PREPARATION OF COPPER-DOPED TiO_2 PHOTOCATALYST FOR DYE DEGRADATION UNDER UV LIGHT (EFFECT ON INCUBATION TEMPERATURE)

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Abstract— **The objective of this study was to investigate the preparation of hybrid CuO/TiO_2 photocatalyst by using wet impregnation method at different incubation temperature. The physical characterization of the photocatalyst was performed using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), Field Emission Scanning Electron Microscope (FESEM) and Brunauer-Emmett-Teller (BET). The photocatalytic activity of Methyl Orange was analyzed by determine the percentage degradation of Methyl Orange under uv light irradiation. The observed results of photocatalytic activity suggest that the incubation temperature of 50 °C is the optimum as the percentage degradation is the highest which is 82.06 %. From the characterization analysis, the copper elements cannot be detected in XRD analysis. The anatase peak at 2 θ show only TiO_2 peak after incorporated with different incubation temperature. In the EDX analysis, the CuO can be detected in the EDX mapping for hybrid CuO/TiO_2 photocatalyst, before and after degradation. The surface area of hybrid CuO/TiO_2 photocatalyst, before and after degradation are higher than bare TiO_2 which are 8.8137 m^2/g and 9.7521 m^2/g while for bare TiO_2 is 2.0801 m^2/g. Among the incubation temperature, the photocatalyts that synthesized at 50 °C has the best uv light response and the highest photodegradation activity.**

Keywords— Degradation of Methyl Orange, Hybrid photocatalyst, Photocatalyst activity, Titanium dioxide, UV light, Wet impregnation method.

I. INTRODUCTION

Water plays an important role in providing and assisting human to a better and complete life. As the large portion of earth's surface covered by the water and only less than a third covered by land (M. Khraisheh et. al., 2012), water is essential to sufficiently provided in order to enhance human life as well as for the healthy growth of agriculture such as farm crops and farm stock. As the populations continues to grow, the water resources become one of the main problem, exclaiming to the serious concern of the water used and the efficiency of the water which might affects the human daily life or versa. The water from manufacturing industry always become the reason of water quality degradation that cause by the unclean water released which contained impurity chemical.

Besides, there are many other reasons to the changes in water quality including the increasing in nutrient loading from organic waste such as sewage and farm waste, industry discharged, construction sites and forestry. In order to treat and prevent the problem from developing into the serious level, there are a number of options available today for water disinfection and treatment including the traditional process for water waste treatment, chlorination, ozonation, iodine treatment, ultraviolet (UV) treatment and boiling treatment. (M. Khraisheh et. al., 2012) However, there is limitation from the options as some of the process, especially the traditional process are not sufficient anymore to purify the highly contaminated water. (M. Khairy et. al., 2014) One of the downside of this problem is the production of more concentrated pollutant-containing phase.

Among the options available for these problem, the direct ultraviolet (UV) treatment has gained interest worldwide due to the UV's effectiveness in inactivating protozoa and its lack of production of treatment byproducts. (R. E. Kalan et. al.,2016) This treatment which include the photocatalysis technique (M. Khairy et. al.,2014) were conducted using titanium dioxide, TiO_2 which known as a highly efficient photocatalyst, cheap and nontoxic to human and has been extensively applied for degradation of photodegradation of organic pollutant. The heterogeneous photocatalysis process which occur in reactive properties of electron hole pairs generated in the semiconductor particle with the presence of light has appeared as an emerging destructive technology leading to the total mineralization of the most organic contaminant. (M. Khairy et. al., 2014)

There are many researches conducted on using titanium dioxide as photocatalyst in photodegradation process. Titanium dioxide has large surface area which offer the reaction rate of photocatalytic reaction when contacted to pollutant molecules. It is an oxide-based semiconductor photocatalyst (Olga M. Ishchenko et. al., 2016) which acts as sensitizers for light-reduce redox process due to their electronic structure, which characterized by a filled valence band and empty conduction band. (M. R. Hoffmann et. al., 1995) Based on the researched conducted by J. A. Cha et. al. (2012), the doped-TiO_2 photocatalyst can achieved the maximum photodegradation efficiency of 99 % and 92 % for UV and visible light respectively under optimum condition.

Despite its ability to react and degrade the pollution in water efficiently, the research has be re-establish by modifying the photocatalyst by doping and hybrid it with various transition metal elements such as Cu, Cr, Co, Fe, Mo, V and W. (A. Di Paola et. al., 2002) The doped-TiO_2 photocatalyst proved to be more efficient than the un-doped TiO_2 photocatalyst. Although titanium dioxide is the most used and popular photocatalyst, some researcher reported that the recombination rate of the electron-hole pairs increased for doped titanium with respect to un-doped titanium dioxide. (A. Di Paola et. al., 2002) The TiO_2-based semiconductor photocatalyst lack a continuum of interband states to assist the recombination of electron hole-pairs in order to assure the sufficiently long period of $e^- - h^+$ pair to diffuse to the catalyst's surface and eventually initiate a redox reaction. (Y. Nosaka et. al., 1998) Thus, the titanium dioxide photocatalyst need to modify as doped-TiO_2 photocatalyst in order to increase and to enhance the photocatalytic activities by reduce the band gap of the photocatalyst because titanium dioxide has wide band gap which limit the light fraction during the photodegradation process. (Y. Chong et. al., 2007)

The other factor need to be investigate in order to increase the efficiency of the photocatalytic activity is the effect of incubation temperature during the preparation process. The incubation

temperature is believed to affect the introduction of metals onto the titanium dioxide's surface as well as the structure of the photocatalyst. The optimum incubation temperature is well determined in this research as well as the photodegradation efficiency.

II. METHODOLOGY

A. Materials

All the chemical reagents used were of analytical grade and were utilized without further purification. The materials used are; titanium dioxide TiO_2 (80 % anatase), copper (II) acetate $CuAc_2$ (99.99 % traces metals basis), sodium hydroxide NaOH (0.25 M), methyl orange MO and hydrochloric acid HCl (37 % solution in water). The distilled water was used throughout all the experiments.

B. Preparation of Hybrid CuO/TiO_2 Photocatalyst With Different Incubation Temperature.

1 g of hybrid CuO/TiO_2 photocatalyst was prepared using wet impregnation method as follows. 0.984 g of TiO_2 powder and 0.016 g of $CuAc_2$ were dissolved into 50 mL of distilled water. The solution was stirred for 1 hour at 90 °C. Next, NaOH was added into the solution after 1 hour and stirred again for 2 hours at incubation temperature of 90 °C. The solution was washed using distilled water and filtered to get the solid phase of the mixture. The mixture is dried in an oven at 105 °C for 24 hours before calcined at 450 °C for 2 hours. The procedures were repeated using different incubation temperature which are room temperature (RT), 50 and 70 °C. Fig. 1 show the experimental set-up of the preparation of hybrid photocatalyst.

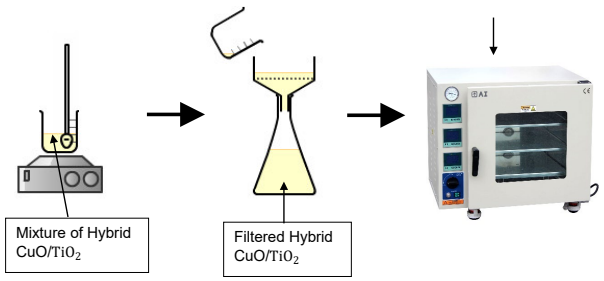


Fig. 1 : The experimental set-up of preparation process.

C. Characterization Methods.

The x-ray diffraction (XRD) analysis was performed in order to determine the pattern of the photocatalyst. The samples were measured at room temperature in the range from $2\theta = 20$ to 90 °.

The morphology of the photocatalyst was examined using energy-dispersive x-ray spectroscopy (EDX) which provide the mapping and the distribution of the copper, oxygen and titanium dioxide elements. The energy graph of the samples also plotted during the analysis.

The surface area of the fresh and used catalyst, the cumulative surface area and volume of pores were determined using Brunauer-Emmett-Teller (BET) analysis. Nitrogen gas was used as the adsorbate in the analysis with the analysis temperature of 90 °C.

D. Photodegradation of Methyl Orange Under UV Light

0.8 g of hybrid CuO/TiO_2 photocatalyst powder was weighted using electrical scale balance. The catalyst was then dispersed into 200 mL of 10 ppm Methyl Orange. The solution was stirred in a dark place for 15 minutes in order to reach the adsorption equilibrium at the surface of the photocatalyst. After 15 minutes, the solution was irradiated under UV light for 180 minute with vigorous stirring and aeration process.

The samples were took for every 15 minutes for the first hour, 30 minutes for the second hour and next after one hour for the third hour. All the samples were analyzed using UV-Vis Spectromenter and the degradation percentage were obtained using the calibration curve. The calculation of the percentage degradation are as follow:

$$\left(\frac{C_o - C}{C_o}\right) \times 100\% \qquad \text{(Eq. 1)}$$

Where C_o is the initial concentration of the Methyl Orange, and C is the concentration of Methyl Orange at time t. The experiments were repeated using the samples from different incubation temperature. Fig. 2 show the experimental set-up of the photocatalytic activity of the hybrid photocatalyst.

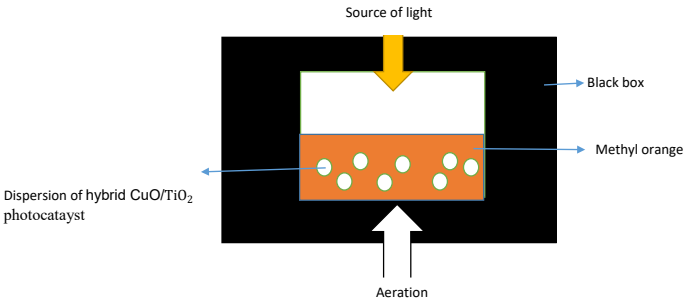


Fig. 2 : The experimental set-up of the photocatalytic activity.

E. The Overall Process Flow Diagram

All the process of this experiments can be interpret into the overall process flow diagram as in Fig. 3.

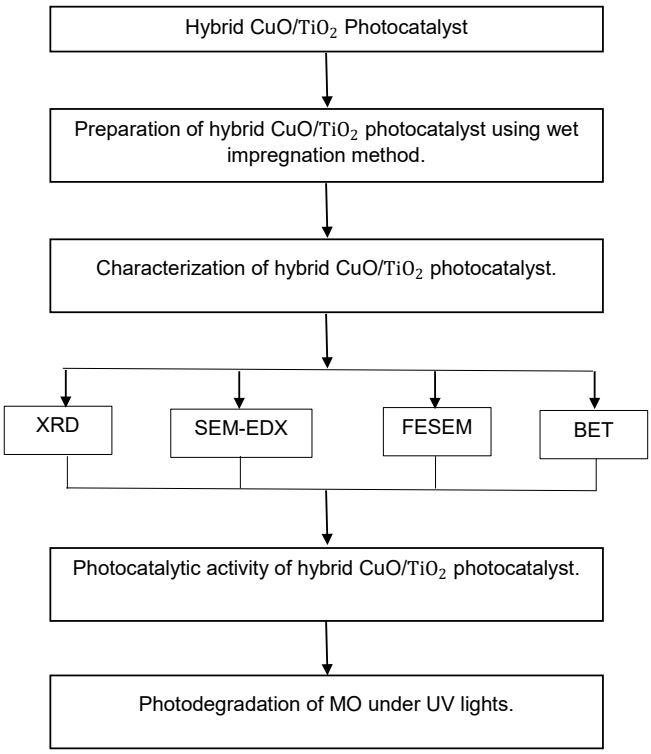


Fig. 3 : The overall process of the experiment.

F. Kinetic Model of Adsorption

The kinetic study on the photocatalytic reaction of hybrid CuO/TiO_2 photocatalyst with Methyl Orange under illumination can be explained using pseudo-first kinetic model. This kinetic model is assumed to characterize the photocatalytic degradation rate for most organic compounds. (I. Bouzaida et. al, 2004; E. Bizani et. al., 2006) The pseudo-first kinetic model can be explained in the Eq. 2 below:

$$-\frac{dC}{dt} = k_{app}C \qquad \text{(Eq. 2)}$$

Integration of the kinetic model equation under condition of **C** = C_o and **t = 0**, will lead to the expected equation in Eq. 3.

$$\ln\left(\frac{C_o}{C}\right) = k_{app}t \qquad \text{(Eq. 3)}$$

Where k_{app} is the apparent rate constant, **t** is the reaction time, C_o is the initial concentration at t=0 and **C** is the concentration at time **t**. The value of k_{app} can be determine from the slop of the graph plotted between $\ln\left(\frac{C_o}{C}\right)$ and the reaction time, **t**.

From the pseudo-first kinetic model in Eq. 3.1, the half-life time can be calculated using the following expression:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \qquad \text{(Eq.4)}$$

III. RESULTS AND DISCUSSION

A. Characterization of Photocatalyst

The hybrid CuO/TiO_2 photocatalyst was prepared by wet impregnation at different incubation temperature which are room temperature (RT), 50 °C, 70 °C and 90 °C. In order to characterize the photocatalyst, all the samples were undergo four characterization analysis which are XRD, EDX, FESEM and BET.

i. XRD

X-ray diffractogram was used to investigate the crystallinity of the material used and also to detect the copper element in hybrid photocatalyst during the impregnation process. Fig. 4 show the XRD pattern of the hybrid CuO/TiO_2 photocatalyst at different incubation temperature. The samples were scanned in 2 θ range between 20° to 90° with Cu K radiation (λ=1.5418). The pattern of the samples were compared to the anatase data which is JCPDS 00-021-1272.

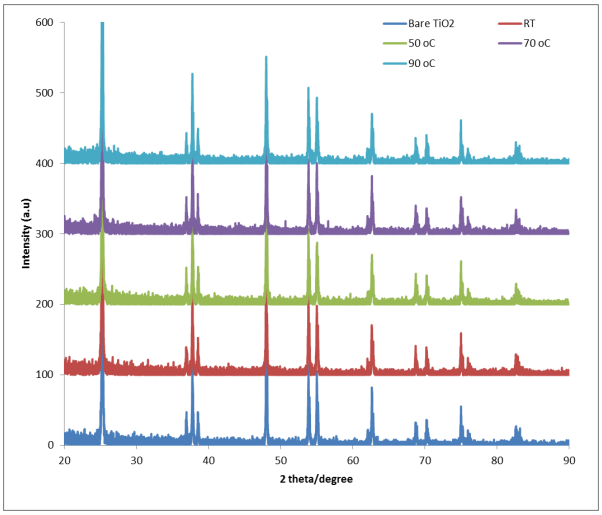
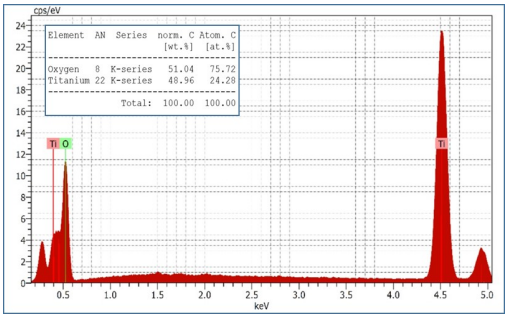


Fig. 4 : XRD pattern of the photocatalyst at different incubation temperature.

Based on the XRD pattern in Fig. 4, there was no significant change between Bare TiO_2 photocatalyst and the hybrid CuO/TiO_2 photocatalyst. After incorporated at different incubation temperature, the XRD results show the anatase peak at 2 θ, assigned as (101), (004), (200), (105), (211), (204), (116), (220), (215) and (224). The observation shows that there were no additional peaks which indicated that there were no copper element traces in the catalyst. It was assumed that copper might be not completely incorporated into the titanium element during the wet impregnation process. The crystallinity of the catalyst might not change as there were no evidence of the incorporation. However, at plane (101), the intensity of the samples were different to each other. The hybrid photocatalyst at room temperature has the highest intensity which 552 a.u. compared to Bare TiO_2, incubation temperature of 50 °C, 70 °C and 90 °C which were 415 a.u, 521 a.u, 489 a.u and 514 a.u, respectively.

ii. EDX Analysis

To further confirm the existence of copper element in the hybrid CuO/TiO_2 photocatalyst, the EDX analysis was performed for the sample with optimum incubation temperature which is 50 °C. The samples powder were tested for photocatalyst before degradation and after degradation. The samples from Bare TiO_2 also being tested as to analyze the differences between doped and un-doped photocatalyst. Fig. 5 show the energy graph of doped and un-doped photocatalyst, before and after degradation.



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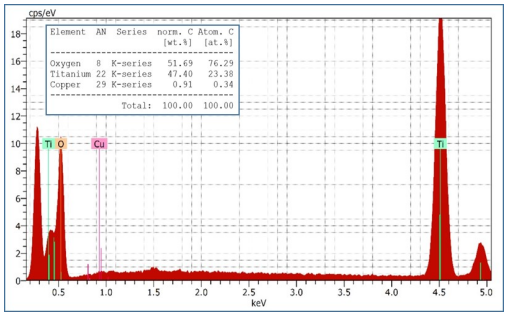

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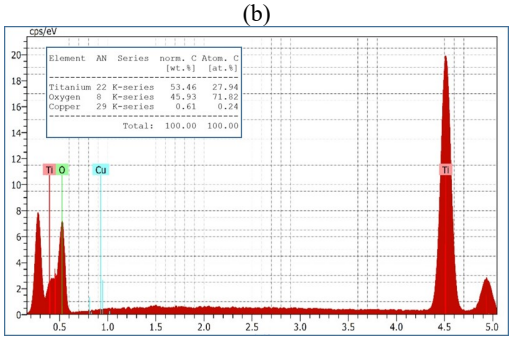

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Fig.5 : The energy graph of (a) bare TiO_2 , (b) CuO/TiO_2 photocatalyst before degradation and (c) CuO/TiO_2 photocatalyst after degradation.

Table 1 : The EDX data of photocatalyst.

Sample	Norm. C (Wt %)		
	Ti	O	Cu
Bare TiO_2	48.96	51.04	-
Cu/TiO_2 (Before)	47.40	51.69	0.91
Cu/TiO_2 (After)	53.46	45.93	0.61

Fig. 5 and Table 1 show the distribution of oxygen, titanium and copper element on the surface of the catalyst. The oxygen and titanium were detected for all the samples tested as both were originated from the same elements which is TiO_2. The bare TiO_2 consist of 51.04 % of oxygen and 48.96 % by weight of titanium. The TiO_2 peak was observed at 4.512 eV and for oxygen at 5.20 eV. This results were matched with theoretical energy table as in Fig. 6. After incorporated with copper elements, there was 0.91 % by weight of copper element detected on in the photocatalyst. The copper peak was detected around 8 to 9.5 eV which almost accurate as the theoretical energy table. This proved that the wet impregnation method was successfully performed as the copper element was perfectly introduced. After photodegradation process, the photocatalyst used was being analyzed in order to observe the changes of copper elements in the catalyst. Based on the EDX results, the amount of copper elements decreased from 0.91 wt % to 0.61 wt %. This is because the copper elements might be deposited in the filter membrane during filtration process.

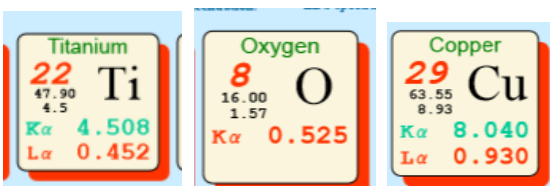


Fig.6 : The theoretical energy data of titanium, oxygen and copper elements. (Retrieved from JEOL : http://www.jeol.com)

The EDX data can be further analyzed using the EDX mapping as in Fig. 7 and Fig. 8. The distribution of oxygen, titanium and copper elements were clearly represented in the EDX mapping. From Fig. 7, the oxygen and titanium elements were well distributed in the bare TiO_2 photocatalyst as the oxygen elements were conquering the surface of the photocatalyst. The copper elements in Fig. 8 (a) and Fig. 8 (b) were represented using pink color and blue color, respectively. The differences between the EDX mapping for both samples can be observed as the copper elements for samples of after degradation in Fig. 7 (b) were barely seen compared to samples of after degradation in Fig. 7 (a). Thus show that, the copper elements were decreased after undergo degradation process.

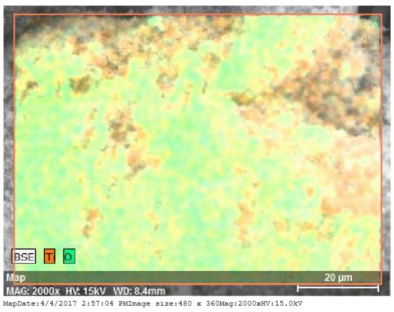
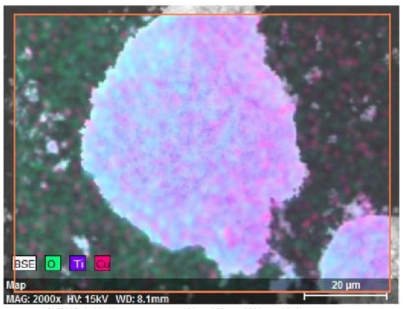


Fig. 7: The EDX mapping for Bare TiO_2.



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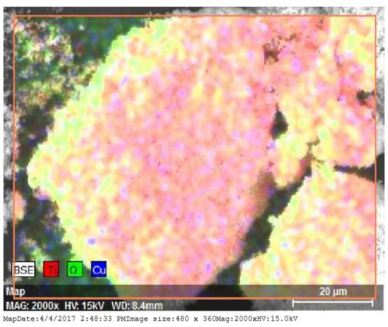


(b)

Fig. 8: The EDX mapping for hybrid CuO/TiO_2 photocatalyst (a)before degradation and (b) after degradation.

iii. FESEM-BET Analysis

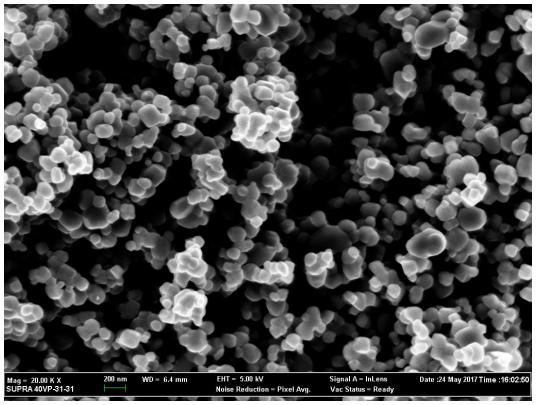
Fig. 9 and 10 show the FESEM images of bare TiO_2 and hybrid CuO/TiO_2 photocatalyst at incubation temperature of 50 °C, respectively. Clearly, the particles of bare TiO_2 photocatalyst samples were in spherical and square-like shape with various sizes which were dominance with the smaller size. The FESEM images in Fig. 10 show the particle shape for the hybrid CuO/TiO_2 photocatalyst were mostly in round or spherical shape with various sizes. This probably caused by the type of precursor used which is copper acetate. Based on the FESEM images, the copper elements were successfully incorporated with TiO_2. The observations were consistent with EDX mapping that show the evidence of copper elements.

To further analyze the specific surface area of the catalyst, the

BET analysis were conducted. The BET analysis explained the physical adsorption of nitrogen on a solid surface for an important technique for the measurement of specific surface area. It can be observed from Table 2 that bare TiO_2 has a rather low BET specific surface area (2.0801 m^2/g). Upon the incorporation with copper element, it can be seen that the BET specific surface area of the hybrid CuO/TiO_2 photocatalyst showed an increment for both before and after degradation (8.8137 and 9.7521 m^2/g). Besides, the pore surface area and volume also increase as well as the BET specific surface area. It is assumed that the copper elements were perfectly diffused into the TiO_2.

Table 2: BET specific surface area and BJH cumulative surface area and volume of pores.

Characterization	Bare TiO_2	Before Degradation	After Degradation
BET surface area (m^2/g)	2.0801	8.8137	9.7521
BJH desorption of cumulative surface area of pores (m^2/g)	3.2823	7.6988	8.3594
BJH desorption of cumulative volume of pores (cm^3/g)	0.006210	0.032336	0.037714



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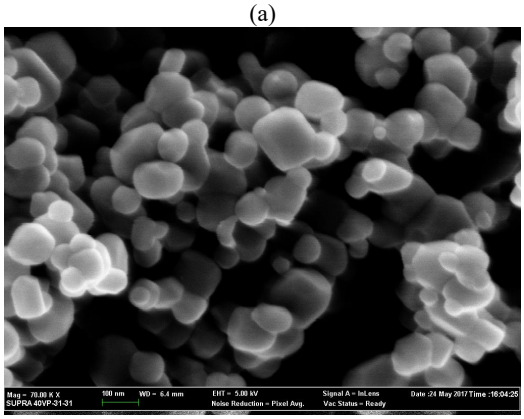

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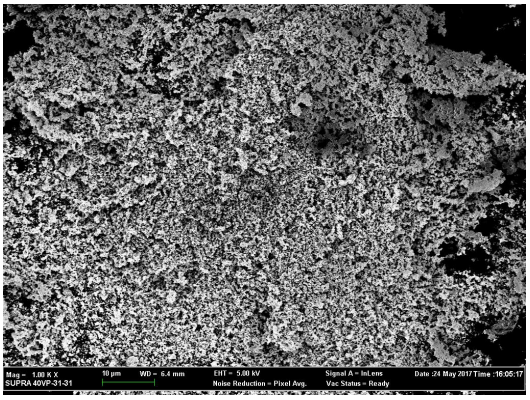

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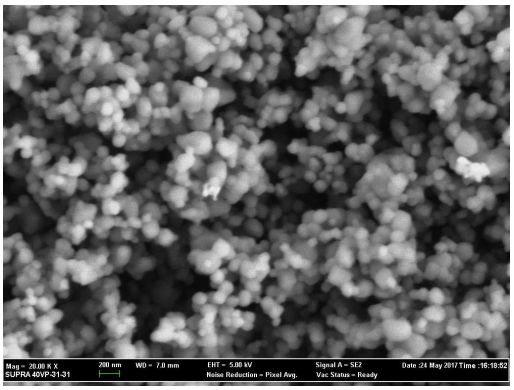
Fig. 9: FESEM images of Bare TiO_2 with different particle sizes.



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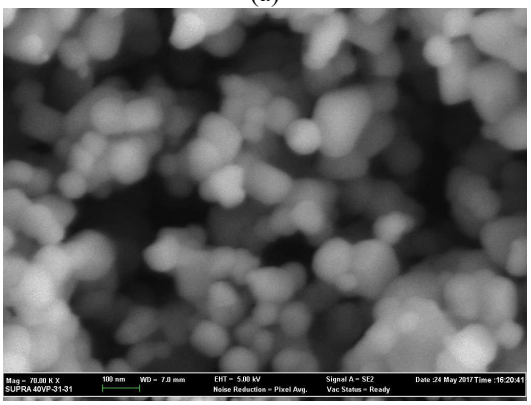

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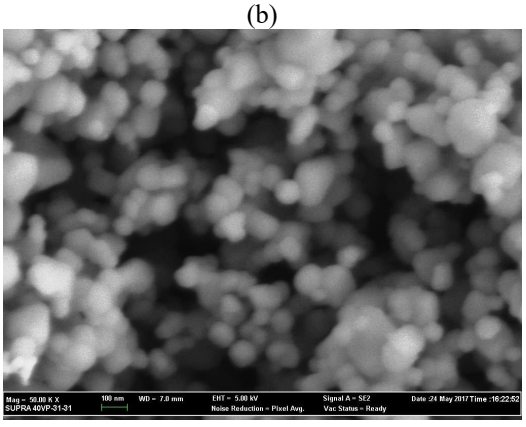

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Figure 10: FESEM images of hybrid CuO/TiO_2 photocatalyst .

B. Photocatalytic Activity

i. Control Test

Control test was conducted to study and observed the photocatalytic activities of the photocatalyst towards Methyl Orange. There were two set of control tests were carried on which are photolysis and adsorption experiments. The degradation of Methyl Orange can be observe from Fig. 11. Photolysis is the degradation of Methyl Orange with the absence of photocatalyst while adsorption is the degradation of Methyl Orange without the presence of UV light. Based on the graph in Fig. 11, the photocatalyst reaction show the rapidly increase of percentage degradation compared to other process. This is because, the photocatalyst help to increase the degradation efficiency as well as to increase the rate of reaction.

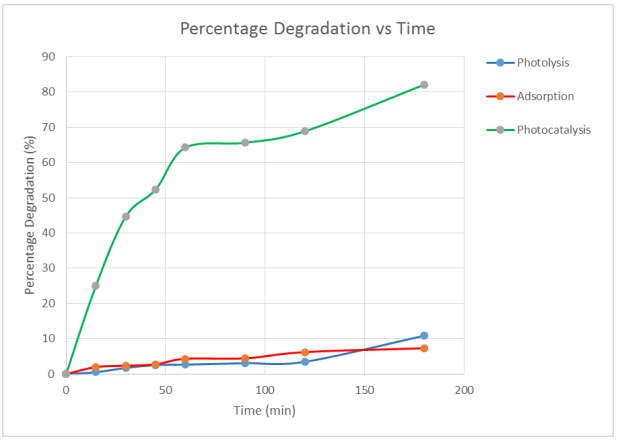

Fig. 11: Percentage degradation against the reaction time.

ii. Application of Hybrid CuO/TiO_2 Photocatalyst In Methyl Orange Degradation.

The study was conducted to observe the degradation of Methyl Orange at different incubation temperature which are room temperature (RT), 50 °C, 70 °C, and 90 °C. Table 3 show the percentage degradation of hybrid photocatalyst at different incubation temperature. From the table, it can be observed that incubation temperature at 50 °C has the highest percentage of degradation which 82.06 % while for room temperature, 70 °C and 90 °C were 45.96 %, 49.17 % and 45.67 %, respectively.

By using the calibration curve at Fig. 12, the concentration of the samples can be calculated and the degradation percentage of Methyl Orange can be obtained. Based on the BET specific surface area, the hybrid photocatalyst at 50 °C of incubation temperature has the larger surface area and larger cumulative surface area and volume of pores. This is because the larger surface area and increased of pore volumes provide more interfacial area for the reaction to occur.

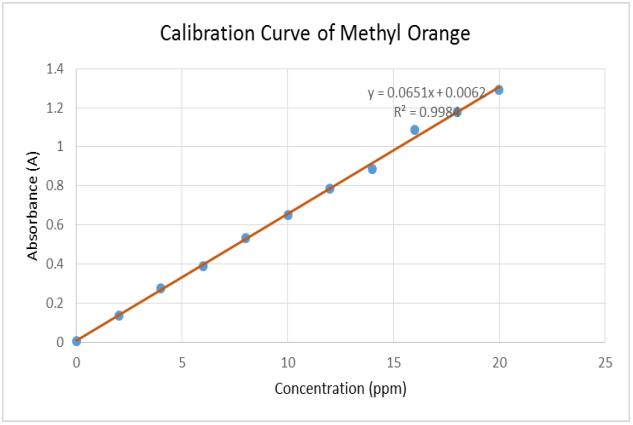

Fig. 12 : Calibration curve of Methyl Orange

Table 3: Percentage of degradation at different incubation temperature.

Incubation Temperature (°C)	Percentage of Degradation (%)
RT	45.96
50	82.06
70	49.17
90	45.67

The phtocatalytic activity of Methyl Orange can also be observed via the color changes from the beginning to the end of UV light exposure. The Methyl Orange was originally in orange color with the pH value around 4 to 4.5. However, in order to increase the surface tension of the solution, a few drops of HCl were added into Methyl Orange solution which decreased the pH value to 3. This results in change of color from orange to light pink which indicated that the solutions were in acidic state.

After few hours exposed to the UV light, the color of Methyl Orange slowly change into yellowish color. This show that the photocatalytic reactions were occur which degrade the Methyl Orange with the helpful of photocatalyst.

C. Kinetic Model of Adsorption

The kinetic model of adsorption used in this experiment is pseudo-first order. Fig. 13 show the pseudo-first order of the photocatalytic activity and Table 4 show the K-value and the R^2 value of the kinetic model. Based on the Fig. 13 and Table 4, the optimum incubation temperature which is 50 °C has the highest K-value (0.0107) but lowest R^2 value (0.8172). The K-value of room temperature, 70 °C and 90 °C of incubation temperature were 0.0036, 0.0043 and 0.0038, respectively. The R^2 value of calibration curve is 0.9984 which is slightly higher than the optimum incubation temperature.

The half-life time of photocatalysis process was 64.78 minutes which is the shortest compared to other photocatalyst. The half-life time can be calculated using K-value obtained from pseudo-first order of kinetic model. As conclusion, the optimum incubation temperature reported for this experiments was 50 °C which has the highest percentage degradation and the shortest half-life time.

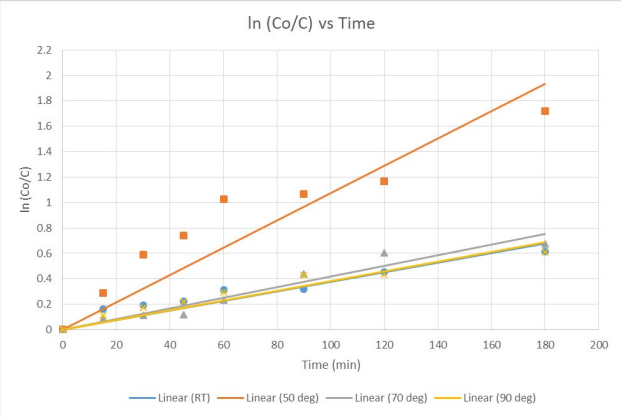

Fig. 13 : The pseudo-first order of the photocatalytic activities.

IV. Conclusion

Incubation temperature of 50 °C has been proven as the optimum incubation temperature for the preparation of hybrid CuO/TiO_2 photocatalyst. The samples are characterized using XRD, EDX, FESEM and BET analysis in order to study and observed the physical and chemical difference between each samples. The samples with different incubation temperature is firstly analyzed using XRD, however, there is no copper traces founded in the results. The characterization is continued with EDX, FESEM and BET analysis. From the analysis, the copper can be founded as the mapping of EDX and the FESEM images analysis show the distribution of the copper and titanium elements. The FESEM images show that the shape of the particles are changed to spherical only shape. For BET analysis, the BET surface area, the BJH desorption surface area and volume of pores are increase from Bare TiO_2 to hybrid CuO/TiO_2 for before and after degradation, respectively. For photocatalytic activity, the optimum incubation temperature obtained the higher degradation percentage which is 82.06 % compared to other incubation temperature. From the pseudo-first kinetic model analysis, the half-life of the photocatalysis process is 64.78 minutes which is the shortest among other catalysts. Thus, it can be conclude that, the optimum incubation temperature of hybrid CuO/TiO_2 is 50 °C.

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