Preparation of Hybrid CuO/TiO_2 Photocatalyst Responsive Towards UV-Light (Effect of Incubation Time)

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***Abstract*—Titanium dioxide (TiO_2) photocatalyst is one of the promising methods used in the treatment of dye removals. However, it has to be doped with other metals such copper oxide (CuO) to increase the efficiency, reactivity and stability under UV-light. This study was carried out to prepare hybrid CuO/TiO_2 using wet impregnation method by varying the incubation times at 1, 2, 4, 8 and 24 hr as well as to evaluate the photocatalytic removal of methyl orange under UV-light irradiation by hybrid CuO/TiO_2 photocatalyst. Then, characterization of the photocatalyst was done by XRD, EDX, FESEM and BET analysis. Hybrid photocatalyst sample was prepared using Copper (II) acetate monohydrate as the precursor for copper loading at a condition of 0.5wt%, 50˚C and various incubation times. Photocatalytic degradation for 10 ppm of methyl orange was studied under UV-light irradiation and the extent of dye degradation was determined using UV-Vis Spectrophotometer. Thus, from the research, the result showed that the sample being incubated at 2 hr during preparation of hybrid photocatalyst is an optimal result as it showed the best decolourization results with 82.06% of methyl orange removal.**

Keywords*—*CuO/TiO_2 photocatalyst, Incubation time, Methyl orange, Photodegradation, Wet impregnation.

1.0 INTRODUCTION

Large amount of synthetic dyes are produced and consumed in many industries such as textile industry, leather industry, food technology and many more. The presence of synthetic dyes in effluent streams can cause environmental pollution such as water pollution and serious health risk as it involve with the removal of inorganic pollutants into the source of water such as river, lake, sea and others. For instance, there are about 20 percent of the total production dyes are released in the textile effluent and remain in the wastewater [1], which cannot be recovered or reused due to the inefficiency of the dyeing process. The effect of these kinds of inorganic effluents in the wastewater can be identified by the change in the vital parameter of the effluent water such as biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity and odor of water [2].

A lot of conventional methods have been utilized for handling the dye removal from water. These methods include incineration, biodegradation, ozonation, reverse osmosis, filtration, adsorption on solid phase and coagulation [3] but it seems like these methods have their own limitations. As an example, most of the dye effluent especially from textile industries is photocatalytically stable towards chemical oxidation which increases their resistant towards decolorization process by conventional methods.

Due to this problem, Advanced Oxidation Processes (AOPs) such as photocatalysis method is applied as it is an increasing approach for the degradation of dyes in industrial wastewater. Photocatalysis method is inexpensive, easy to operate and efficient as compared to other methods. In this method, titanium dioxide, TiO_2 is the most widely used semiconductor photocatalyst as it has high chemical stability, inexpensive, non-toxic, long durability and environmental friendly [4]. TiO_2 photocatalyst exist in a form of anatase, rutile and brookite but anatase phase is widely used as it is the most active phase, has metastable phase, high photosensitivity and high stability [5], [6]. However, Akpan and Hameed [7] determined that TiO_2 has relatively high value of bandgap, around 3.2 eV which limit its using under ultraviolet (UV) light and it has high sensitivity to the electron-hole recombination which result in small specific surface area, low adsorption abilities and low quantum efficiency.

In order to explore efficient photocatalysis process and further improvement in the catalytic stability and activity, some modification of TiO_2 such as metal doping is carried out. Doping method has been introduced in which ion metal such as copper is being doped with TiO_2. Copper is cheaper-earth abundant material and it is found to be an effective material in metal doping due to its economical factor, good thermal stability, strong adsorption selectivity, facilitate charge separation, active and have polymorphs [4], [8]. Other than that, copper doping has limited exploration and inadequate literature as compared to other metals. It is suitable for implementing copper-dopant with TiO_2 for further study.

There are many methods on preparation of stable and effective ion-metal doped TiO_2 photocatalyst including wet impregnation, hydrothermal treatment, sol-gel, co-precipitation, reverse micro emulsion, spray drying and deposition-precipitation. Among all the methods, the wet impregnation method seems to be the most convenient method. Although it was rarely being focused as the main synthesis technique of doped TiO_2, it is a simple technique which related to ion-exchange or adsorption process, produce low waste streams and provides dominant interaction with the support. Therefore, this method has been utilized for further study.

The objective of the present work is to prepare copper-doped TiO_2 photocatalyst using wet impregnation technique by varying the incubation time. Characterization of the photocatalyst sample also has been done by following standard procedures using XRD, EDX, FESEM and BET. Besides that, the research is to evaluate the photocatalytic removal of methyl orange under UV-light irradiation by the hybrid CuO/TiO_2 photocatalyst.

2.0 METHODOLOGY

2.1 Chemicals and materials

In this study, Titanium dioxide (TiO_2) in powder form was used as a support which also acts as the semiconductor in photocatalysis. Copper (II) acetate monohydrate (Cu $(CO_2CH_3)_2$. H_2O) was used as dopant metal. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH of solution. Methyl orange (MO) was used as a dye for photocatalytic degradation study. All chemicals were used without further purification.

2.2 Preparation of photocatalyst

Wet impregnation technique was used in the preparation of CuO/TiO_2 photocatalyst. Wet impregnation is a method in which active metal precursor solution is contacted with a porous support and is dissolved in an aqueous or organic solution [5]. In a typical process, 2.593 g of TiO_2 powder was dispersed into 100 mL of distilled water, followed by addition of 0.0471 g of copper (II) acetate monohydrate and was stirred continuously for well mixing. The mixture was being incubated in a water bath at 50˚C for 1 hr under stirring. Then, a proper amount of NaOH solution was added to the suspension to modify the pH to 9-10 and allowed to incubate for another 2 hr. The prepared suspension was calcined in the furnace at 450˚C for 2 hr. All the steps were repeated for 1, 4, 8 and 24 hr of incubation time.

2.3 Characterization of photocatalyst

After preparing the CuO/TiO_2 photocatalyst sample, the samples were activated by calcination process. The dried samples were ground into fine powder and sent for the characterization. It is important to characterize the samples to identify the physical and chemical properties of photocatalyst samples in order to relate their properties with the photocatalytic performance.

The crystalline structure of photocatalyst sample was characterized by X-ray Diffraction (XRD). The accelerating voltage and applied current were 40 kV and 40 mA, respectively and the scan range is from 20˚ to 90˚ for 2θ. Elemental mapping of samples and image analysis were identified by Energy Dispersive X-Ray Spectroscopy (EDX) analysis which is attached to Scanning Electron Microscopy (SEM) instruments. EDX will detect the x-rays emitted from the samples with energy of 0.5 to 30.0 kV. Next, in this study, the surface morphology of CuO/TiO_2 photocatalyst such as crystallite particle shape, particle size and particle distribution was observed using Field Emission Scanning Electron Microscopy (FESEM). The surface area and porosity analysis were determined by Brunauer-Emmet-Teller (BET) analysis based on the physical adsorption and desorption of gas molecules at 77 K using liquid nitrogen (N_2) as an adsorbate gas. The amount of nitrogen gas being adsorbed is corresponding to the total surface area of particles including pores in the surface.

2.4 Control tests

Control test was conducted for methyl orange in photolysis and adsorption process. For photolysis, 10 ppm of methyl orange was illuminated under UV-light for 180 minutes without the presence of TiO_2 photocatalyst. Next, the adsorption process was carried out by immersing TiO_2 photocatalyst in methyl orange solution without UV-light irradiation and it was conducted for 180 minutes.

2.5 Photocatalysis Experimental Procedures

Photodegradation experiment was performed in a container or box equipped with UV-light source and it was covered by aluminium foil to prevent UV-light leakage. Then, 0.8 g of prepared sample of CuO/TiO_2 photocatalyst was put into 200 mL of methyl orange solution for 3 hours with continuously supply of oxygen by using air pump into the stirred suspension. The pH of methyl orange solution was adjusted to 3 by adding certain amount of hydrochloric acid, HCl into the prepared dye solution to enhance the influence of pH on the ionization state of titania [7].

For pre-absorption reaction, the sample was stirred constantly for 15 minutes without light to achieve adsorption equilibrium state between photocatalyst and dye solution. The photocatalytic activity was started by switching on the light and conducted under stirring. The sample solution of 3 mL was withdrawn using syringe at a fixed time interval for every 15 minutes. Next, the collected sample was filtered through a 0.5 µm filter to obtain clear solution of sample. The progress for photocatalytic degradation of methyl orange was monitored by measuring the absorbance in a UV-Vis spectrophotometer to determine the efficiency of dye removal. The experimental setup for photodegradation of methyl orange is shown in Fig 1.

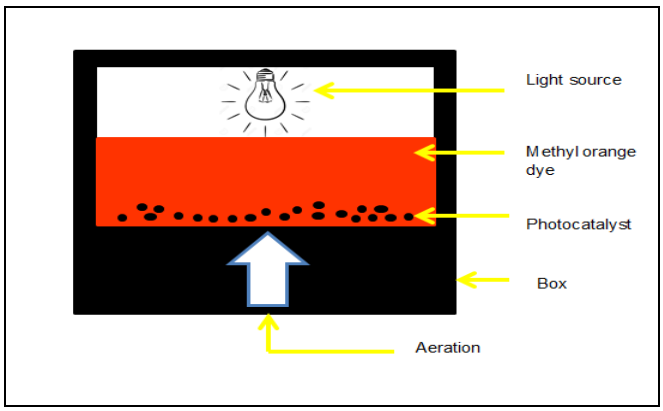

Fig 1: Experimental setup for photodegradation of methyl orange

2.6 Kinetic of Adsorption

In order to describe the relationship between the ratio of initial methyl orange concentration and methyl orange concentration at t time with irradiation time within 180 minutes, the first order kinetic model was applied. The first order kinetic formula is shown by Equation 3.1 [9].

$$\ln\frac{C_o}{C} = -k_1 t \qquad (3.1)$$

The pseudo-first order rate constant, k can be obtained from the slope of the straight line by plotting ln (C_o/C) against irradiation time, t which yields linear relationship. Then, half-life time was computed in order to determine the time taken for photodegradation to precede half-way to completion. Hence, the relationship between the first order rate constant and half-life time is shown in Equation 3.2 [9].

$$t_{1/2} = \frac{\ln 2}{k_1} \qquad (3.2)$$

3.0 RESULTS AND DISCUSSION

3.1 Characterization of photocatalyst

3.1.1 XRD

The XRD patterns of bare TiO_2 and CuO/TiO_2 photocatalyst prepared by using wet impregnation at different incubation time is shown in Fig 2. As shown in Fig 2, the strong diffraction peaks at 2θ= 25.3˚, 36.9, 37.8˚, 38.6˚, 48.1˚, 53.9˚, 55.1˚, 62.1˚, 62.7˚,

68.8˚, 70.3˚, 75.0˚, 76.0˚, and 82.7˚ appear in all samples. These correspond to the main peak of anatase structure of TiO_2 photocatalyst, which is similar with typical diffraction characteristics from JCPDS 00-021-1272. However, the peak of Cu species was less noticeable for the hybrid samples due to the very low amount of copper being doped with TiO_2 photocatalyst.

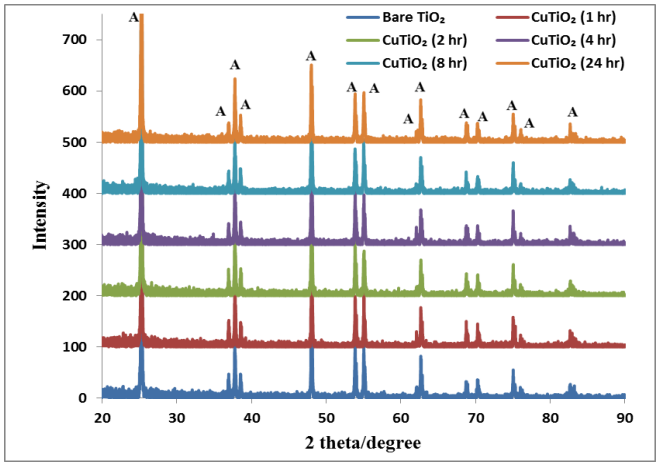

Fig 2: XRD patterns for bare TiO2 and hybrid CuO/TiO_2 photocatalyst at different incubation time (1, 2, 4, 8 and 24 hr)

Lei et al. [10] found that no copper peaks can be detected in XRD for Cu content lower than 1wt% but it can be observed for Cu content with relatively higher than 5wt%. It revealed that the Cu content in the samples was below the detection limits of the XRD to allow the detection of diffraction peaks [11] and indicated that the CuO clusters was evenly dispersed on the surface of TiO_2 photocatalyst during preparation of the hybrid samples. Therefore, to further confirm the presence of Cu in the hybrid photocatalyst, EDX analysis was carried out.

3.1.2 EDX

The correlation between elemental composition and morphological changes of particles can be identified by EDX which then further confirms the presence of Cu in hybrid CuO/TiO_2 photocatalyst. After incorporation of Cu at different incubation time during preparation of the samples, Cu was successfully detected by EDX. The presence of Cu was originated from copper precursor (copper (II) acetate monohydrate) used for hybrid preparation. The EDX analysis is shown in Fig 3 in which Ti peak was observed at 0.45 and 4.50 keV and O peak was detected at 0.52 keV. Meanwhile, Cu peak was detected 0.94 and 1.02 keV which further confirm the presence of Cu in the sample.

Additionally, the detailed weight percentages for each element analyzed with EDX spectroscopy (before and after photodegradation process) is shown in Table 1. Based on Table 1, the amount of copper loading after degradation is less than before degradation process. After removal of methyl orange for 180 minutes, a significant change is identified by the amount of copper loading in the samples shown by EDX result. It was decreasing from 0.91wt% to 0.61wt%. Hence, the decreasing amount of copper loading in the samples cause the loss of photocatalytic activity for reusability purpose of the photocatalyst [12].

After the presence of Cu had been confirmed by EDX analysis, mapping analysis is shown in Fig 4 to see the elemental distribution of Ti, O and Cu in the photocatalyst sample. From the mapping analysis, it can be concluded that Cu was homogeneously distributed on the TiO_2. Hence, it can be analysed that after copper loading, copper particles could be detected but at low amount and thus, it is believed that the copper clusters were evenly incorporated into the support during preparation of hybrid CuO/TiO_2 [11].

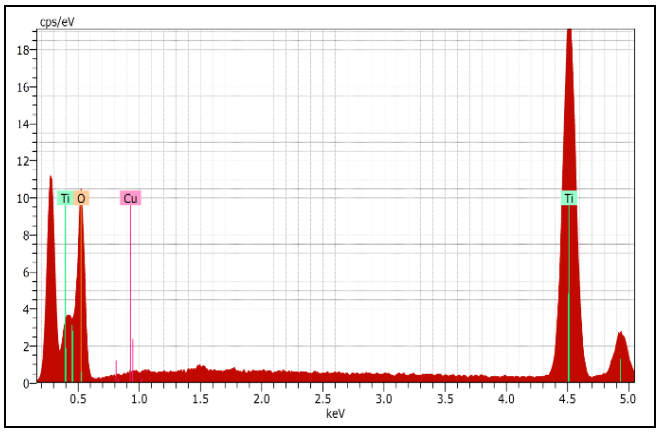

Fig 3: EDX Spectrum of CuO/TiO_2 at optimum condition

Table 1: Quantitative analysis of weight percentage for CuO/TiO_2 at optimum condition (before and after photodegradation).

Element	AN	Series	Norm. C (wt%)	
			Before	After
Oxygen	8	K-series	51.69	45.93
Titanium	22	K-series	47.40	53.46
Copper	29	K-series	0.91	0.61

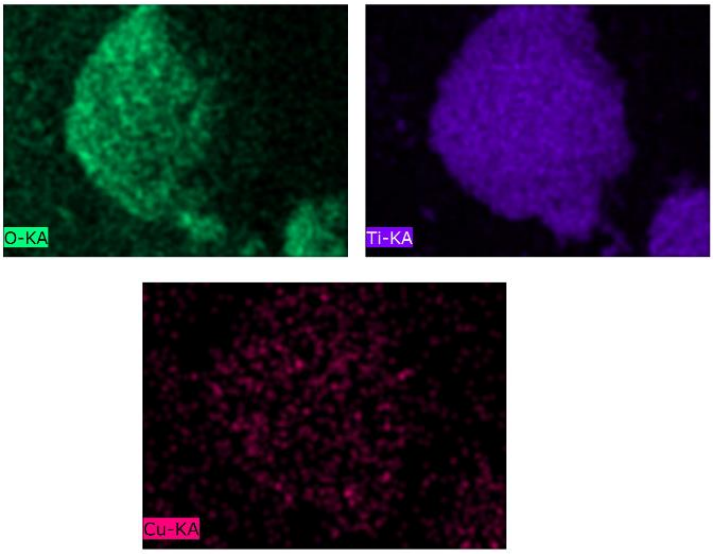

Fig 4: Elemental distribution of CuO/TiO_2 at optimum condition.

3.1.3 FESEM

The surface morphologies of bare TiO_2 (commercial TiO_2) and CuO/TiO_2 photocatalyst prepared by wet impregnation method were studied by FESEM. Fig 5 shows the FESEM images of bare TiO_2 photocatalyst of size around 200 nm. From the figure, bare TiO_2 consists of some spherical and square-like shape with various sizes. Fig 6 depicts the image of CuO/TiO_2 photocatalyst of size around 200 nm which were uniformly distributed on TiO_2 surface by adhering [10] as indicated by XRD analysis and were confirmed as Cu particles by EDX analysis. This is because after Cu was incorporated with TiO_2, the morphology of the CuO/TiO_2 photocatalyst sample was homogeneous and most of the particles appear were spherical shapes with various sizes, probably as the precursor used during hybrid preparation is the copper (II) acetate monohydrate.

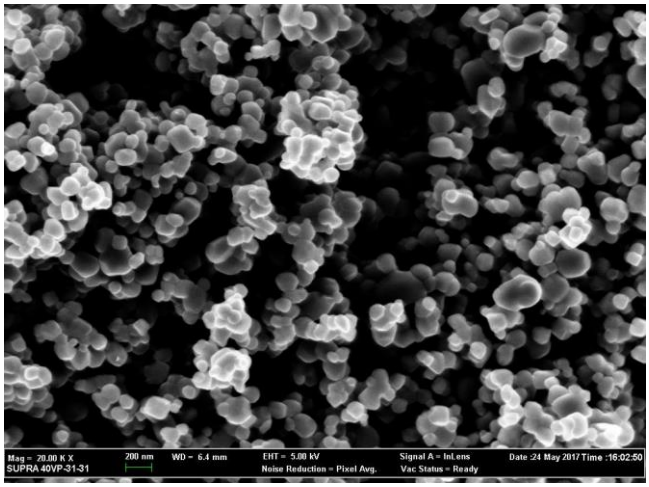

Fig 5: FESEM micrograph of bare TiO_2

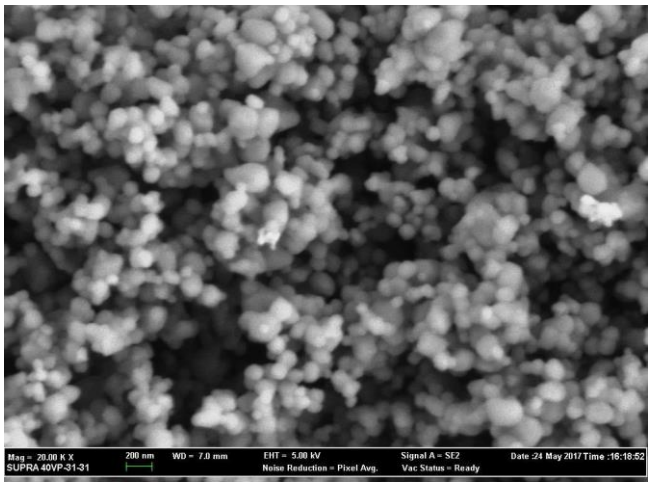

Fig 6: FESEM micrograph of CuO/TiO_2 photocatalyst

3.1.4 BET

As the photocatalyst is used for methyl orange removal, surface area and porosity of the photocatalyst become an important factor for determining the efficiency of photodegradation. This is due to the fact that photocatalysis is highly dependent on the surface area of photocatalyst to provide the surface active sites for the adsorption process. Table 2 shows the BET surface area, pore volume and pore width of hybrid CuO/TiO_2 photocatalyst at the optimum condition. Theoretically, photodegradation process may reduce the surface active sites for the adsorption of the photocatalyst sample as the methyl orange particles will agglomerate on the surface of photocatalyst. However, based on the table, it showed insignificant effect on the surface area, pore volume and pore width of hybrid CuO/TiO_2 photocatalyst before and after photodegradation process.

Table 2: BET surface area, pore volume and pore width of photocatalyst sample before and after photodegradation.

	Before photodegradation	After photodegradation
BET surface area (m^2/g)	8.8137	9.7521
Pore volume (cm^3/g)	0.032336	0.037714
Pore width (m^2/g)	7.6998	8.3594

3.2 Application of photodegradation

3.2.1 Control test

Two sets of control experiments such as photolysis and adsorption were carried out on methyl orange for 180 minutes to verify photocatalytic performance of the samples. Photolysis was carried out by direct illumination of UV-light without TiO_2 while adsorption was taken place with presence of CuO/TiO_2 without UV-light irradiation.

Fig 7 shows the percentage of methyl orange removal for different reaction condition. Photocatalysis process showed the highest percentage about 45.67% of methyl orange removal followed by photolysis and adsorption with 10.86% and 7.26% of methyl orange removal, respectively. From the research, photolysis and adsorption led to little removal of methyl orange. Thus, it can be concluded that the photocatalytic performance can be enhanced by reacting the photocatalyst samples under UV-light irradiation as it can excite more electron and hole in TiO_2 [13].

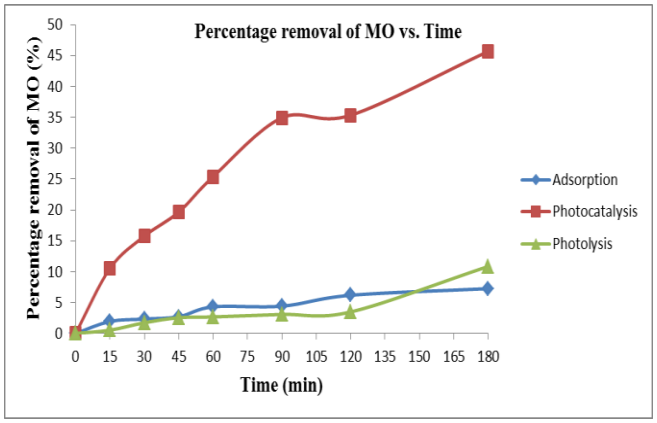

Fig 7: Percentage removal of MO vs. time at different reaction condition.

3.2.2 Photodegradation of methyl orange under UV-light

Before conducting the experiment for photodegradation of methyl orange, a calibration curve of absorption against concentration (ppm) was plotted linearly as depicted in Fig 8. It was obtained by using standard methyl orange solution with known concentration at 465 nm of absorbance peak [14] which representing the peak for methyl orange concentration.

The experiment was carried out at 4 g/L of CuO/TiO_2 photocatalyst dosage and 10 ppm of initial concentration of methyl orange. The samples were collected for different time intervals up to 180 minutes. Fig 9 shows the degradation of methyl orange within 180 minutes under UV-light irradiation. It can be observed that the decolourization of methyl orange occurred as the colour was changed from orange solution to almost colourless.

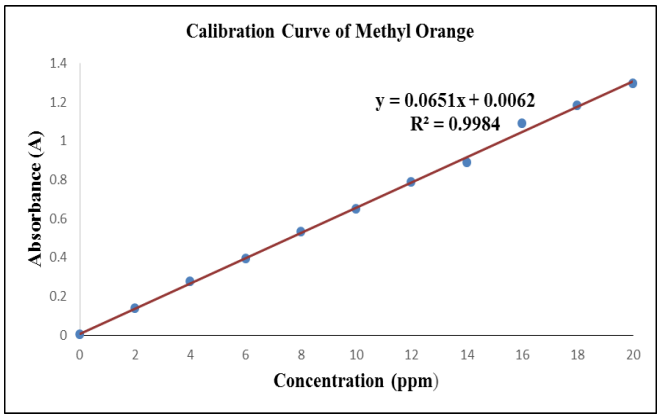

Fig 8: Calibration graph of absorbance versus concentration of methyl orange solution at 465 nm.

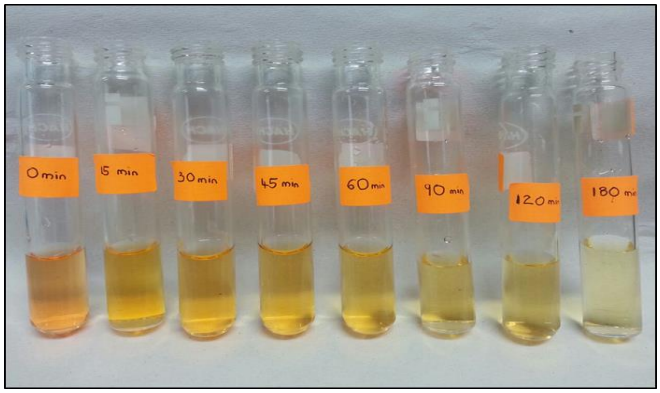

Fig 9: Degradation of methyl orange dye after 3 hours under UV-light irradiation.

Fig 10 depicts the overall result for effect of different incubation time of photocatalyst sample towards the percentage removal of methyl orange. The percentage degradation of methyl orange shown in Fig 10 were 42.47%, 82.06%, 39.12%, 30.29% and 40.21% for different incubation time at 1, 2, 4, 8 and 24 hr, respectively. In contrast, the percentage degradation of methyl orange for bare TiO_2 was only 29.87%, which is lower than hybrid CuO/TiO_2 photocatalyst. From the data, it can be concluded that the performance of TiO_2 photocatalyst under the UV-light irradiation can be enhanced by undergoing some modification of TiO_2 such as by metal doping with copper.

It clearly shows that the sample being incubated at 2 hr during preparing of hybrid photocatalyst is an optimal result with 82.06% of methyl orange percentage removal. Incubating the sample at 1 hr increased the photodegradation of methyl orange until it reach optimum time but it kept decreasing when the samples were incubated longer than 2 hr. The reason is that, prolonging the incubation time promoted the growth of crystalline particle which tend to agglomerate on the surface [15]. As a result, it would reduce the surface area of hybrid photocatalyst sample as well as photocatalytic activity due to weaken interaction between CuO/TiO_2 photocatalyst [16]. In addition, the part of photocatalyst surface becomes unavailable for photoabsorption which may result in lower photodegradation of methyl orange. Reli et al. [15] studied the photocatalytic activity by investigating the effect of calcination time and temperature of kaolinite/TiO_2 composite. He suggested that only optimum time and temperature could reach the maximum photocatalytic activity.

Furthermore, in terms of p-n junction principle, it is known that CuO is p-type semiconductor with negative charge while TiO_2 is n-type semiconductor with positive charge, which created electron-hole pairs under UV-light illumination. The holes will flow into the negatively charged field and the electrons will migrate to the positive field under the effect of inner electric field. Lei et al. [17] found that the electron-hole separation will be separated effectively by the built-in electric fields in the p-n heterojunction formed in CuO/TiO_2. When the incubation time is shorter than 2 hr, p-n junction photocatalyst may not be formed due to n- TiO_2 and p-CuO only play their own photocatalytic role [17] and this may lowering the photocatalytic activity of the hybrid photocatalyst as well as percentage removal of methyl orange. However, studied by Lei at al. [10] and Riaz et al. [14] towards CuO/TiO_2 and Cu-Ni/TiO_2 photocatalyst, respectively showed the different result. The effect of incubating the samples at 1 hr showed higher photodegradation of tetra-dibromo-diphenylether and methyl orange dye. They explained that n- TiO_2 and p-Cu could play their role together.

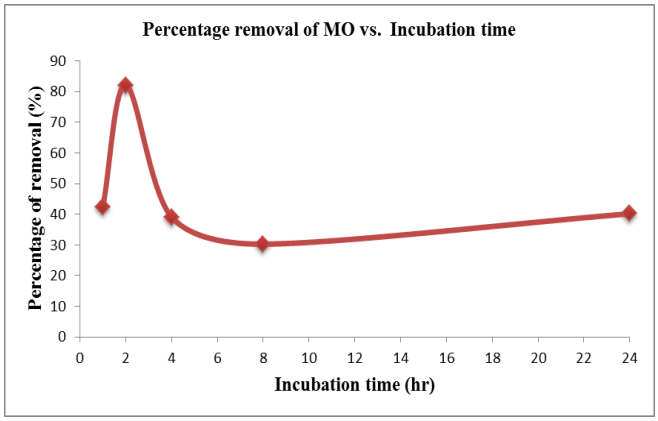

Fig 10: Percentage removal of methyl orange against incubation time at 1, 2, 4, 8, and 24 hr.

When the sample of hybrid photocatalyst was incubated longer than 2 hr, the p-n junction was formed but the electrons and holes tend to recombine which reduce the thickness of the space charge layer on the TiO_2 surface and prevent interfacial charge transfer to degrade methyl orange adsorbed on the surface of particles [17]. From this chronology, it is known that the higher the electron-hole recombination rate, the lower the photocatalytic activity of the samples. Hence, these factors will reduce the photodegradation of methyl orange in photocatalytic activity.

From the analysis, the removal of methyl orange is dependent on the incubation time during the preparation of hybrid samples which in return affects the crystallinity of particles, surface area, p-n junction principle and recombination rate of electron-hole on the structure. The percentage of removal of methyl orange at 1, 4, 8 and 24 hr of incubation time does not enhance the photocatalytic activity as the methyl orange removal is lower than 82.06%, implying that 2 hr of incubation time may be enough during preparation of CuO/TiO_2.

3.2.3 Kinetic model of adsorption

Basically, kinetic models are classified into three categories which are pseudo-first order, second order and intra particle diffusion. However, for the effect of incubation time towards CuO/TiO_2 photocatalyst, the pseudo-first model is well-fitted to this study which eliminating the other two models. The pseudo-first order kinetic model can be expressed as ln (C_o/C) which is a ratio between original concentration of methyl orange and the concentration after photodegradation of methyl orange against time of irradiation. Hence, the pseudo-first order model is shown in Fig 11. Thus, from Fig 11, the graph was linearized in order to obtain the value of regression coefficient, R^2 and the rate constant of pseudo-first order, k from the slope of the straight line. The value of R_2 and k for bare TiO_2 and CuO/TiO_2 photocatalyst at different incubation time is shown in Table 3.

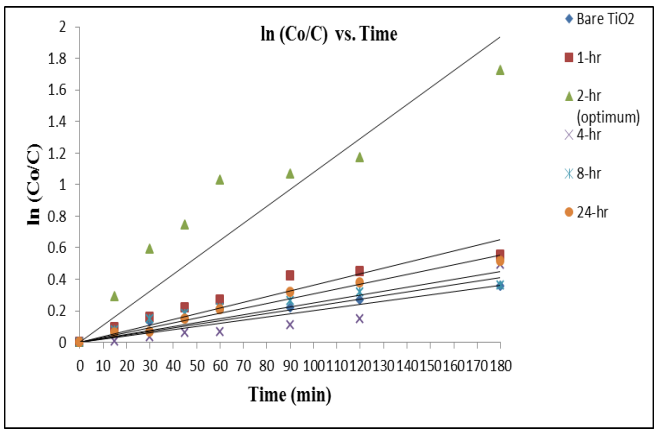

Fig 11: Pseudo-first order kinetic model

Table 3: The value of R^2 and k of pseudo-first order kinetic model

Parameter	Regression coefficient, R^2	Rate constant, k (min^{-1})
Bare TiO_2	0.8022	2.30×10^{-3}
CuO/TiO_2:		
1 hr	0.8880	3.60×10^{-3}
2 hr (optimum)	0.8183	1.08×10^{-2}
4 hr	0.7993	2.00×10^{-3}
8 hr	0.7467	2.50×10^{-3}
24 hr	0.9782	3.10×10^{-3}

Based on Table 3, the optimum incubation time at 2 hr showed the highest k value which is 0.0108 min^{-1}. This k value was used to calculate the value of half-life time, $t_{1/2}$ using Equation 3.2. In this study, half-life is the time taken for the initial concentration of methyl orange to be degraded into half of adsorption time. Hence, the half-life time of CuO/TiO_2 photocatalyst at 2 hr was 64.18 min, which is shorter than other parameter. Apparently, higher rate constant will lead to shorter half-life time and hence, faster the removal rate of methyl orange.

4.0 CONCLUSION

The hybrid CuO/TiO_2 photocatalyst was successfully prepared by wet-impregnation method. From the characterization, XRD patterns exhibited strong diffraction peaks of pure anatase TiO_2 similar to standard spectrum characteristics. The copper loading cannot be detected by XRD analysis due to the low amount of copper content and beyond equipment limit but it can be found via EDX. The surface morphologies of bare TiO_2 and CuO/TiO_2 photocatalyst were studied by FESEM and it indicated the relative uniform distribution of CuO on TiO_2 surface. For BET analysis, it showed insignificant change on the surface area, pore volume and pore width before and after photodegradation process. The study on different incubation time (1, 2, 4, 8 and 24 hr) has shown that it has significant influence on the photocatalytic activity. Based on the result obtained, it can be concluded that photocatalyst prepared at 2 hr of incubation time is the optimal result which showed the best photocatalytic activity with 82.06% of methyl orange removal. Meanwhile, the lowest percentage is shown by bare TiO_2 with only 29.87%. Therefore, it can be stated that preparing of the samples at shorter and longer than 2 hr of incubation time may affected the crystallinity of particles, surface area, p-n junction principle and recombination rate of electron-hole on the structure as well as the performance of photocatalytic activity. From the pseudo-first order of kinetic model, it can be concluded that the half-life time at optimum incubation time (2 hr) was the lowest with 64.18 min. It revealed that the shorter time was required for the initial concentration of methyl orange to be degraded into half of adsorption time and thus, faster the removal rate of methyl orange. Therefore, the viewpoint of incubating CuO/TiO_2 photocatalyst at 2 hr is very favourable.

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