

Photocatalytic Activity of Modified TiO₂ for Methyl Orange Removal

Lim Ying Pei, Tan Huey Ling, Lim Ying Chin

Abstract: In this study, the researcher review on the modified TiO₂ preparation via wet impregnation method for dye removal application. The bare TiO₂ and Ag-TiO₂ that have been synthesized undergo characterizations using XRD, FESEM-EDX and UV-Vis spectroscopy. The XRD pattern showed that the synthesized TiO₂ was of pure anatase phase. The crystal structure of anatase TiO₂ was not disturbed upon doping with Ag. FESEM images revealed that the TiO₂ constitutes of various sizes of spherical and square-like shapes. EDX mapping illustrates that dopant metals are dispersed in a uniformed manner onto the TiO₂ support and appeared as metal oxide. The bare TiO₂ that has been modified acts as a photocatalyst to remove MO through the batch method. The effects of initial dye concentrations (5-25 ppm), pH solutions (2–9), catalyst loadings (0.5–4) g/L, and light sources (visible, solar, UV) were analyzed. It was discovered that photocatalytic experiment performed using Ag-TiO₂ has greater efficiency of MO removal that ranges from 32% to 100% in contrast to bare TiO₂ with MO removal of 12%-67% for comparable dosages of photocatalyst at initial MO concentration of 5 ppm in both alkaline and acidic conditions under UV irradiation. It was postulated that Ag-TiO₂ photocatalyst is the better candidate for effective dye removal.

Keywords: Ag-TiO₂, methyl orange, photocatalyst

I. INTRODUCTION

Various synthetic dyes were employed in numerous industries such as leather industry, textile industry, cosmetics, and others [1]. The current domination of about 100 000 different categories of dyes is led by the textile industries which produces at 7×10^5 per annum [2]. Additionally, the fabric dyeing stage has led to a total loss of more than 20% of the world dyes manufacture and become a main source of color that was discharged into the environment [3], [4]. The wastewater resulted from the textile industries contains various organic compounds that could be detrimental and harmful to the environment and humans.

Advanced Oxidation Processes (AOPs) has been proposed as a favorable alternative for the treatment of dye wastewater [5]. Among AOPs, the capability of heterogeneous photocatalysis to thoroughly eliminate dye from the water and mineralization organic water pollutant compounds is garnering more attention. In regard to this, titanium dioxide, TiO₂ is extensively used as photocatalyst because it has high

photo-activity, chemical resistant, low cost, and non-toxic. However, TiO₂ has a rather large bandgap value of 3.2 eV and high sensitivity to electron recombination that leads to a small specific surface area, low quantum efficiency and low adsorption abilities which therefore limits its uses in practical applications [6].

Noble metals such as platinum (Pt), silver (Ag), palladium (Pd) and gold (Au) were usually chosen as dopant material in order to solve these problems as they can capture the electron from photo-excitation TiO₂ faster and reduce the recombination rate of photo-generated charge carriers effectively. Specifically, silver (Ag) was favored due to its exceptional electrical and thermal conductivity as well as its high stability [7], [8].

In this work, preparation of bare TiO₂ and Ag-TiO₂ were carried out via wet impregnation method. The prepared photocatalyst undergoes characterizations using X-ray diffractometry (XRD), ultraviolet-visible spectroscopy (UV-Vis), energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM). The efficiency of Ag-TiO₂ to remove methyl orange was analysed through its photocatalytic property by varying the effect of Ag-TiO₂ dosage, dye concentration, pH and light source.

II. METHODOLOGY

A. Materials

Titanium dioxide (TiO₂) and sodium hydroxide (NaOH) were acquired from R&M Chemicals. Methyl orange (MO) with the molecular formula (CH₃)₂NC₆H₄NNC₆H₄SO₃Na and λ_{\max} of 460–480 nm was obtained from Sigma-Aldrich. Hydrochloric acid (HCl) was purchased from Fisher Scientific (M) while silver nitrate was purchased from Bendosen. All the chemicals used were of analytical grade and distilled water was used to prepare the solutions

B. Preparation of Ag-TiO₂ Photocatalyst

The Ag-TiO₂ photocatalyst was produced using commercial TiO₂ with silver nitrate as a precursor. The Ag-TiO₂ photocatalyst synthesis was done via wet impregnation method. In brief, 9.212 g of TiO₂ powder was dissolved into 50 mL distilled water, followed by the addition of 0.787 g of silver nitrate (AgNO₃) while being continuously stirred. Then, the solution was incubated in a water bath at 70 °C for 8 hours. Finally, the acquired sample was washed and annealed in a furnace at 450°C overnight. For comparison purposes, the preparation of bare TiO₂ was carried out using the same procedure excluding the metal dopant.

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C. Characterization of Ag-TiO₂ Photocatalyst

The morphology of selected samples was determined by characterizing with Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss SUPRA 40VP) together with the attached Energy Dispersive X-ray (EDX, Oxford Instruments). A gold coating was not necessary before the imaging due to the conducting property of TiO₂. Meanwhile, X-Ray Diffraction (XRD) (X'Pert Pro-MPD, Panalytical) system was used to analyze the crystal structure of photocatalyst, using a scanning range of 2θ = 10-90° with Cu Kα (λ=1.504Å) which was operated at 40 kV and 30 mA. The diffuse reflectance spectra (DRS) of the photocatalyst sample was acquired using Shimadzu 3600, UV-visible NIR spectrophotometer with BaSO₄ as the reference scatter.

D. Photocatalytic of Methyl Orange

The batch photocatalytic experiments of prepared Ag-TiO₂ was conducted in a 400 mL Pyrex glass beaker containing a varied amount of photocatalyst and 200 ml MO with an initial concentration of 10 ppm at pH 3. Continuous stirring was applied for the solution in all experiments. To develop equilibrium in adsorption, the reactor was initially kept in the dark for 15 minutes. Subsequently, 11W UV lamps (Philips) placed 8 cm from the glass beaker was irradiated to the reactor. The influence of catalyst loadings (0.5-4 g/L), pH solution (2-9), initial dye dosages (5-25 ppm) and light sources (visible, solar, UV) were investigated. The pH of the solution was modified by using 0.1M NaOH or 0.1M HCl. A 3 mL sample was obtained at different intervals for 180 minutes. The MO concentration in the samples was identified by UV-Vis spectrophotometer (Hach, DR2400 absorption at 460 nm, and standard calibration curve). The removal efficiency of MO was calculated using the following equation:

$$\xi = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

where ξ is MO removal efficiency, C_o and C_t are the concentration of MO at initial and after treatment in ppm

III. RESULTS AND DISCUSSION

A. Characterization of Synthesized Photocatalyst

1) X-Ray Diffractometer (XRD)

Fig.1 illustrates the XRD pattern for bare TiO₂ and Ag-TiO₂ photocatalyst. From the Fig.1, several significant diffraction peaks were observed at 2θ = 25.5°, 37.9°, 48.2°, 55.0°, 62.6°, 75° and 83° which corresponds to the general pattern of crystal plane anatase structure of TiO₂ photocatalyst (JCPDS card (PDF # 21-1272)). A similar analysis was also stated by [9]-[13]. Plus, no peaks were detected at 30° which would have indicated the absence of brookite (B). However, there were no diffraction peaks found in the XRD pattern for Ag-TiO₂ that correspond to the Ag phase. It is plausible that this occurred because of the low Ag loading which resulted to an insignificant change in crystallinity as the Ag⁺ ion radii are too big to substitute Ti⁴⁺ ions in the TiO₂ matrix [10]. Another possible reason is the uniform dispersion of silver particles among the anatase crystallites (as proven by the EDX analysis). This observation conforms to the report by [12] in regard to XRD

pattern where the low Ag concentration has resulted in no identification of characteristics peaks attributed to the transition metal oxides.

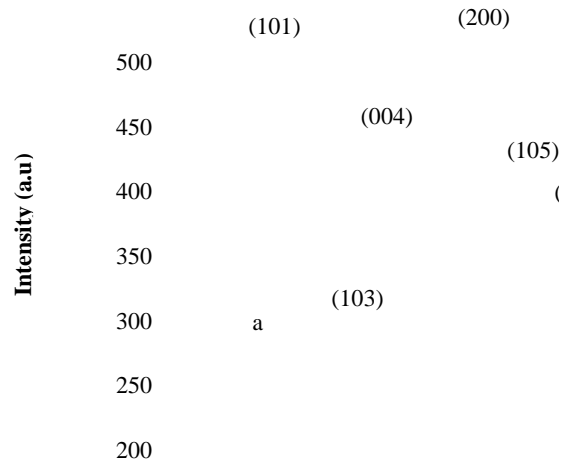


Fig. 1: XRD patterns for (a) bare TiO₂ and (b) Ag-TiO₂

2) Energy Dispersive X-ray Spectroscopy (EDX) Through EDX mapping, the relationship between elemental composition and particle morphological changes could be determined. Fig. 2 illustrates the EDX mapping for bare TiO₂ and Ag-TiO₂.

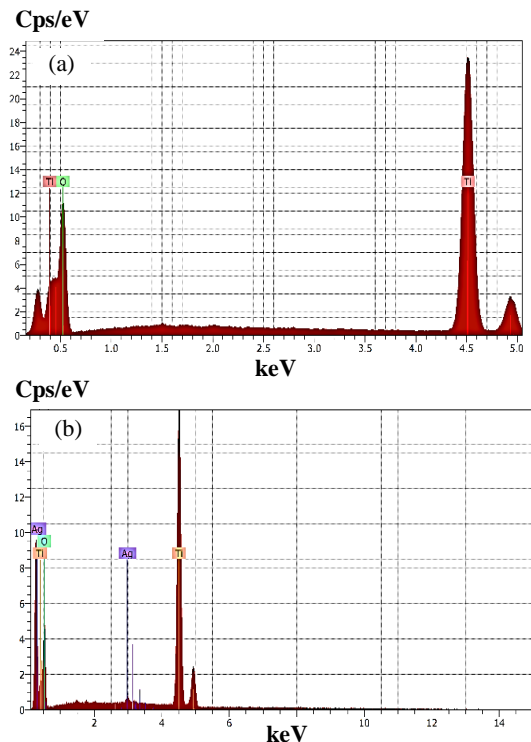


Fig. 2: EDX spectrum of (a) bare TiO₂ and (b) Ag-TiO₂ photocatalyst

Titanium (Ti) peaks can be detected at 0.45 keV and 4.51 keV while the oxygen (O) peak was observed at 0.52 keV. These elements (Ti and O) were derived from the TiO₂ compound and comprises of 75.72 atomic% of Ti and 24.28 atomic% of O as demonstrated in Table I.

Meanwhile, Ag was successfully detected upon the incorporation of the element as shown in Fig. 2(b), where Ag peaks were observed at 0.25 keV and 2.9 keV. The source of Ag particles is from the silver nitrate (AgNO₃) precursor handled during the Ag-TiO₂ photocatalyst preparation. Compounds Ti, O, and Ag in Ag-TiO₂ photocatalyst have content of 33.07 atomic%, 66.58 atomic%, and 0.34 atomic%, respectively. This EDX spectrum verifies the successful doping of Ag particle into the TiO₂ matrix.

Table I: Quantitative analysis of weight percentage bare TiO₂ and Ag-TiO₂

Element	Atom, C (at, %)	
	Bare	Ag-TiO ₂
Titanium	75.72	33.07
Oxygen	24.28	66.58
Silver	0	0.34

Based on Fig. 3, a highly uniform dispersion of Ag can be observed on the TiO₂ surface from the EDX mappings, which further confirmed the Ag element presence which had failed to be identified via the XRD analysis.

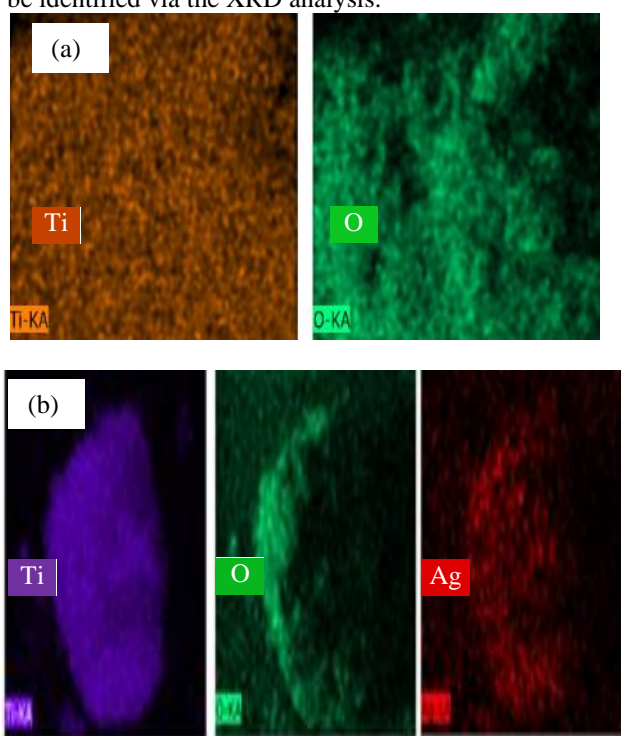


Fig. 3: EDX mappings of (a) bare TiO₂ and (b) Ag-TiO₂

3) Field Emission Scanning Electron Microscopy (FESEM)

Fig. 4 shows the FESEM images on the morphology of Ag-TiO₂. Bare TiO₂ constitutes of various sizes of spherical and square-like shape. Incorporation of Ag showed no noticeable changes in the shape of TiO₂. On top of that, there is an apparent color change from grey to white during the impregnation process. The EDX analysis predicts an even distribution of Ag on the TiO₂ surface and the color change upon doping of Ag also confirms the successful incorporation of Ag into TiO₂.

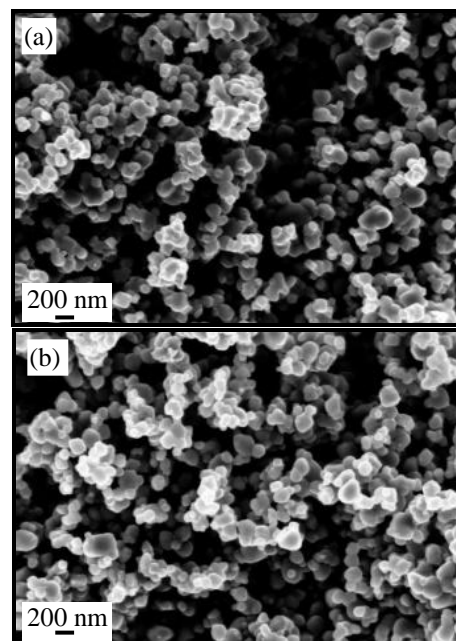


Fig. 4: FESEM images of (a) bare TiO₂ and (b) Ag-TiO₂

4) UV-vis spectroscopy

Fig. 5 shows the UV-vis spectra of bare TiO₂ and Ag-TiO₂ photocatalyst. It was investigated that Ag-TiO₂ photocatalyst has slightly higher optical absorption. Additionally, an increase in the maximum absorption was observed upon incorporation with Ag with bare TiO₂ and Ag-TiO₂ photocatalyst having the wavelength of 372 nm and 378 nm, respectively. Therefore, a higher absorption intensity has a quicker rate of electron-hole pairs formation on the surface of photocatalyst [1].

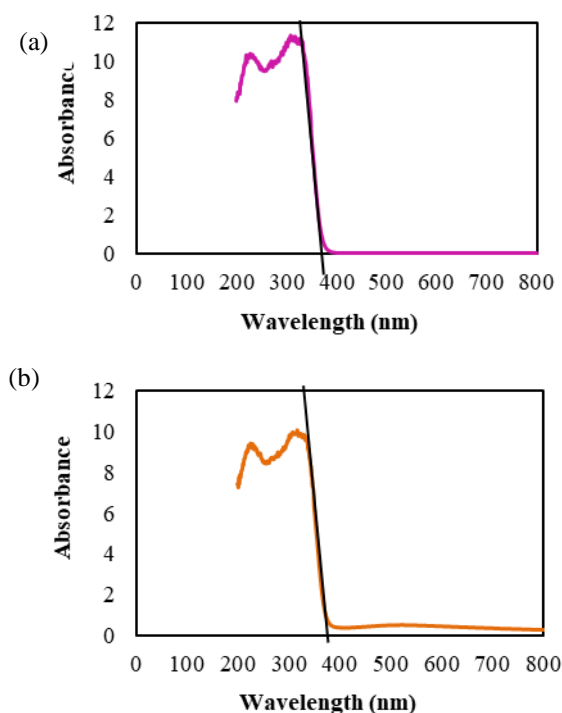


Fig. 5: UV-vis spectra for (a) bare TiO₂ and (b) Ag-TiO₂
The bandgap energy can be calculated by using [14] :

$$\text{Band gap energy}(E) = \frac{hc}{\lambda} \quad (2)$$



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where:

h = Plank's Constant = 6.626×10^{-34} Js

C = Speed of light = 3.0×10^8 m/s

λ = Wavelength = 374 nm

Since, $1\text{eV} = 1.6 \times 10^{-19}$ J (conversion factor)

Table II shows the TiO₂ and Ag-TiO₂ photocatalyst calculated bandgap energy. The result revealed that bare TiO₂ and Ag-TiO₂ photocatalyst has a bandgap energy of 3.33 eV and 3.28 eV respectively. Despite the slight reduction in the bandgap energy, the catalysts still require an activation under UV light irradiation, indicating an improvement of photocatalytic activity upon irradiation of UV-light. UV irradiation makes the generation of active species such as HO•, OH₂•, and H₂O₂ easier for Ag-TiO₂.

Table II: The wavelength and bandgap energy for bare TiO₂ and Ag-TiO₂

Sample	Wavelength, nm	Bandgap energy, E_g
Bare TiO ₂	372	3.33
Ag-TiO ₂	378	3.28

B. Photocatalytic Activities for Bare TiO₂ and Ag-TiO₂

Fig. 6 shows the color removal profile of MO under UV light irradiation for bare and Ag-TiO₂ photocatalyst. At pH 3, Ag-TiO₂ displayed a greater MO removal efficiency of 88% in comparison to bare TiO₂ with 65% within the duration of 3 hours. This investigation also demonstrated the improved TiO₂ photocatalytic performance when the metal dopant is present. The working mechanism of silver as a dopant is as shown below [15]:

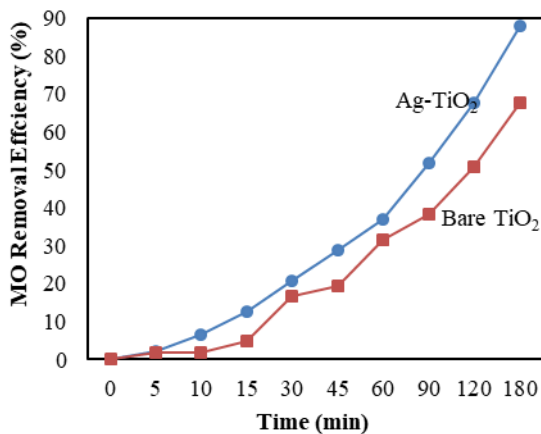
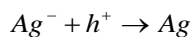
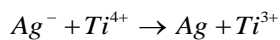
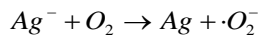
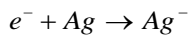


Fig. 6: Removal efficiency of MO for bare and Ag-TiO₂ under UV light irradiation (initial MO concentration = 10 ppm, pH 3, catalyst loading = 2 g/L)

Due to the inappreciable outcome on the bandgap energy improvement for bare and modified TiO₂ as well as adsorption efficiency (result not shown), it could be assumed that improvement in photocatalytic performance is responsible for the Ag particles increased capability to capture electron from photo-excitation TiO₂ and effectiveness in minimizing the recombination rate of photogenerated charge carriers [16].

1) Effect of Catalyst Loading

Fig. 7 shows the relationship between the effects of catalyst loadings and the removal efficiency of MO from 0.5 g/L to 4.0 g/L Ag-TiO₂ at pH 3 upon irradiation of UV light. It is investigated that a higher amount of photocatalyst leads to a higher removal efficiency of MO. This is because an increase in catalyst loadings usually increases the number of photons absorbed by the catalyst, which eventually generate a high number of hydroxyl radicals and produces higher removal efficiency of MO [17].

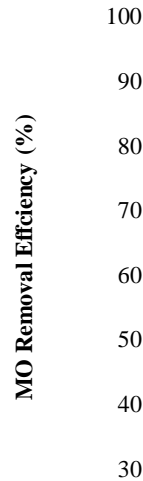


Fig. 7: Removal efficiency of MO for Ag-TiO₂ under UV light irradiation with different catalyst dosage initial MO concentration = 10 ppm, pH 3)

2) Effect of Dye Concentration

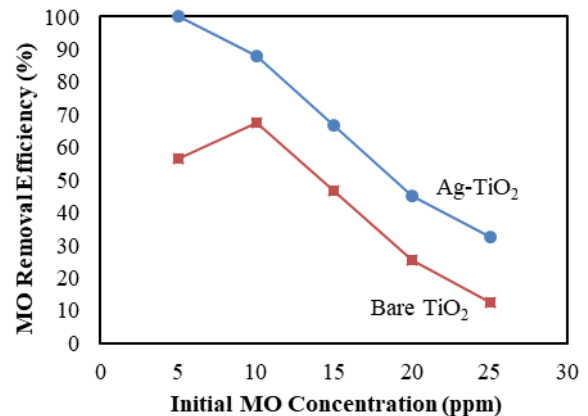


Fig. 8: Removal efficiency of MO for Ag-TiO₂ under UV light irradiation with different initial dye concentrations (pH = 3, catalyst loading = 2 g/L, t = 180 minutes)

Photocatalytic investigations were carried out with different initial MO concentrations of 5, 10, 15, 20 and 25 ppm with initial pH 3 and 2 g/L Ag-TiO₂ loading. Fig. 8 suggests that the MO removal efficiency is highly dependent on MO initial concentration. It was discovered that 100% of MO is removed within 180 minutes at 5 ppm MO concentration. As the dye concentration of 5 ppm is increased to 25 ppm, the removal efficiency of MO removal reduces from 100% to 35%. Similar results have been produced by [13] and [18].

Apparently, MO dye molecules are adsorbed on the active surface of the catalyst at low dye concentration followed by reaction with photogenerated holes and hydroxyl radicals on the surface of the catalyst. MO molecules are effectively degraded by these reactive species. However, as the concentration of MO increases with the fixed catalyst loading, photogenerated holes accounted for ·OH generation does not increase. There is competition for active sites among the MO molecules to perform the catalytic reaction, therefore MO removal efficiency experiences a reduction.

3) Effect of pH

Generally, the role of solution pH is very crucial in the photocatalysis process because this parameter identifies the charge of dye molecules, the adsorption of dyes onto the photocatalyst surface and the concentration of hydroxyl radicals. Trabelsi *et al.* (2016) suggest that point zero charges (pH_{zpc}) for TiO_2 is about to 6.8 [19], while co-doped Ag into TiO_2 shifted the pH_{zpc} to slightly acidic region. At pH lower than pH_{zpc} , TiO_2 surface turns into positive and vice versa, as shown in the following equation [20]:

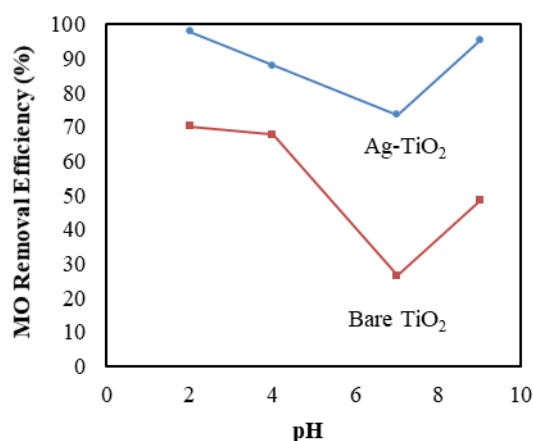
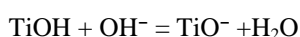
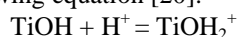


Fig. 9 : Removal efficiency of MO for bare TiO_2 and $Ag-TiO_2$ under UV light irradiation with different solution pH (initial MO concentration = 10 ppm, catalyst loading = 2 g/L, UV irradiation)

Fig. 9 illustrates the effect of pH on the removal efficiency of MO for bare and $Ag-TiO_2$ photocatalysts. Bare TiO_2 photocatalyst has a degradation efficiency of 70.2%, 67.7%, 26.4% and 48.3% at pH 2, 4, 7 and 9 respectively. Meanwhile, $Ag-TiO_2$ witnesses an increase in the MO removal efficiency at all pHs range investigated in comparison to bare TiO_2 . This is because metal-dopant is present which substantially enhances the interfacial electron transfer rates and charge carrier recombination rates, thus resulted in better photoreactivity [21].

Additionally, it is also suggested that MO molecules decomposed much easier and faster under both alkali and acidic conditions rather than in neutral condition (pH 7), inclining more towards the acidic condition. This analysis agrees with reports made by [22] and [23]. The catalyst surface was negatively charged in alkaline solutions while positively charged in acidic conditions. Moreover, MO molecule is found to be an anionic dye [24]. An increase in degradation efficiency of MO observed in acidic pH is attributed to the availability of photocatalyst surface with a

positive charge for the MO molecules absorption. Plus, there is more formation of hydroxyl radicals in acidic solution which leads to improvement in removal efficiency. Contrarily, hydroxide ions predominate when the solution pH is increased to alkaline medium. Ag presence in the $Ag-TiO_2$ diminishes the recombination rate which increases the availability of generated holes, allowing interaction with hydroxide ions to form reactive hydroxyl radicals which are responsible for MO molecules oxidation. This eventually leads to high removal of MO at alkali condition.

4) Effect of Light Source

According to Fig. 10 and Fig. 11, it is apparent that the MO solution under irradiation of UV yields the best color removal efficiency. The graph analyzes that bare TiO_2 attained 67.7% MO removal in 180 minutes in contrast to visible and solar light, which documented only 2.12% and 16.1%, respectively. This outcome was predicted and the difference in removal efficiency of MO was attributed to the input energy differences. Meanwhile, $Ag-TiO_2$ yields better MO removal efficiency compared to bare TiO_2 when similar experimental conditions were applied. This is probably because the silver particles able to capture electrons entrapped in the valence band, excited and jumped up into conduction band which generates charge carriers. Subsequently, this increased electrons-holes separation [25]. The lowest removal efficiency of MO is observed in photocatalytic degradation under visible light because the modified TiO_2 has bandgap energy that is still under UV range.

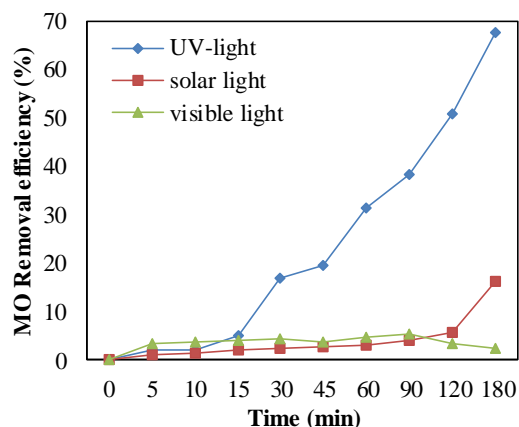


Fig. 10: Removal efficiency of MO dye under a different light source for bare TiO_2 (initial MO concentration = 10 ppm, catalyst loading = 2 g/L, pH 3)

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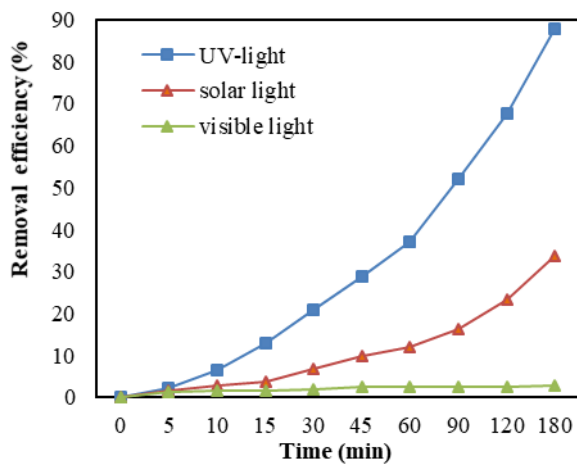


Fig. 11: Removal efficiency of MO dye under a different light source for Ag-TiO₂ (initial MO concentration = 10 ppm, catalyst loading = 2 g/L, pH 3)

IV. CONCLUSION

In brief, the preparation of Ag-TiO₂ photocatalyst was successfully carried out via the wet-impregnation method. The samples were all characterized using FESEM-EDX, UV-DRS, and XRD. The XRD patterns displayed intense diffraction peaks identified as bare anatase TiO₂ while no Ag phase was observed in the samples due to the low silver amount. The EDX result proves the existence of Ag in the sample. The result showed that Ag has an even distribution on the TiO₂ surface based on the surface morphology of bare TiO₂ and Ag-TiO₂. MO removal efficiency becomes the performance indicator to measure the photocatalytic activity. Ag-doped TiO₂ yields a better photocatalytic activity compared to bare TiO₂ because of the enhanced electron-hole separation. The initial dye concentration, catalyst loading, solution pH solution and light sources proved to affect the photocatalytic degradation. Use of Ag-TiO₂ photocatalyst at initial MO concentration of 5 ppm using 4 g/l catalyst loading at pH 2 under UV irradiation is the optimal experimental conditions for removal of MO.

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