

The Study of Methylene Blue Removal by Using Mixed-TiO₂ as a Catalyst under Solar Light Irradiation

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Abstract- To investigate the removal efficiency of Methylene blue (MB) by using TiO₂ with second metal (M) such as Cu, Al, Mg, Fe, Tb, La and Ce as catalyst which were prepared by impregnation method in amount of 2% M/TiO₂. The catalyst ratio that used in this reaction was 2 g/L, pH 5, temperature 30°C and 100 min in reaction time. The most effective catalyst was 2%Cu/TiO₂. Then the preparations of 2%Cu/ TiO₂ were compared; impregnation and sol-gel process. The study found that 2%Cu/ TiO₂ prepared by the im-pregnation method performed better activity. Therefore, we selected to prepare the catalyst by the impregnation method to study the amount of Cu in Cu/TiO₂ which was 0.5%, 1%, 4% and 8%Cu / TiO₂, results showed that 0.5%Cu/ TiO₂ performance is the highest. Then, the used amount of 0.5%Cu/ TiO₂ in reaction was studied which were 0.5, 1, 1.5 and 2 g/L. It found that 0.5 g/L showed the best ratio in MB removal. Moreover, the effects of pH in the range of 3-10, temperature between 30°C - 70°C, concentration of the MB solution and influence of irradiated light were examined. The results showed that at pH 9, temperature 30°C, lower concentration of MB solution were suitable for the removal of MB and the solar light is effective to degrade MB in solution.

Index Terms- Photodegradation; Mixed- TiO₂; Methylene blue; Catalyst

I. INTRODUCTION

Nowadays, we cannot refuse that the environmental concern has been attracted much attention in every organizations. For the industrial that participated in dye usages could also enhance the pollution to environmental through the waste water without proper treatment. The main chemical in waste water from this industrial was the excess dyes from their product. The main industrial which have been faced these problem such as textile, leather, cosmetic and printing – publication business. It is about 10,000 industrial worldwide which is dye consumed and it is excess of 107 kg/year [1]. In this number, it is about 1-15% of the dyes used are released to waste water.

There are water treatment methods such as such as coagulation, chemical oxidation, membrane separation, electrochemical process, adsorption techniques and photodegradation. Photodegradation has been considered as the promising method for organic waste removal from solution. [2] According to this reaction could be environmentally friendly and the catalyst could be re-used. Moreover, the solar light is effective enough for being irradiation light and it is inexpensive. The most well-known catalyst is the TiO₂ because it shows high

photocatalytic activity, photo-stability, non-toxic and commercial availability [3], [4]. The process is initiated by the photo adsorbed over the surface of TiO₂, the energy of photon need to be equal to or greater than band gap energy of semiconductor catalyst. Then, the electron may then be promoted from the valence band (VB) to the conduction band (CB). After the electron transit from VB, the electron hole (h⁺) is generated, this is electron deficiency. This step is induced the redox process with the adsorbed pollutant such as dye or other organic pollutant. The adsorbed water over the surface of TiO₂ which reacted with hole was proposed to produce the hydroxyl radical [5], [6], [7]. These radical could then react with the pollutant as well. However, the electron and hole could also recombine, leading to low photodegradation activity. The improvement of this process can be divided into 2 main categories. First, the catalyst could be reduced the possibility of the recombination. Second, increasing the pollutant adsorbed over the surface of catalyst. However, some of the researchers also improve other properties of catalyst such as the porous structure, the agglomeration over surface, crystal structure etc.

The enhancement of photocatalytic properties of TiO₂ by doping transition metal is the promising and attractive method because this could improve the separation of electron – hole and surface modification (porous, surface area,) [8], [9]. The normal doping metals such as Sn, V, Cr, W, Co, Cu, Fe, Ta, Ga, Tb, Ce, La, etc because they are found to be effective and the active site for these gas species easy to be produced [10] –[14]. After these metal mixed with TiO₂, they could from the rare earth oxide over surface of TiO₂. These species are found have polymorph, strong adsorption selectivity, good thermal stability, etc, due to their f-electron and multiple-electron configuration [15].

In this study, the second metal such as Cu, Fe, Tb, Ce, La, Al and Mg was added to TiO₂ for preparing as mixed TiO₂ catalyst. The suitable catalyst was then studied the optimum conditions in Methylene Blue (MB) through photodegradation process such as preparation method, pH, temperature, catalyst content, concentration of MB and reaction time.

II. EXPERIMENTAL

1. The preparation of M/TiO₂

For impregnation method, TiO₂ pellets which was purchased from CARLO ERBA was calcined at 500 °C for 4 hours and grinded in mortar before used. Then, the proper amount of metal salt (preparing Mg/TiO₂, used Mg(NO₃)₃.6H₂O) in solution was dropped to TiO₂. The mixture was stirred for well mixing and dried at 100 °C for overnight. The dried sample was crunched

and calcined at 500 °C for 4 hours. The resulting mixed oxide was then used as catalyst. The different mix oxide with TiO₂ was prepared in similar method but the specific metal salts were required.

The second method which is in interesting is sol-gel method, for preparing TiO₂-CuO₂. The starting metal salts of Ti and Cu are Titanium (IV) n-butoxide and Cu(NO₃)₂ which are dissolved in ethanol and water, respectively. Poly-ethylene glycol (PEG) was added to Cu(NO₃)₂ solution under vigorous stirring. Then the titanium (IV) n-butoxide solution was dropped into the mixture. The white precipitate was produced during dropping. Then, the 5 M NaOH and 5 M hydrazine were sequentially in to above slurry and the yellow precipitate was formed. The mixture was kept stirring for 15 min. The mixture was then washed by water and acetone and filtrated. The cake was then dried at 100 °C for overnight and calcined at 500 °C for 4 hours. [16]

2. Photocatalytic reaction

In order to study the effect of the second metal in M/TiO₂ catalyst which prepared by impregnation method, the different M which are Cu, Fe, Tb, Ce, La, Al and Mg over TiO₂ was selected. The solution of Methylene Blue (MB) was prepared at specific concentration and adjusted pH at 5. The solution of MB was stirred and heated to 30 °C, then the M/TiO₂ catalyst was added to the solution at content 2 g/L. The mixture was kept stirring and heated for 100 min while some of mixture was sampled at every 10-20 min. The mixture was subjected to centrifuge and the supernatant was measure the concentration of residual MB by Spectrophotometer at 665 nm.

For different parameter study, the experiment was similarly as above procedure whereas the interested parameter was varied.

3. Analytical method

The efficiency of catalyst was related to the % of MB removal which was calculated by following equation;

$$= \frac{C_{in} - C_{final}}{C_{in}} \times 100$$

% MB removal

where C_{in} and C_{final} denote to the initial and final concentration of MB (M), respectively.

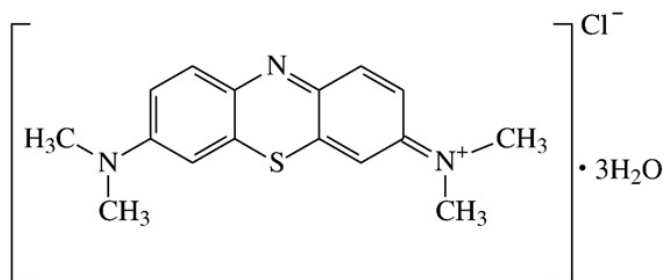


Figure1 Formular structure of MB

III. RESULTS AND DISCUSSION

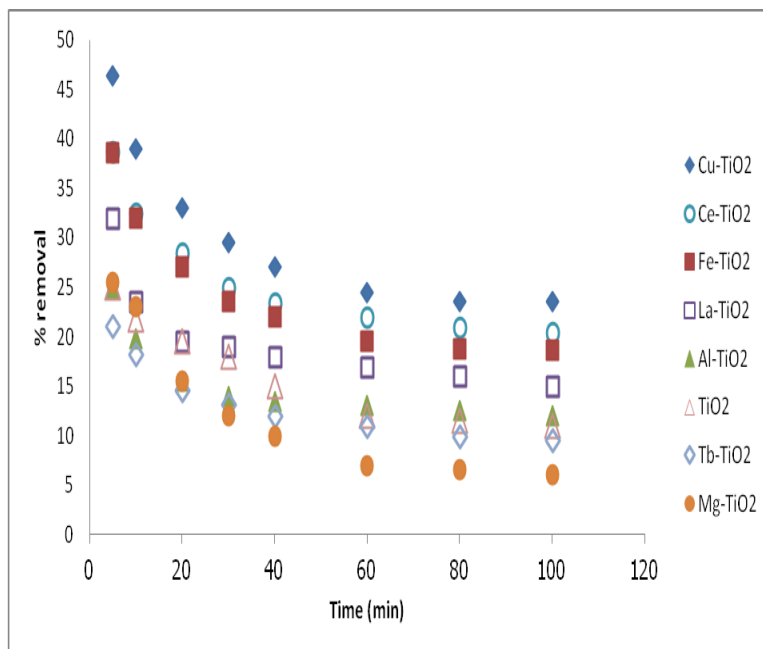


Figure1: Photodegradation of MB over mixed-oxide at pH 5, temperature; 30 °C, MB concentration; 3.2 mg/l, catalyst content; 2 g/l

Figure1 shows the effect of different second metal loading to TiO₂ by impregnation method. It is clearly that some mixed oxide showed lower activity than pure TiO₂ which are Tb-TiO₂ and Mg-TiO₂ whereas Cu-TiO₂ showed the highest photodegradation activity. Firstly, Hara et al. [17] found that the Cu₂O powder could be a catalyst for the decomposition of water to H₂ and O₂ under solar light. This could due to the easiness of the electron and hole generation over CuO₂ because the band gap of CuO₂ is only 2.0 eV. However, the main problem of pure Cu₂O in photocatalysis reaction is the recombination of electron and hole. Therefore, the mixed oxide with Cu₂O was prepared to discover the solution for this problem. Sevevirathna et al. [18]deposition nanoparticle of Cu₂O over TiO₂ powder and found that this composite catalyst could be active catalyst for the decomposition of water under light irradiation. Bessekhoud et al. [19] also studied the photoactivity of the same type of composite material using as catalyst in photodegradation of Orange II. The results show that this composite showed the superior photoactivity in the degradation of Orange II. They seem to suggest that the Cu₂O generated electron and hole, and then electron was transferred to the conduction band of TiO₂; resulting the preventing of the recombination process. Therefore, more electron from catalyst was produced and transferred to the target pollutant in solution. The enhancement of photodegradation of this composite system was achieved when compared to pure Cu₂O and TiO₂. This could be the reason to explain the results from Figure1 in the high activity of Cu-TiO₂.

The well known and simple methods to prepared mixed oxide for using as heterogenous catalyst are impregnation and co-precipitation (sol-gel process) methods. Therefore, this mixed oxide was prepared by these 2 methods and then the resulting catalyst was studied the activity in photodegradation of MB

under solar light irradiation. The results were shown in Figure 2 and suggested that the sol-gel process show higher activity. It has been mentioned that the photocatalyst activity was strongly related to the preparation method. For example, Au-TiO₂ was used as catalyst in water dissociation and the different fabrication methods were investigated [20]; deposition-precipitation, photo-deposition and wet impregnation methods. The results showed that the photo-deposition showed greater activity than others techniques. Boccuzzi et al. [21], [22] were also studied the properties and activity of Cu-TiO₂ in the hydrogenation of 1,3-cyclooctadiene. They found that the catalysts fabricated from different methods showed different properties and activity up to 100 times different. Recently, Shiping Xu et al. [23] studied 5 different methods which is widely used for prepared mixed oxide (metal-TiO₂) such as sol-gel, wet impregnation, chemical reduction of Cu salt by NaBH₄ (NR) and in situ photo-deposition in hydrogen generation from water. The results showed that the catalyst prepared from sol-gel method show highest activity which similarly to our results.

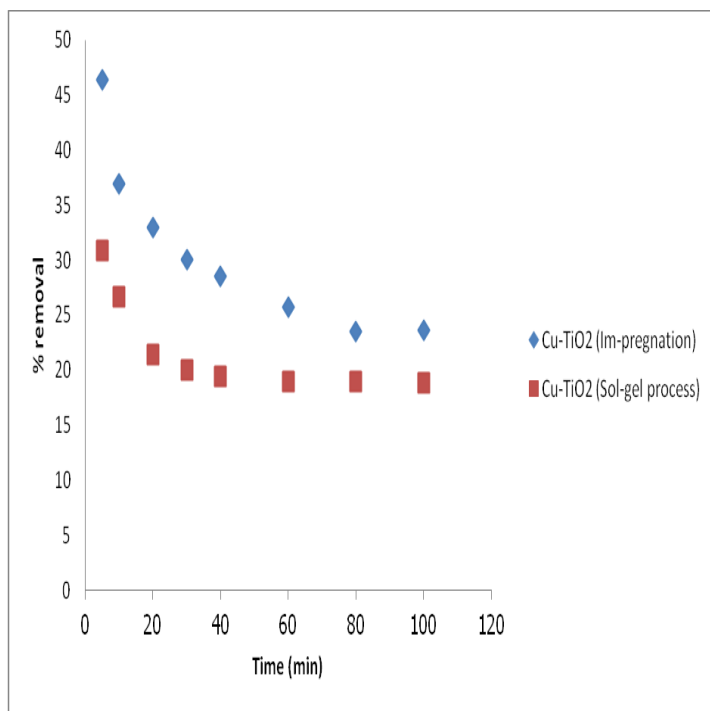


Figure 2: Photodegradation of MB over different Cu/TiO₂ at pH 5, temperature; 30 °C, MB concentration; 3.2 mg/l, catalyst content; 2 g/l

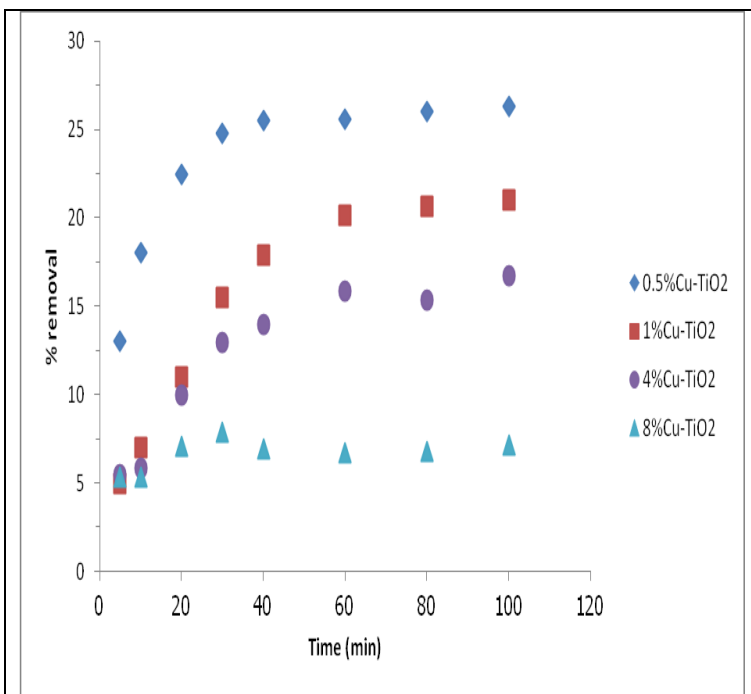


Figure 3: Photodegradation of MB over different loading Cu over TiO₂ at pH 5, temperature; 30 °C, MB concentration; 3.2 mg/l, catalyst content; 2 g/l

Figure 3 showed the effect of Cu loading in TiO₂ which are 0.5, 1, 4 and 8%. It clears that at lower Cu loading showed higher photocatalytic activity. It has been studied that the amount of metal in mixed oxide clearly effects the activity of catalyst [23], [24], [25]. They [23], [24], [25] claimed that only the optimum amount of the metal in mixed oxide could enhanced the activity with specific reaction and condition. M. Zhou et al. [24] studied the photodegradation of surfactant by investigates the effect of Fe loading in TiO₂. They also suggested that only specific ratio of Fe:Ti at 0.25 could reach the maximum activity of catalyst. Similarly, the results was supported in the studied of Mst. S. Nahar et al. [26] which investigated Fe-TiO₂ activity over the phenol degradation over visible light and also K. Melghit et al. [25] which studied the Congo red degradation under solar light with M-TiO₂ (M=V, Fe) as catalyst. However, the same catalyst could showed the different results as found in the investigation of N. A. Jamalluddin [27]. They studied the degradation of reactive dye by Fe-TiO₂ under ultrasonic irradiation. The effect of Fe loading study showed that at lower amount of Fe (between 0.2 – 1%) showed higher activity. They explained that crystal phase of TiO₂ could played the rule. The interfacial between the Fe and TiO₂ could be sufficiently factor. At higher loading could present the less interfacial surface. Therefore at lower loading of second metal could result in the high dispersion of second metal over TiO₂ and related to higher interfacial area. This reason could also explain our results and also support with the mechanism of normal photo degradation that the produced electron at CB will be transferred to the second metal surface. If the catalyst shows the higher interfacial area this process could occur easily and this will prevent the recombination of electron and hole effectively. This will result in the higher photoactivity of the catalyst.

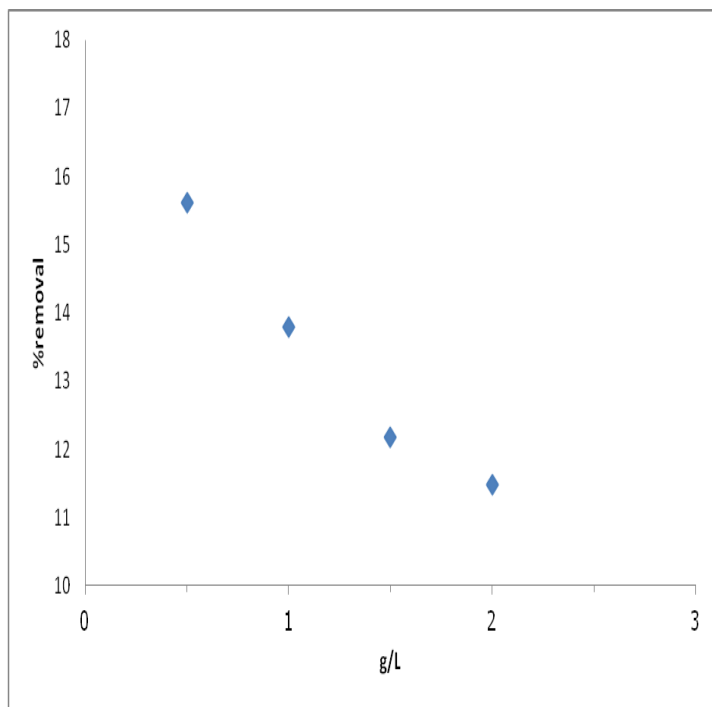


Figure 4: Photodegradation of MB over 0.5%Cu/TiO₂ with different content at pH 5, temperature; 30 °C, MB concentration; 3.2 mg/l.

The effect of catalyst amount which is 0.5%Cu/TiO₂ in the degradation of MB under solar light was studied and the results showed in Figure4. The catalyst amount between 0.5 – 2 g/L illustrated that at higher loading the % removal was lower than at less amount of catalyst. This showed that the more working sites over surface of catalyst were found in reaction at catalyst at 0.5 g/L. The similarly results were found in C. Chen et al. [28]. They studied the effect of catalyst concentration between 0.1-0.5 g/L in the photodegradation of Malachite green over TiO₂ under UV light. They confirm that at lower concentration, the increasing of photodegradation rate was achieved. Their results were also in agreement with the study of M. Saquib et al. [29]. They [28] were explained that at higher dosage of catalyst could enhance the aggregation of catalyst particles which causing the decreasing of surface area of catalyst. However, they also claimed that the light scattering by TiO₂ could occur when using high concentration of TiO₂, leading to the less photon adsorption to the catalyst and causing the decreasing of catalyst activity. This could be also the reason to explain our results in Figure4.

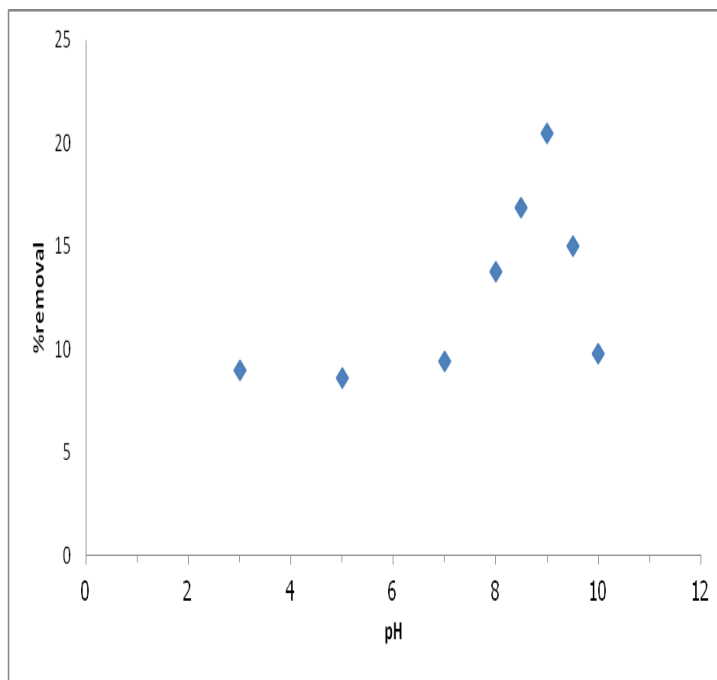


Figure 5: Photodegradation of MB over 0.5%Cu/TiO₂ at different pH, temperature; 30 °C, MB concentration; 3.2 mg/l, catalyst content 0.5 g/l.

The surface charge of TiO₂ could also effect by pH, therefore, effect of pH was also studied (pH between 3-10). The results were showed in Figure5 and clearly showed that pH = 9 was the optimum condition for the MB degradation under 0.5%Cu-TiO₂ catalyst. Normally, TiO₂ in aqueous system is amphoteric [30]. Therefore, at pH higher than isoelectric point the surface of TiO₂ is mainly in negatively charge. Thus, the electrical property of the TiO₂ is dependent with pH and this will affect the adsorb species. According to MB is cationic dyes, pH of dispersion should be in basic range or higher than zero point charge. S. Senthikumar et al. [31] studied the photodegradation of textile dye (MB) by TiO₂ under ultrasonic irradiation. The results showed that at higher pH, the % removal of MB was increased and stayed constant from pH at 10. Similarly, the optimum pH for the degradation of phenanthrene in surfactant solution containing TiO₂ was about 8 when compare pH at 3, 8 [32]. They also explained the results using the iso-electric point (IEP) of catalyst which claimed that IEP of TiO₂ is about 6.8 [33]. Therefore, roughly the proper pH for adsorption the positively species should be higher than 6.8. Regarding to our results, it could be also explained by using the IEP of Cu-TiO₂ which is below 7 as well as pure TiO₂ [34]. Therefore, the optimum pH for our system should be higher than 7 as in agreement with results from Fig 5 (pH higher than 6, the % removal was gradually increasing). However, at higher pH than 9 the % removal was slowly decreasing again, this could be due to the strongly negatively charge of TiO₂ was protonated and loss the negatively property for adsorption cationic dye.

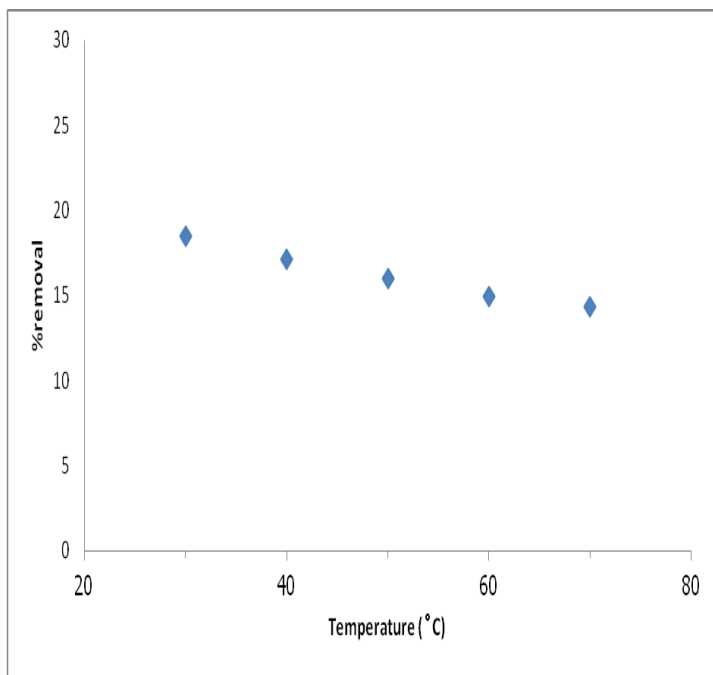


Figure 6: Photodegradation of MB over 0.5%Cu/TiO₂ at different temperature, pH 9, MB concentration; 3.2 mg/l, catalyst content 0.5 g/l.

From Figure6, the % removal of MB is slightly constant. It indicated that the MB degradation is independent with temperature. In the other hand, it could be concluded that the mixed oxide is tolerant to temperature or stable with temperature between 30- 70 °C. This means that the temperature could not change the surface morphology and property of TiO₂ to methylene blue. However, Ling et al. [36] studied the photodegradation of phenol and methylene blue using immobilized TiO₂ film. They found that the temperature between 30 – 50 °C could not affect the photoactivity of this catalyst. They explained that this reaction need very low activation energy or zero which achieved from photonic activation (5-20 kJmol⁻¹) [37]. These level is closed to the hydroxyl radical; reaction, suggested that this reaction may be involved hydroxyl radical reaction.

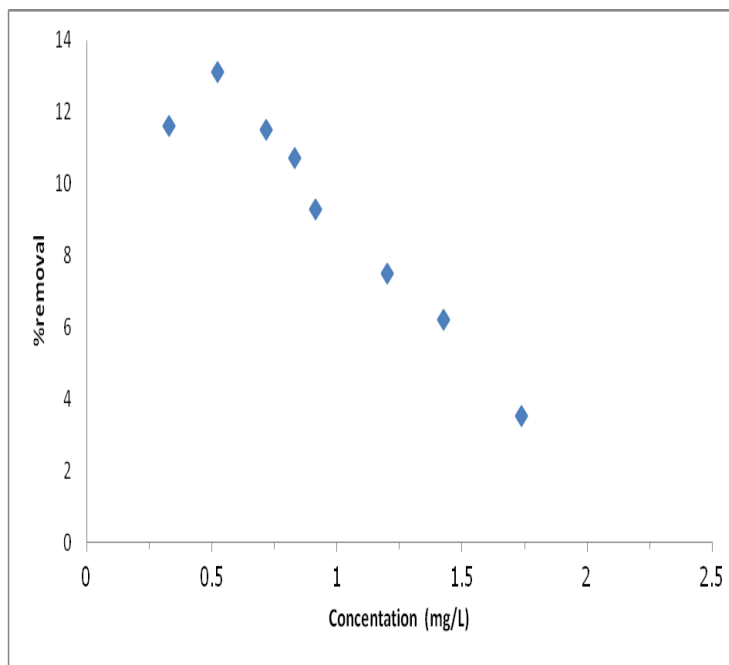


Figure 7: Photodegradation of MB over 0.5%Cu/TiO₂ at different initial MB concentration, pH 9, temperature 30 °C, catalyst content 0.5 g/l.

Figure7 showed the effect of the initial MB concentration in MB removal by using TiO₂ as photocatalyst. It clears that at lower concentration of MB, the removal of MB was increased. The similarly results were found in the study of Chen et al. [28], Ling et al. [36], Liang et al. [35]. Chen et al. [28] studied the degradation of Malachite green using TiO₂, at lower concentration of Malachite green can enhanced the % degradation. They explained that at higher concentration, the adsorption rate of malachite green was high and these could cause the competition of OH⁻ adsorption over TiO₂. Therefore, the OH⁻ production was low. These will cause the lower degradation efficiency. Ling et al. [36] also explained shortly of this influence that it is typical application of photocatalysis.

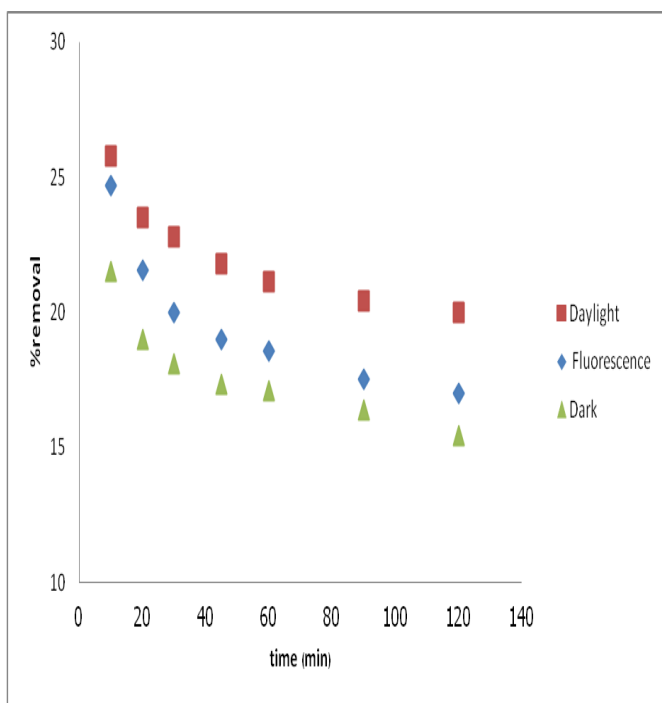


Figure 7: Photodegradation of MB over 0.5%Cu/TiO₂ at different light irradiation, initial MB concentration 0.5 mg/l, pH 9, temperature 30 °C, catalyst content 0.5 g/l.

The results in Figure 7 studied the effect of light irradiation. The reaction was taken place at 3 different conditions which were at daytime about noon (called daylight), at night and turn on the fluorescent light (called fluorescence) and at night time but turn off the light (called dark). These reactions were operated in the same laboratory and used the same condition. The results showed that the reaction at day time showed higher % MB removal, followed by the reaction at night time which turned on and off the fluorescence light. The reaction that operated in the dark is the removal of MB by adsorption process only whereas the reaction with light irradiation contained both adsorption and photodegradation of MB. Therefore, the % removal of MB was higher for the reaction with light irradiation. The comparison of the reaction with solar light and fluorescence, it is clearly that the reaction at day time showed higher % degradation. It is well known that the higher light density can excite more e⁻ and hole in TiO₂ and these will enhance photodegradation activity. The fluorescence light that used in this study was the normal fluorescence lamp at ceiling, it was not contact directly to the solution. Therefore, the excitation of TiO₂ could be less effective than the solar irradiation.

IV. CONCLUSIONS

A series of mixed oxide with TiO₂ were prepared by impregnation of metal salt to TiO₂ commercial grade. Tb/TiO₂ and Mg/TiO₂ show lower photodegradation activity than pure TiO₂ whereas Cu/TiO₂ showed the highest activity. The preparation of Cu/TiO₂ was then investigated, resulting that co-precipitation was the proper method. Then the experiment parameters was examine, % Cu loading, catalyst content, pH, temperature, MB concentration and reaction time. The results

showed that the optimum conditions were lower % Cu loading, catalyst content, MB concentration and temperature. In term of pH, it clears that pH about 9 showing the high % MB removal. The source of light irradiation was also studied; day light showed better activity than fluorescence. The reaction took place in the dark was the lowest activity.

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