A BASIC STUDY ON THE ORGANIC DYE DEGRADATION BY BINAO3PHOTOCATALYST

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Abstract- Organic degradation by photocatalyst has proven to beone of the best ways to overcome environmental pollution problems. This is because it is low in cost and has high efficiency. Besides, it is easy to employ. In this study, we are conducting a research on other possible materials and their optimum condition that can aid in the organic degradation of dyes, besides the titanium dioxide (TiO_2) which is already widely used in treating and degrading the dyes, pesticides and other organic contaminants. Based on the previous study, the bismuth sodium trioxide ($BiNaO_3$) is one of the best photocatalyst in degradation of the dye. Therefore, we further our study in finding the optimum condition for the $BiNaO_3$ in order to have a higher degradation efficiency. The methylene blue (MB) and methyl orange (MO) dye was used as the organic dyes and the experiment was conducted under three different pH conditions (pH 3, 7, 11) with and without the presence of visible light. The result shows that the bismuth sodium trioxide work best under the acidic (pH 3) condition, with the presence of visible light for both dyes. As for the methyl orange (MO) dye, bismuth sodium trioxide took a longer time in degrading the dye compared to the methylene blue (MB) dye. It took only 20 minutes to degrade the methylene blue dye under the presence or without the presence of visible light condition. For the methyl orange (MO) dye degradation, it took about 60 minutes to degrade with the presence of visible light. As a conclusion, bismuth sodium trioxide under acidic solution has been proven as one of the possible photocatalyst in the treatment of the dyes contaminants.

Index Terms- $BiNaO_3$, environmental friendly, methylene blue dye, methyl orange dye, organic degradation, photocatalytic degradation, visible light.

I. INTRODUCTION

The environmental pollution, especially the industrial waste contaminants has been a critical subject in the environmental study in recent years. There are a lot of methods that had been proposed and studied, to overcome these problems. The advanced oxidation process (AOP) such as the photocatalytic degradation is one of the promising methods in treating the contaminants.

Photocatalysis functions like the natural photosynthesis (Fig.1). It uses the visible light or ultraviolet light as irradiating source which capable of mineralizing end product such as CO_2 and NH_3 that exist in the contaminants and leads to a complete degradation [1]. The scope for mineralization originates from ・OH radicals that is produced in the photocatalytic processes, which distribute many complex organic compounds that is prone todecomposition [2].

The photocatalyst will aid in the forming of electron hole pairs on the surface of thesemiconductor by the irradiation of visible light. Then, the holes with a higher oxidation potential state will oxidize the reactive dye.
The photocatalytic degradation efficiency can be affected by many parameters such as the pH, temperature, type of semiconductors, pollutant concentration and other [3].
Bismuth has been proven to be suitable in the degradation of contaminants by photocatalysis. This is because bismuth compound has appropriate band gap. In addition, it is stable and environmental friendly. Based on the previous study [4], it shows that bismuth sodium trioxide ($BiNaO_3$) is the best photocatalyst and has high rate of degradation compared to the other four photocatalysts which are the bismuth vanadate ($BiVO_4$), bismuth (III) oxide (Bi_2O_3), bismuth titanate(Bi_2O_3 ・ $2TiO_2$) and titanium dioxide P25 (TiO_2).

In this study, we are trying to find an optimum condition for the bismuth sodium trioxide by creating three different pH conditions which are the acidic condition (pH 3), neutral condition (pH 7) and alkaline condition (pH 11), with and without the presence of visible light.

As for the dye contaminants, we have chosen two dyes, which are the methylene blue (MB) dye, and the methyl orange (MO) dye. Both of these dyes were chosen because it is one of the frequently used dyes in the industries. The MB dye and MO dye has the chemical structure of $C_{16}H_{18}N_3SCl$ and $C_{14}H_{14}N_3NaO_3S$ each. The chemical structure of MB dye and MO dye is shown in Fig.2 and Fig.3. In addition, MB dye and MO dye has the maximum wavelength of 663nm and 464nm respectively.

II. EXPERIMENTAL PROCEDURE

A. Materials

For this experiment, we used aqueous solution of methylene blue (MB) and methyl orange (MO) with

the concentration of 40mg/100mL and the bismuth sodium trioxide ($BiNaO_3$) powder (Wako Pure Chemical Industries) hydrochloric acid (HCl) solution (Wako Pure Chemical Industries) and sodium hydroxide (NaOH) pallet (Wako Pure Chemical Industries).

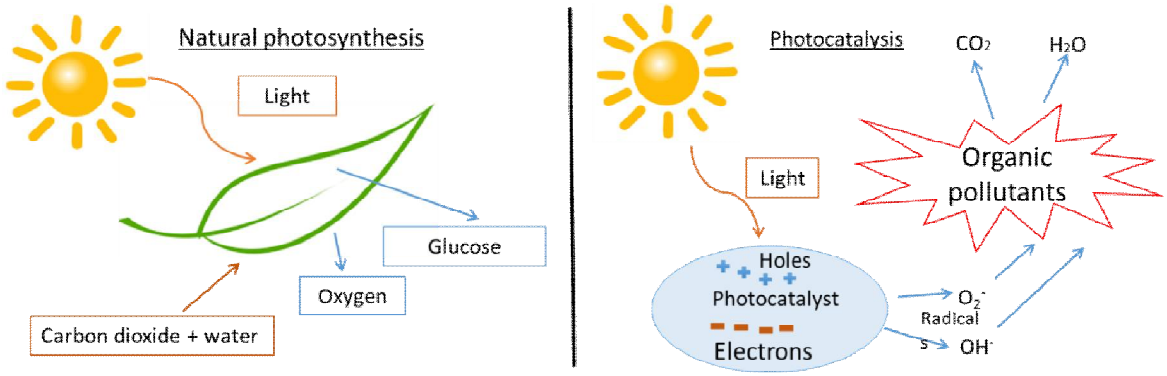

Fig.1 The natural photosynthesis and photocatalysis

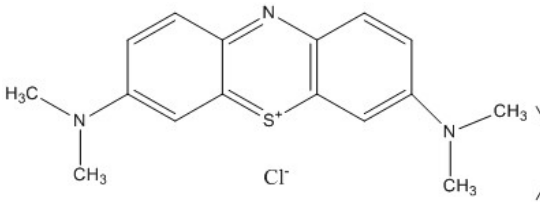

Fig.2 The chemical structure of methylene blue dye

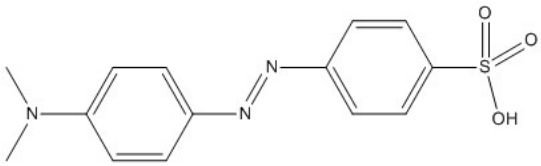

Fig.3 The chemical structure of methyl orange dye

B. 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 for a neutral condition (pH 7). For acidic condition (pH 3), 0.1mL of HCl was added to 95.9mL of ultrapure water, and for the alkaline condition (pH 11) 0.4mL of NaOH solution was added to 95.6mL of ultrapure water. After that, 0.3g of compound powder $BiNaO_3$ was added for each experiment. The experiments were conducted under the presence of visible light (λ> 400nm) and without the presence of light. 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 placed inside a visible-Vis spectrophotometer cell in order to measure the maximum absorption of wavelength for the dye and the rate of degradation.

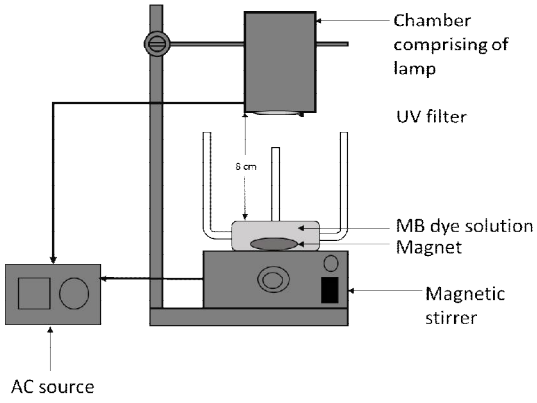

Fig. 4Photomineralization Experiment Setup

III. RESULTS AND DISCUSSION

In this study, we are going to discuss based on the rate of absorbance, rate of degradation and the time required for a complete degradation. The rate of absorbance may be differ based on the type of the dye used, the conditions and the type of photocatalyst used.

In the MB dyes degradation experiment, the result is as shown in Fig.5. From the graph, we can conclude that the rate of absorbance for $BiNaO_3$ is best under pH 3, followed by pH 7 and pH 11, under the presence or without the presence of visible light.

For the MO dye, the result is shown in Fig. 6. It shows that for MO dye, it took a longer time to degrade compared to the MB dye. With the presence of visible light, the optimum degradation pH is as follows; pH 3, pH 7 and pH 11. However, in pH 11, the dye almost does not degraded at all without the presence of visible light.

As for the rate of degradation, the time for MB and MO dye to undergo a complete degradation is different. This might be influenced by the chemical structure of each of the dye. From the results in Fig.7 and Fig.8, the MB dye can be degraded faster than the MO dye.

The time taken for the degradation of the MB dye was only 40 minutes with the presence of light, and 60 minutes without the presence of light, at pH 3. At pH 7, it took about 120 minutes with the presence of light and 140 minutes without the presence of light and at pH 11, it took about 80 minutes with the presence of light, and

more than 180 minutes without the presence of light. On the other hand, for the MO dye degradation, in acidic condition, it took about 60 minutes to degrade about 100% with the aid of the visible light. It took more than 60 minutes without the presence of the visible light. In a neutral condition (pH 7), it took about 200 minutes with the presence of visible light, and more than 200 minutes without

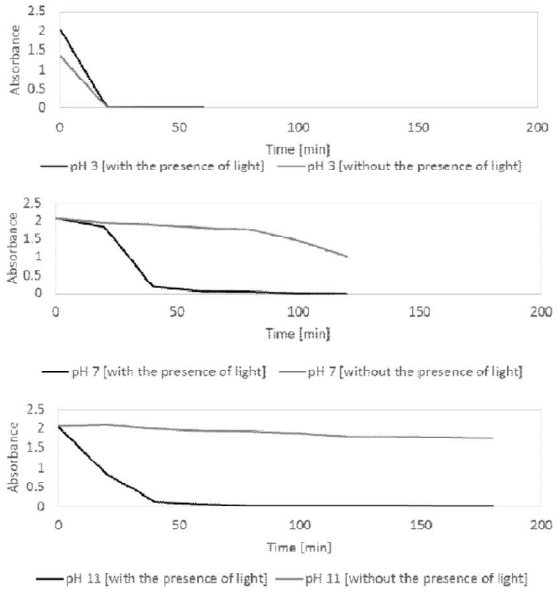

Fig.5 The absorbance over time for methylene blue (MB) dye under pH 3, 7 and 11 with and without the presence of light

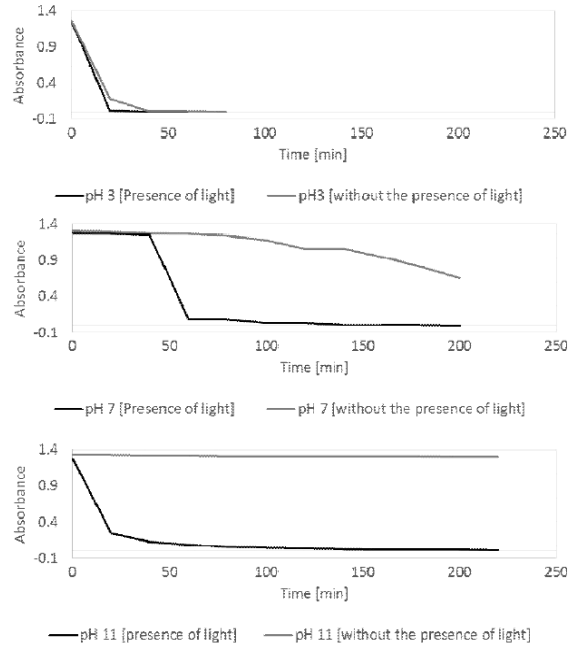

Fig.6 The absorbance over time for methyl orange (MO) dye under pH 3, 7 and 11 with and without the presence of light

the presence of visible light. In addition, for pH 11, it took about 220 minutes to completely degrade the MO dye under visible light, and only degraded about 2% within 220 minutes without the presence of visible light.

The results achieved are influence by the pH value of the experiment condition. This is because, in a low pH value (acidic condition, which in this study is pH 3), the hydroxyl radicals can be formed by the reaction between the hydroxide ions and the positive holes. Furthermore, the positive holes presence are considered as the major oxidation. However, in a neutral (pH 7) or high pH value

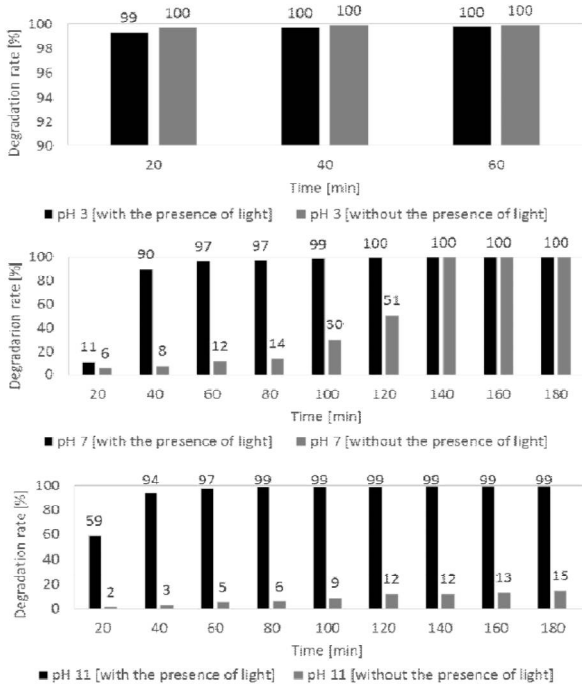

Fig.7 The rate of degradation over time for methylene blue (MB) dye under pH 3, 7 and 11 with and without the presence of light

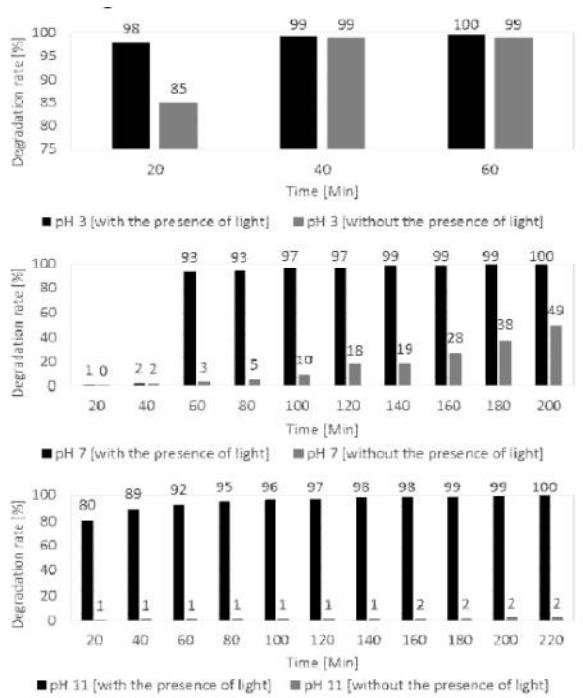

Fig.8 The rate of degradation over time for methyl orange (MO) dye under pH 3, 7 and 11 with and without the presence of light (alkaline condition, pH 11), hydroxyl radicals are considered as the potent species [5].

It has been reported in previous study that the alkaline

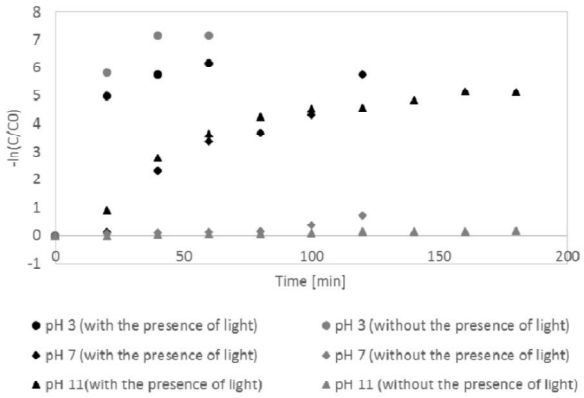

Fig.9 The kinetic study of methylene blue (MB) dye under pH 3, 7 and 11 with and without the presence of light

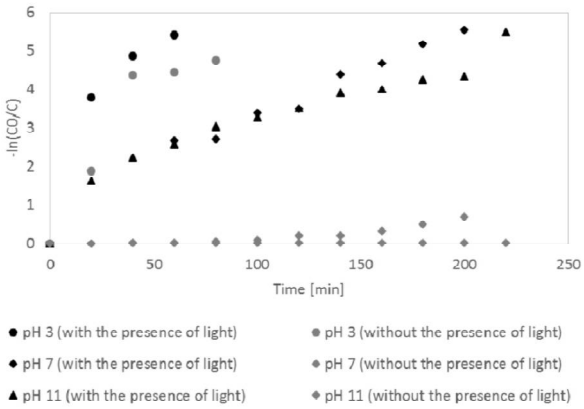

Fig.10 The kinetic study of methyl orange (MO) dye under pH 3, 7 and 11 with and without the presence of light

condition, has a higher probability of the hydroxyl radical (•OH) formation, which is an oxidant. Therefore, it increasesthe efficiency of the degradation of the dye [6]. But, there is also a Coulombic repulsion between the negative charged surface of photocatalyst and the hydroxide anions which can prevent the formation of •OH and thus decrease the photooxidation [7], which leads on why it took a longer time to degrade the MO dye in the alkaline condition.

The kinetic study of MB and MO dye degradation for $BiNaO_3$ was also studied. The result shows that a plot of $-\ln (c/c_0)$ versus time(Fig.9 and Fig.10) has the linear correlation coefficients (R) of ca. 0.6494, 0.951 and 0.6969 with the presence of light and 0.6382, 0.7221 and 0.9447without the presence of light for MB dye. In addition, for MO dye degradation, it has the the ca. 0.7721, 0.9301, and 0.7283 with the presence of light and 0.8002, 0.745, 0.7075 without the presence of light. The degradation of MB and MO dye were observed as a function of irradiation time.It can be concluded that both degradation in all conditions follow the first-order kinetics.

$$\ln [C] = -kt + \ln [C]_0 \quad (1)$$

C and C_0 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 0.1249, 0.047 and 0.0361 min^{-1} with the presence of light for MB dye and 0.1488, 0.004 and 0.0009 min^{-1} without the presence of light. On the other hand, the rate of constant for MO dye degradation with the presence of light is as follows:- 0.1062, 0.0295 and 0.0261 min^{-1}while without the presence of light is as follows:- 0.0717, 0.0022 and 0.0001 min^{-1}.

CONCLUSION

In this study, we can conclude that the bismuth sodium trioxide work best under the acidic (pH 3) condition, with the presence of visible light for both dyes. However, in the degradation of MO dye, it took a longer time compared to the degradation of methylene blue (MB) dye, which is only 20 minutes to degrade the MB dye under the presence of visible light condition.

As a conclusion, bismuth sodium trioxide under acidic solution has been proven as one of the possible photocatalyst in the treatment of the dyes contaminants. With further study, we believe that the usage of the bismuth sodium trioxide as a wide-range organic contaminant degrader can be achieved.

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