Preparation of Hybrid Ag_2O/TiO_2 Photocatalyst Responsive Towards UV Light (Effect of Incubation Time)

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***Abstract*—The objectives of the present study are to prepare hybrid Ag_2O/TiO_2 photocatalyst by wet impregnation method at different incubation time as well as to determine its photocatalytic performance on the degradation of Methyl Orange (MO). Ag_2O/TiO_2 photocatalyst was prepared by mixing 5 wt% of Ag with TiO_2 in 50 mL of distilled water. The solution was incubated for one, two, four, eight and 24 hours at 70 °C and was washed and calcined overnight in a furnace at 450 °C. The degradation of MO was conducted by adding 1 g of photocatalyst in 200 mL of MO solution with concentration of 10 ppm. The solution was supplied with oxygen and was stirred during the reaction for three hours with the presence of UV light. The presence of Ag on TiO_2 surface was confirmed from the characterization analysis. The degradation of MO increased until eight hours of incubation time and then decreased. Thus, the Ag_2O/TiO_2 photocatalyst with eight hours of incubation time was the optimum photocatalyst in which the percentage removal of MO reached 84.94%. It also obtained the highest rate coefficient as well as coefficient of determination, which were 0.01078 min^{-1} and 0.992, respectively. The half-life calculated was 64.29 minutes.**

***Keywords*— Methyl Orange, photocatalyst, titanium dioxide**

I. INTRODUCTION

Photocatalysis is described as the alteration of rate of chemical reactions in the presence of light without being involved in the particular chemical transformation. The word photocatalysis itself actually came from Greek words; *phos* which means light and *katalyo* which means break apart or decompose. In the photocatalysis process, the light photons with specific amount of energy are irradiated on a particular substance in order to enhance the chemical reaction.

The photocatalysis process is categorized into two methods which are homogeneous and heterogeneous photocatalysis. Homogenous photocatalysis is a process in which the photocatalyst and the reactant are in the similar phase, usually in liquid phase. Other than that, the solid catalyst may be dissolved in water during the reaction. The homogeneous photocatalysis normally involves the utilization of ozone, photo-Fenton system or photo-Fenton-like system [1]. Heterogeneous photocatalysis is the photocatalysis process in which the reactant and the catalyst are in different phases. The process has caught attentions from researchers especially from the photochemistry field due to its potential in environment and energy-related applications such as water splitting and wastewater treatment. The heterogeneous photocatalysis implies a reaction scheme between a solid photocatalyst and a fluid reactant. The solid photocatalysts that are normally used are metals and semiconductors.

Researchers often choose semiconductors as photocatalyst in their studies due to its electronic structure of metal atoms which is the filled valence band and empty conduction band. When they are irradiated by light with particular energy, the electrons are photoexcited and will jump out from the valence band and fill the conduction band, at the same time producing holes in the valence band [2]. TiO_2 is one of the most common semiconductors used in the photocatalysis process. The semiconductor is known for its inertness chemically and biologically, photocatalytically stable, cheap and has high redox potential. However, the pure TiO_2 photocatalyst also has its disadvantages. TiO_2 actually has lower quantum efficiency and due to its wide bandgap, the semiconductor only response towards UV light irradiation. For these reasons, researchers came out with a solution in which semiconductor photocatalysts should be incorporated with other chemical substance; metals or non-metals in order to improve its photocatalytic activity. This alternative is known as hybrid photocatalyst. Hybrid photocatalyst is a photocatalyst doped with other chemical substance in order to enhance its properties as well as to improve the photocatalytic activity.

Discovered in 1980s, a number of techniques of co-catalyst loading have been studied ever since. The co-catalyst loading was proven to improve the performance of a particular photocatalyst including the alteration of Fermi level as well as increases the number of active sites on the photocatalyst surface [3]. Deposition, sol-gel, wet impregnation and co-precipitation techniques are among the common doping techniques widely utilized by researchers in their studies. Jasso-Salcedo et al. in his study has incorporated Ag nanoparticles on ZnO surface by photodeposition and wet impregnation method in which both hybrid photocatalysts resulted in an increment of the reaction rate constant in the degradation of bisphenol-A, although the photocatalyst developed by photodeposition method showed higher reaction rate constant than by the impregnation method [4]. Zuas and Budiman also have loaded 3 wt% of Cu with TiO_2 by using co-precipitation method. The result showed that 90% of Congo Red dye was decolourized over Cu/TiO_2 photocatalyst, while in case of pure TiO_2, only 53% of the dye decolourized within a minute [5]. In addition, the impregnated Cu/TiO_2 also showed better photocatalytic performance over pure TiO_2 photocatalyst in the degradation of both decabromodiphenyl ether (BDE209) and tetrabromodiphenyl ether (BDE47) when exposed to UV irradiation in anoxic atmosphere [6]. Besides, Wang et al. also conducted a study on the degradation of salicylic acid over iodine and nitrogen co-doped TiO_2 photocatalyst. They found that the presence of iodine increased the rate constant of the acid removal and 78.3% of total organic carbon was eliminated upon 180 minutes of visible light irradiation [7]. Research by Chen et al. also indicated that 66%

antibiotic oxytetracycline was removed in the presence of pure TiO_2 photocatalyst and it was further increased when $Au/CuS/TiO_2$ photocatalyst were utilized [8]. Chang et al. reported that *Mycrocystis aeruginosa* cells have degraded after 12 hours-exposure of light/dark cycles for 12 days when Ag/TiO_2 photocatalyst was added [9]. These findings prove the effectiveness of photocatalysis, although the photocatalytic performance can be enhanced by doping chemical substances over pure photocatalysts.

Dyes are substances used to add or alter colours. They are used primarily in the production of consumer products including paints, textiles, cosmetics, plastics and papers. Natural dyes are first discovered million years ago in plants and ever since 1800s, most of the industries are using synthetic dyes as they give richer colour and better protection against exposure either by adsorption, mechanical retention or formation of covalent bonds with salts and metals. However, these dyes are not easily treated and as a result, most industries dump tons of dye effluents into surface waters. Due to this reason, the dye industry is ranked the tenth most polluted industries by the Pure Earth and Green Cross Switzerland [10]. The worst problem is dyes contain a number of dangerous chemical substances such as dioxin and formaldehyde as well as heavy metals. These substances harm ecosystems and human health. Dyes also can cause acute and chronic effects on the exposed living organisms and due to their stability, dyes last longer in the environment. Besides, the presence of dyes on water surface prevents the sunlight to penetrate into water and thus retards algae photosynthesis.

Thus, removal of dyes has received much attention and a number of methods were offered by researchers around the world. Some of the early methods introduced are adsorption, coagulation, ultrafiltration and reverse osmosis. However, these methods only transfer the pollutants from water to other phases rather than eliminating them. As a result, secondary pollution may occur and further treatments will be required.

Photocatalysis, however, offers better solution for the problems. The method is advantageous due to its ability to completely mineralize the pollutants. TiO_2 photocatalyst has proved its ability by degrading 87% of Brilliant Green within one hour [11]. According to Zhang et al., Rhodamine B also showed 100% degradation when it was mixed with $BiWO_3$ nanopowders for two hours in sunlight exposure [12]. Other than that, $Ag_{10}Si_4O_{13}$ removed 98% of Methylene Blue dye upon seven minutes of visible light irradiation [13]. The applications of TiO_2 have been wider each day ranging from dye-sensitized solar cells, degradation of organic pollutants and production of hydrogen from water splitting. Nonetheless, it still has its own limitations, for example, in terms of its cost competitiveness. Henschel in his research has compared the TiO_2 photocatalysis and granular activated carbon adsorption from the factor of operation cost. It was found that the estimated cost of photocatalysis was seven to ten times higher than that of activated carbon adsorption. Therefore, in order to be cost competitive, the photocatalytic activity must be improved by boosting the quantum efficiency under UV light or employing visible light activity that is absent with pure TiO_2 photocatalyst [14].

Other than that, the photocatalyst surface is also modified by coupling the photocatalyst with a semiconductor. Coupling n-type and p-type semiconductors will create a p-n heterojunction which will improve the electrons and holes separation. Ren and Yang in their research has loaded Ag_2O on TiO_2. Due to the energy band structure and inner electric field built at the heterojunction, the electron transfer between Ag_2O and TiO_2 is constrained. However, the holes generated can be transferred, causing an effective electron-hole separation. As Ag_2O has narrower bandgap energy than TiO_2, the generated electrons in TiO_2 conduction band are transferred to Ag_2O conduction band. The electrons in both conduction bands are captured by the oxygen and produces hydroxyl radicals. At the same time, the photocatalytic activity is enhanced when the holes in the valence band of TiO_2 reacts with water, also producing hydroxyl radicals while the holes in Ag_2O directly react with the pollutant [15]. Fig. 1 shows the mechanism of coupled semiconductors as photocatalyst.

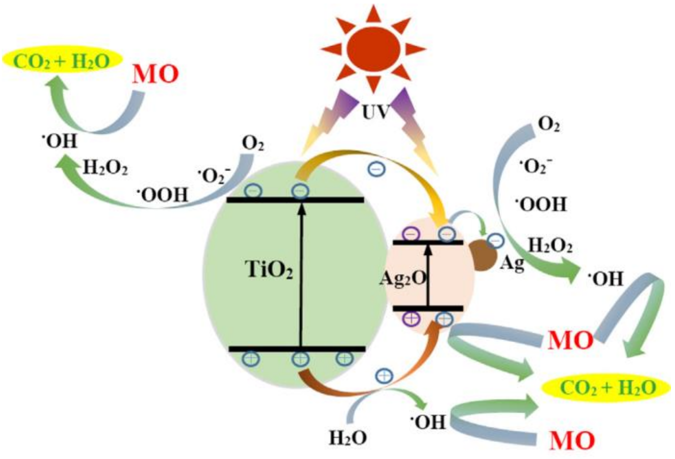


Fig. 1: Photocatalysis mechanism [15].

The method of wet impregnation is one of the methods of coupling metals into photocatalyst that has caught a lot of interest among scientists. The metal precursor is first contacted with porous support and added into the solution. Usually water is used as solvent for inorganic salts while organic solvents are used for organometallic precursors. The solution is stirred for a few hours and dried at 100 °C for two hours to remove any volatile components and to obtain the powder photocatalyst. The powder is then washed repeatedly and dried again before it is calcined at high temperature for a few hours.

One of the advantages of this method is its simplicity and that it facilitate the synthesis of nano-sized TiO_2 photocatalyst with high purity and at low temperature [16]. Besides that, it also produces low waste streams and gives uniform and complete pore filling [17].

Scientists from various fields of study has done researches on the types of photocatalyst to be used and the factors influenced the photocatalytic performance including the substance concentration and pH, light intensity, irradiation time and method of metal coupling as well. To date, infinite methods of metal coupling on photocatalysts have been investigated. Previous investigations showed that the method of coupling also gives impacts on the photocatalytic activity as it affects the particles distribution [3], charges separation as well as reactions in the solution [18], [19].

The effect of incubation time on the physical properties of photocatalyst is not extensively studied even though the photocatalysis process has shown quite a potential in various applications. Jasso-Salcedo et al. reported that there was no change on the crystalline structure of zinc sulphide (ZnS) and Ag upon impregnation either in one hour, two hours or five hours of incubation when analyzed using x-ray diffraction (XRD) analysis. The peaks from the analysis showed the hexagonal wurtzite structure of ZnS and the face-centered cubic structure of Ag [3]. Lei et al. has incubated the solution of CuO/TiO_2 for one hour. He also obtained similar results in which the crystalline structure of CuO and TiO_2 showed no changes upon incubation [6]. However, Di Paola et al. claimed that the XRD analysis of various dopants on TiO_2 photocatalyst showed mixtures of anatase and rutile in the ratio of 4:1 upon 24 hours of incubation [20].

The previous reported investigations showed lack of understanding on the effect of incubation time on the properties of the prepared photocatalyst. Therefore, it is suggested to conduct further studies on the respective topic.

In this research, the potentials of TiO_2 as photocatalyst is further developed in which the effect of incubation time during the preparation of hybrid Ag_2O/TiO_2 photocatalyst and its photocatalytic activity on the degradation of Methyl Orange (MO) dye is investigated.

The objectives of the study include to prepare hybrid Ag_2O/TiO_2 photocatalyst by wet impregnation at different incubation time, to characterize the prepared photocatalyst using X-ray diffraction (XRD), energy dispersive X-ray (EDX) and field emission scanning electron microscopy (FESEM) as well as to determine the photocatalytic performance on the degradation of MO.

II. METHODOLOGY

A. *Chemicals and Materials*

The chemicals used in this research were commercial TiO_2, $AgNO_3$ and MO powder. Distilled water and water bath was used in the preparation of Ag_2O/TiO_2 and MO solution.

B. *Preparation of Ag_2O/TiO_2 Photocatalyst*

The hybrid Ag_2O/TiO_2 photocatalyst was prepared according to the procedures outlined in Lei et al. [6]. For 5 wt% of Ag, 9.2126 g of TiO_2 was first dispersed in 50 mL of distilled water. 0.7874 g of silver nitrate ($AgNO_3$) was added into diluted TiO_2 solution and was stirred. The solution was next incubated in water bath in which the incubation time was varied for one hour, two hours, four hours, eight hours and 24 hours at the temperature of 70 °C. The product was washed and calcined overnight in a furnace at 450 °C.

C. *Preparation of Methyl Orange Solution*

The MO stock solution was prepared by diluting 1.0 g of MO powder with 1000 mL of distilled water in a volumetric flask. 200 mL of 10 ppm of MO was used for the degradation procedure in which 2 mL of MO stock solution was diluted in 198 mL of distilled water. Another MO solution at the concentration of 0 ppm to 20 ppm was prepared with interval of 2 ppm for the construction of calibration curve.

D. *Characterization of Ag_2O/TiO_2 Photocatalyst*

The characterization analysis of Ag_2O/TiO_2 photocatalyst was conducted in order to study the physical and chemical properties of the photocatalyst. The methods of characterization employed were XRD, EDX, and FESEM. X-rays have a wavelength in the range of interatomic distances. The range makes them capable of studying crystalline materials. XRD analysis is known as a very useful instrument in the characterization of single phase materials. It is normally used to identify the phase, crystal size, strain and preferred orientation of crystalline materials. Meanwhile, EDX is used in the identification of elements as well as the composition of the existing elements. The data obtained from the analysis consist of spectra which show peaks corresponding to the composition of elements in the particular sample as well as the mapping of the sample. The EDX analysis is considered as a rapid, inexpensive and non-destructive surface analysis. FESEM is an instrument used with high-energy beam of electrons which are released from a field of emission source. The instrument is normally used to obtain topographic details on the surface of a sample. FESEM gives topographical information at magnifications of 10 to 300, 000 times with unlimited depth of field.

E. *Adsorption of Methyl Orange on Ag_2O/TiO_2 Photocatalyst*

The adsorption of MO dye solution in Ag_2O/TiO_2 photocatalyst was conducted by adding 1.0 g of photocatalyst in 200 mL of MO solution. The solution was stirred and supplied with oxygen using air pump so that the reaction atmosphere was protected by oxygen during the adsorption reaction for three hours. A UV light was placed on top of the solution to allow irradiation on the MO solution. Fig. 2 shows the experimental setup for the degradation of MO solution.

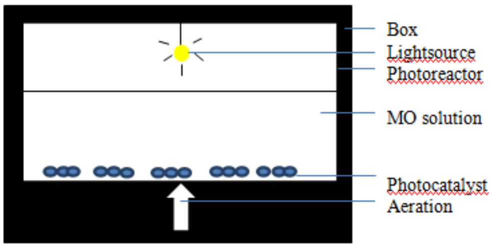


Fig. 2: Experimental setup for MO photodegradation.

III. RESULTS AND DISCUSSION

A. *Characterization of Ag_2O/TiO_2 Photocatalyst*

The XRD patterns of bare TiO_2 and hybrid Ag_2O/TiO_2 photocatalysts with different incubation time are shown in Fig. 3. The TiO_2 anatase peaks can be seen at 2θ = 25.28°, 37.8°, 48.05°, 53.89°, 55.06° and 62.69° corresponding to crystal planes of (101), (004), (200), (105), (211) and (204) (JCPDS 21-1272). However, the metallic Ag diffraction peaks cannot be seen at concentration lower than 10 wt%, probably due to the detection limit of XRD instrument.

To further confirm the XRD result, EDX analysis was performed. Fig. 4 shows the EDX spectra of bare TiO_2 and Ag_2O/TiO_2 photocatalyst at two hours of incubation time. From Fig. 4(a), Ti peaks was observed at 0.45 keV and 4.51 keV while the O peak was detected at 0.52 keV. The peaks of Ti and O were originated from TiO_2. The compound consists of 75.72 atomic% of Ti and 24.28 atomic% of O. After the incorporation of Ag, the element was successfully identified at 2.9 keV and 3.15 keV as shown in Fig. 4(b) in which the peaks came from $AgNO_3$ used in the preparation of Ag_2O/TiO_2. The amounts of Ti, O and Ag in Ag_2O/TiO_2 were 33.07 atomic%, 66.58 atomic% and 0.34 atomic%, respectively.

To observe the dispersion of Ag on TiO_2 surface, the mapping analysis was performed. From Fig. 5, the mappings show high uniform dispersion of Ag on the surface of TiO_2. The results prove the presence of Ag when XRD instrument could not identify the element.

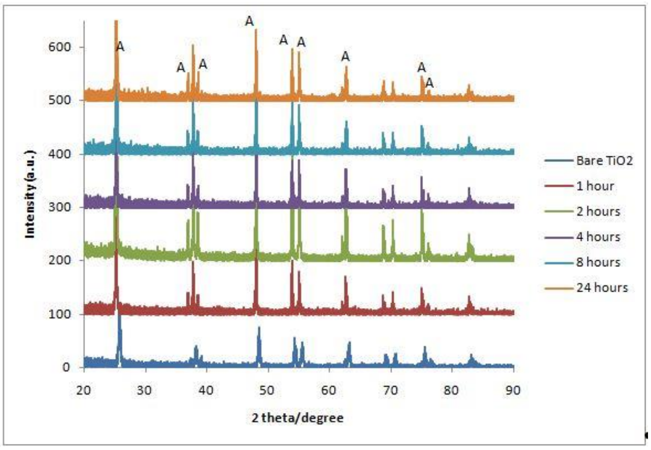
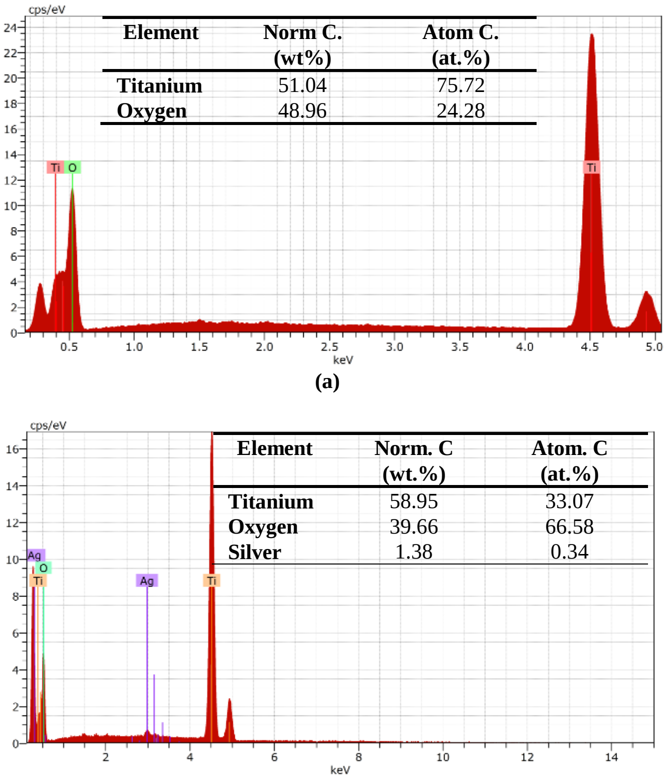


Fig. 3: XRD pattern of Ag_2O/TiO_2 with different incubation time.



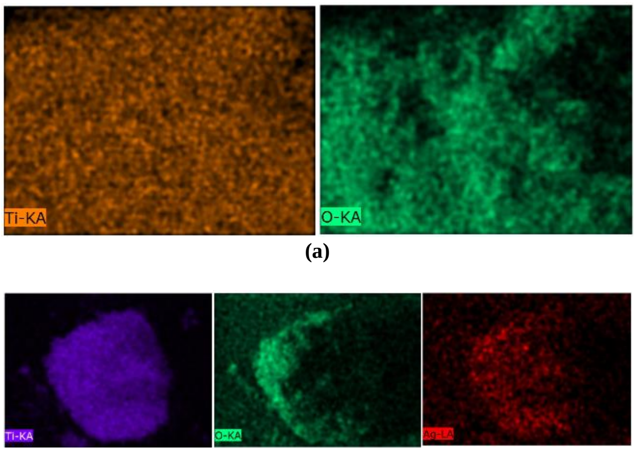
Element	Norm C. (wt%)	Atom C. (at.%)
Titanium	51.04	75.72
Oxygen	48.96	24.28

(a)

Element	Norm. C (wt.%)	Atom. C (at.%)
Titanium	58.95	33.07
Oxygen	39.66	66.58
Silver	1.38	0.34

(b)

Fig. 4: EDX spectra of (a) bare TiO_2 and (b) Ag_2O/TiO_2 with 2 hours of incubation time.

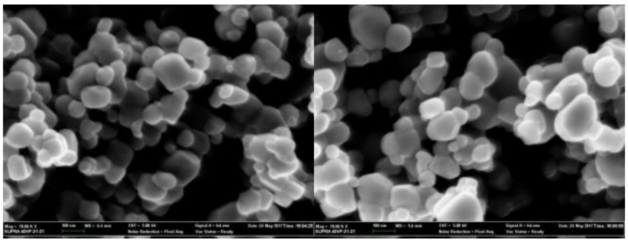


(a)

(b)

Fig. 5: EDX mappings of (a) bare TiO_2 and (b) Ag_2O/TiO_2 with 2 hours of incubation time.

FESEM analysis was performed in order to observe the changes of TiO_2 structure when Ag was incorporated. Fig. 6 shows the FESEM images of bare TiO_2 and Ag_2O/TiO_2. Based on the figure, bare TiO_2 is comprised of spherical and square-like shape with various sizes. There were also no significant changes on the shape of TiO_2 when Ag was impregnated. However, it can be seen that the colour changed from gray to white upon impregnation. The changes in the colour proved that Ag was successfully impregnated on TiO_2 surface.



(a) (b)

Fig. 6: FESEM images of (a) bare TiO_2 and (b) Ag_2O/TiO_2 photocatalyst.

B. Photocatalytic Performance of Ag_2O/TiO_2 Photocatalyst

The photocatalytic performance of Ag_2O/TiO_2 photocatalyst was studied based on the calibration curve of MO, the photodegradation of MO by Ag_2O/TiO_2 as well as the reaction kinetics of the MO degradation by Ag_2O/TiO_2 photocatalyst at different incubation time.

A calibration curve was constructed in order to obtain the concentration of the MO samples. Upon degradation, the samples of MO were collected at a certain interval time. The samples were then analyzed by UV-vis spectrometer in which the concentration of the samples was identified corresponding to the absorbance values. The calibration curve was constructed in order to obtain the concentration of MO at a particular absorbance value. Fig. 7 shows the calibration curve of MO dye.

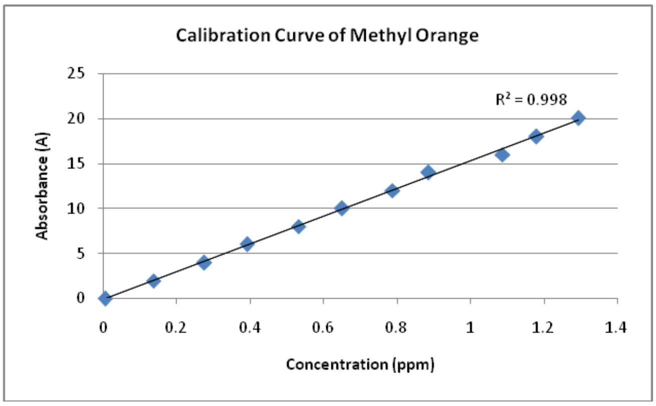


Fig. 7: Calibration curve for MO dye.

The adsorption and photolysis of MO were first conducted as control tests in which the adsorption of MO on bare TiO_2 was conducted without the presence of UV light, while the photolysis experiment was performed without the presence of photocatalyst under the UV light.

Based on Fig. 8, the degradation rate of MO was improved with increasing incubation time between one and eight hours and then decreased. The highest MO removal obtained was 84.9% at eight hours of incubation time. This is because Ag^+ ions consume electrons rather faster than the reduction of oxygen and more metallic Ag was formed with longer incubation time, thus, a higher degradation rate was obtained [21].

Behnajady et al. has prepared Ag-loaded TiO_2 photocatalyst by wet impregnation and photodeposition methods, and compared their photocatalytic activity on the removal of Acid Red 88 (AR88) upon UV light irradiation. The percentage removal of the dye was the highest when using photodeposition method, followed by wet impregnation and bare TiO_2 photocatalyst [18].

Wei et al. also has prepared the hybrid Ag_2O/TiO_2 nanobelt heterostructures via chemical precipitation method. The photocatalytic performance was tested by observing the degradation rate of MO under UV, visible, near-infrared (NIR) and simulated sunlight. Generally, Ag_2O/TiO_2 photocatalyst showed the best performance compared with pure Ag_2O, TiO_2 and P25 in which the degradation efficiency reached 87% within 35 minutes under the UV light [22].

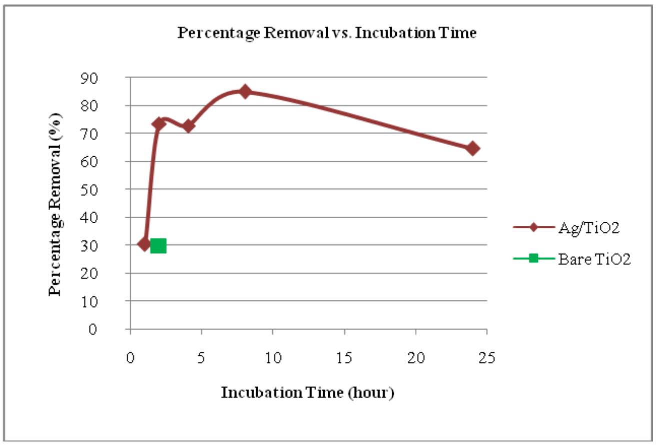


Fig. 8: Total % removal of MO with different incubation time.

Besides that, Meng et al. has prepared Ag_3PO_4/TiP_2O_7 photocatalyst. The photocatalytic activity was observed from the degradation of Rhodamine B (RhB) under simulated sunlight irradiation. The photocatalyst was prepared by deposition-precipitation method with different Ag_3PO_4/TiP_2O_7 weight ratios. The degradation rate of RhB was improved when hybrid photocatalyst was introduced and it was significantly enhanced when using 2:8 weight ratio in which RhB was 99% removed in 120 minutes [23].

Fig. 9 compares the optimum performance of Ag_2O/TiO_2 photocatalyst on the removal of MO with the control tests. From the figure, the degradation of MO was clearly enhanced with the photocatalysis of Ag_2O/TiO_2, followed by bare TiO_2 photocatalyst, photolysis and lastly adsorption of MO by TiO_2 without the presence of light.

The kinetics analysis of the degradation of MO by Ag_2O/TiO_2 photocatalyst at different incubation time was performed. The photocatalytic degradation of MO was assumed to obey the Langmuir-Hinshelwood kinetic model in which the model describes the relationship between the rates of degradation of MO as a function of incubation time. The reaction rate is written in the form of:

$$r = \frac{-dC}{dt} = kC \qquad \text{(Eq. 1)}$$

where k is the pdeuso-first order reaction rate coefficient and C is the concentration of MO. The integration of the expression with C = C_0 at t = 0 gives:

$$\int_{C_0}^{C} \frac{-dC}{C} = k \int dt \qquad \text{(Eq. 2)}$$

$$-(\ln C - \ln C_0) = kt \qquad \text{(Eq. 3)}$$

$$\ln \frac{C_0}{C} = kt \qquad \text{(Eq. 4)}$$

The construction of ln C_0/C versus time with different incubation time was shown in Fig. 10. The degradation rate coefficients were determined from the slope of the graphs.

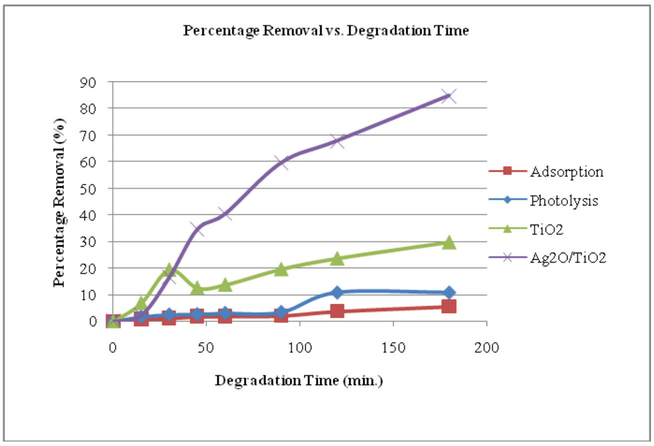


Fig. 9: Removal of MO using different method.

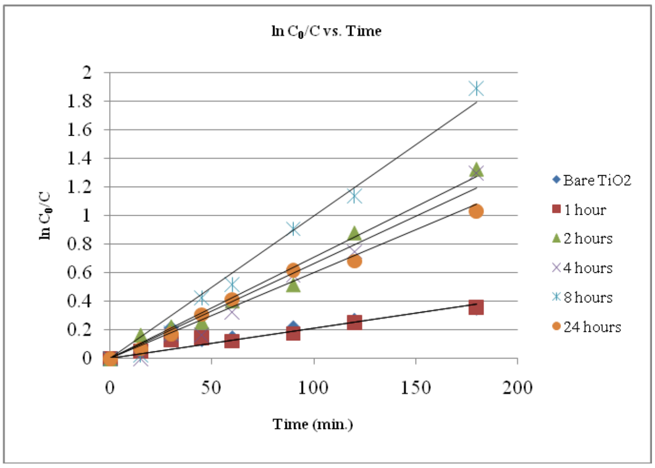


Fig. 10: Kinetics of photodegradation of MO at different incubation time.

Table 1 summarizes the reaction rate coefficients obtained from the slope of the graphs as well as the coefficients of determination or also known as the R-squared values. From the table, the degradation of MO using Ag_2O/TiO_2 photocatalyst prepared at eight hours of incubation time obtained the highest rate coefficient as well as the R-squared value, which was 0.01078 min^{-1} and 0.992, respectively.

Table 1: Rate coefficients and R^2 values at different incubation time

Parameter	k (min^{-1})	R^2
Bare TiO_2	1.71×10^{-3}	0.827
1 hour	1.83×10^{-3}	0.946
2 hour	7.19×10^{-3}	0.98
4 hour	7.38×10^{-3}	0.984
8 hour	1.08×10^{-2}	0.992
24 hour	5.79×10^{-3}	0.984

From the reaction rate coefficients obtained, the half-life of Ag_2O/TiO_2 photocatalyst was calculated in which the half-life is described as the time taken for the amount of photocatalyst to decrease by half. The half-life was calculated using the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \qquad \text{(Eq. 5)}$$

Using the equation, the half-life obtained for the optimum Ag_2O/TiO_2 photocatalyst was 64.29 minutes. As a conclusion, Ag^+ was successfully impregnated on TiO_2 surface in which it gives significant impacts on the degradation of MO. Ag_2O/TiO_2 photocatalyst at eight hours of incubation time showed the best photocatalytic performance as the percentage removal of MO obtained was 84.94%.

IV. CONCLUSION

The objectives of the research were to prepare hybrid Ag_2O/TiO_2 photocatalyst by wet impregnation method with different incubation time as well as to observe the photocatalytic activity on the degradation of MO. Other than that, the prepared hybrid photocatalyst samples were also characterized using XRD, EDX and FESEM analysis. The XRD analysis illustrated the anatase structure of TiO_2. The EDX spectra showed the composition of Ag on TiO_2 surface while the mappings showed the presence of Ag with uniform distribution on TiO_2 surface. The FESEM images showed the spherical and square-like shape of TiO_2. The colour also changed from gray to white when Ag was incorporated. From the experiment, the Ag_2O/TiO_2 photocatalyst proved better photocatalytic performance than bare TiO_2, photolysis and also adsorption in the removal of MO dye. Moreover, the photocatalytic performance was also improved with increasing incubation time. The photocatalyst prepared at eight hours of incubation time showed an optimum result in which the photocatalyst was able to remove 84.9% of MO in three hours. The reaction kinetics also showed that the rate coefficient of Ag_2O/TiO_2 was 0.01078 min^{-1} and the half-life obtained was 64.29 minutes.

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