradation

1 Introduction
In recent years, due to the rise of fashion business, the demand in textile industries has increased. This leads to the growth of waste products and contaminants from textile industries that severely affected water. It does not only present adverse aesthetic coloration, but also contains significant amount of carcinogenic and mutanic organic substances [1,2]. It is estimated to be about 30,000 to 150,000 tons of dyeing materials are being discharged into the environment yearly[3]. Besides being poisonous, these contaminants will also absorb the oxygen amount in the water [4,5].

The conventional treatment of wastewater contaminants are ineffective for removing the dyes since many dye compounds are highly resistant to biological, physical or chemical treatments [3]. There are many kind of methods have been intensively studied, including biological method, chemical coagulation and advanced oxidation process(AOP). The AOP such as the photocatalyst, has been the subject of research for these past few years. The degradation by photocatalytic activity is known to be one of the best method because it uses the visible light or ultraviolet light as irradiating source. It is also capable of mineralizing end product such as CO₂ and NH₃ presence in organic dye molecules, which leads to a complete degradation[6]. The scope for mineralization originates from OH radicals achieved in photocatalytic processes, which distribute many complex organic compounds that is prone to decomposition [1].

In the presence of photocatalyst, the electron hole pairs are formed on the surface of the semiconductor by the irradiation of UV light. Then, the holes with a higher oxidation potential will oxidize the reactive dye. The total reaction between the photocatalyst and the reactive dye could be written as follow [7].

Semiconductor + hv → 
(semic) (e₋B + h₊B) 
(h₊B + dye → dye + (oxidation of the dye) 

In decades, photocatalyst such as TiO₂ has been acknowledge for its effectiveness in treating the contaminants of industries such as dyes and
pesticides. In this research, we are trying to find alternative materials that can endeavor better results or at least, identical to TiO$_2$ in the degradation of methylene blue (MB) dye.

Bismuth has been proven to be suitable in the degradation of contaminants by photocatalysis. This is because bismuth compound has appropriate band gap besides it is stable and environmental friendly. Therefore, we are focusing on the bismuth compounds which are sodium bismuthate (BiNaO$_3$), bismuth vanadate (BiVO$_4$), bismuth titanate (Bi$_2$O$_3$・2TiO$_2$), and bismuth oxide (Bi$_2$O$_3$). Degussa P25 TiO$_2$ is used as a control experiment.

As for the dye contaminants, we chose methylene blue (MB), C$_{16}$H$_{18}$N$_3$SCl dye. This is because MB dye is mainly used in textile industries for acrylic, nylon, silk and wool dyeing which can cause allergic dermatitis, skin irritation in direct contact, and give rise to short-term rapid of difficult breathing upon inhale. Therefore, the degradation of MB in wastewaters has attracted attention of researchers from this field. The chemical structure of MB dye is shown in Fig.1 and the maximum wavelength of this dye is 663nm.

Fig.1 The chemical structure of methylene blue dye

2 Experimental Procedure

2.1 Materials
For this experiment, we used aqueous solution of methylene blue (MB), BiNaO$_3$ powder (Wako Pure Chemical Industries), BiVO$_4$ (Alfa Aesar), Bi$_2$O$_3$ powder (Wako Pure Chemical Industries), Bi$_2$O$_3$・2TiO$_2$ (Wako Pure Chemical Industries) and P25 TiO$_2$.

2.2 Photomineralization Procedures
4mL of methylene blue solution was placed in a 100mL Pyrex vessel. Then, 96mL of ultrapure water was added to the aqueous solution. After that, 0.3g of compound powder (BiNaO$_3$, BiVO$_4$, Bi$_2$O$_3$, Bi$_2$O$_3$・2TiO$_2$, P25) was added for each experiment. The experiments were conducted under the presence of visible light (λ > 400nm) and the solution was magnetically stirred to ensure uniformity. The samples were then filtered by using syringe membrane filter to remove the photocatalyst particles. Samples were taken from the solution for every 20 minutes and were put inside a UV-Vis spectrophotometer cell in order to measure the maximum absorption of wavelength for the dye and the rate of degradation.

3 Results and Discussion
In this study, we are focusing on the photocatalytic evaluation by studying the rate of absorbance over time (Fig.2), the rate of degradation over time (Fig.3), the rate of degradation at 120 minutes (Fig.4) and finally the kinetic rate of MB degradation by 5 different photocatalysts (Fig.5).

Among all of these five photocatalysts, the degradation rate of BiNaO$_3$ shows huge difference at 20 minutes reading and 40 minutes reading (Fig.2). This is because BiNaO$_3$ has a high photocatalytic performance which attribute to the strong visible light absorption ability and the rapid mobility of
photo-generated electrons [8]. Therefore, it contribute to a higher rate of degradation of MB dye, which is 100% degradation at a shorter time of 120 minutes (Fig.3).

Besides BiNaO₃, BiVO₄ (band gap of 2.4eV) generates holes (h⁺) in valence band (VB) when exposed to visible light will eject photogenerated electrons (e⁻) from VB to conduction-band (CB). These photogenerated holes can react with adsorbed water on the surface of the BiVO₄ nanoparticles to generate highly reactive hydroxyl radical (OH⁻). On the other hand, O₂ acts as an electron acceptor to form a superoxide anion radical (O²⁻) that can act as an oxidizing agent or as an additional source of OH⁻. The presence of these reactive radicals contribute to the strong oxidizing ability which results in a shorter time of MB dye degradation into non-toxic organic compounds compared to the other three photocatalysts [9].

Furthermore, Bi₂O₃ which has the band gap of 2.58-2.85eV, has been proven to be suitable for decomposition of dye contaminants [10-11]. However, it took almost 5 hours to undergo complete degradation and only degrade 56% at 120 minutes when compared to BiNaO₃ which is 100% (Fig.4). This is because it has quick recombination of photo-generated charge carriers which decreased the photocatalytic performance of Bi₂O₃ [10,12].

TiO₂ has a large band gap of 3.2eV. When TiO₂ is combine with Bi₂O₃, the band gap is minimize, and the absorption spectra is enlarge. The structure formed from the combination will effectively encourage separation of photogenerated charge carriers and the absorption wavelength to the visible region is broaden. The electrons (e⁻) in the valence band (VB) of Bi₂O₃ were excited to its conduction band (CB), so the VB of Bi₂O₃ was rendered partially vacant [10,13] and the electrons in the VB of TiO₂ could be transferred to the VB of Bi₂O₃. As a result, holes (h⁺) were generated in the VB of TiO₂, and this results in the trapping of charge carriers, which react as oxidation–reduction centers for generation of hydroxyl and superoxide radicals from adsorbed water and oxygen, respectively [16].

The kinetic study of MB degradation for BiNaO₃, BiVO₄, Bi₂O₃ • 2TiO₂, Bi₂O₃ and P25 TiO₂ was also investigated. The result shows that a plot of −ln(c/c₀) versus time (Fig.5) has the linear correlation coefficients (R) of ca. 0.8938, 0.8352, 0.8712, 0.8429 and 0.7704 respectively. The degradation of MB was observed as a function of irradiation time and it can be concluded that it follow the first-order kinetics.

\[ \ln[C] = -kt + \ln[C]_0 \]  

where C and C₀ are the concentration of pollutant at irradiation time 0 and t, k is a first-order rate constant (min⁻¹) and t is the irradiation time (min). The rate constants were calculated to be 0.75, 0.28, 0.23, 0.21 and 0.26 h⁻¹.

![Fig.4 The degradation rate at 120 minutes for five different photocatalyst](image)

![Fig.5 MB degradation rate kinetics for five different photocatalysts](image)

**4 Conclusion**

In this study, we can conclude that all of these bismuth compounds have the potential to be used as the photocatalyst in the degradation of dye contaminants. For a complete degradation of methylene blue, BiNaO₃ took about 2 hours, BiVO₄ 2 hours and 40 minutes, Bi₂O₃ 5 hours, Bi₂O₃ • 2TiO₂ 4 hours and 40 minutes and finally P25 TiO₂ took about 6 hours and 20 minutes. The degradation rate at 120 minutes is as follows: BiNaO₃ (100%) > BiVO₄ (88%) > Bi₂O₃ • 2TiO₂ (58%) > Bi₂O₃ (56%) > P25 TiO₂ (47%).

As a conclusion, sodium bismuthate, BiNaO₃ is one of the best photocatalyst to be used in degrading the MB dye since it can undergoes almost 100%
degradation in only two hours. With further study, the time for a complete degradation can be reduced and the possible usage of bismuth compounds as better photocatalyst alternative can be applied to treat other industrial pollutants.

References: