

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

This research studied the activity of bilayer films, which are ZnO/TiO₂ and V₂O₅/TiO₂ films for the degradation of AO7 via photocatalytic reaction. In order to explain the optimum calcination temperature of ZnO and V₂O₅, the catalysts were characterized by scanning electron microscopy, and point of zero charge analysis.

4.1.1 Scanning Electron Microscopy

The surface of bilayer films was studied by using scanning electron microscopy (SEM, Hithachi, S-4800), and the results are shown in Figures 4.1 - 4.3. Figure 4.1 shows the SEM micrographs of the TiO₂ first layer that illustrates the uniform TiO₂ surface. The homogenous TiO₂ solutions covers all over the glass slide substrate. Figures 4.2 and 4.3 are the morphology of the 300ZnO/TiO₂ and V₂O₅/TiO₂ bilayer films, respectively. It can be seen in Figures 4.2a and 4.3a that the ZnO and V₂O₅ particles deposite thoroughly on the TiO₂ layer. Figures 4.2b and 4.3b show the porous structure of ZnO and V₂O₅ particle. The porous structure of ZnO and V₂O₅ particles is the result from the addition of PEG in the preparation step. This structure would allow the light and active radicals to penetrate into the TiO₂ first layer. However, the porosity of the V₂O₅ particles is lower than that of ZnO particles. It is possible the PEG may not be suitable to form the porous structure for V₂O₅ particles.

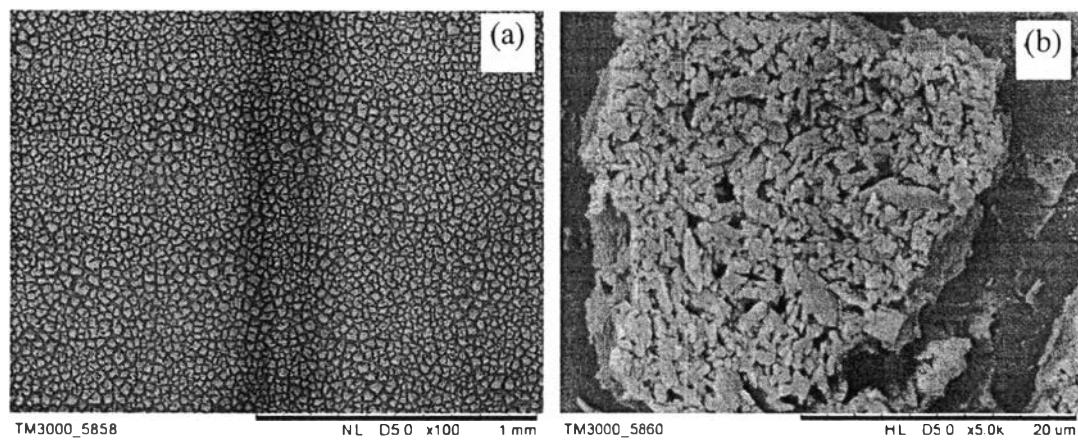


Figure 4.1 SEM micrographs of TiO₂ film at (a) 100X and (b) 5,000X magnification, respectively.

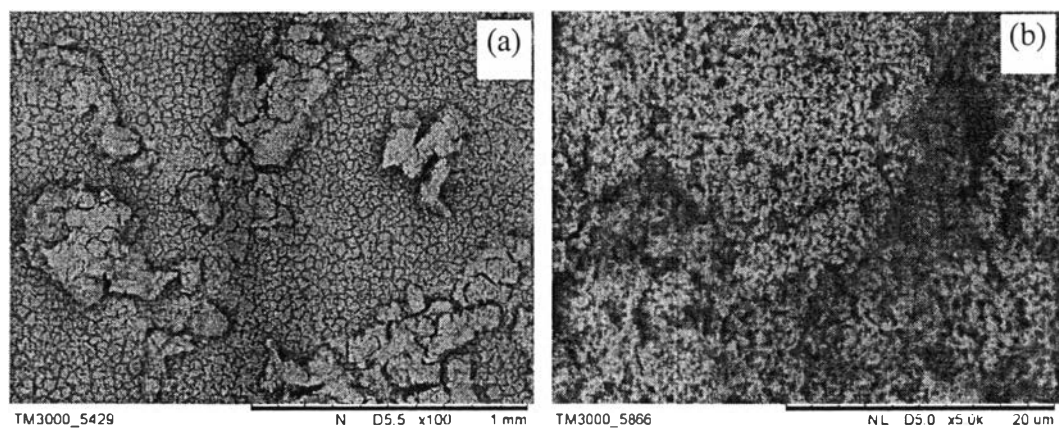


Figure 4.2 SEM micrographs of ZnO/TiO₂ film (a) 100X and (b) 5,000X magnification, respectively.

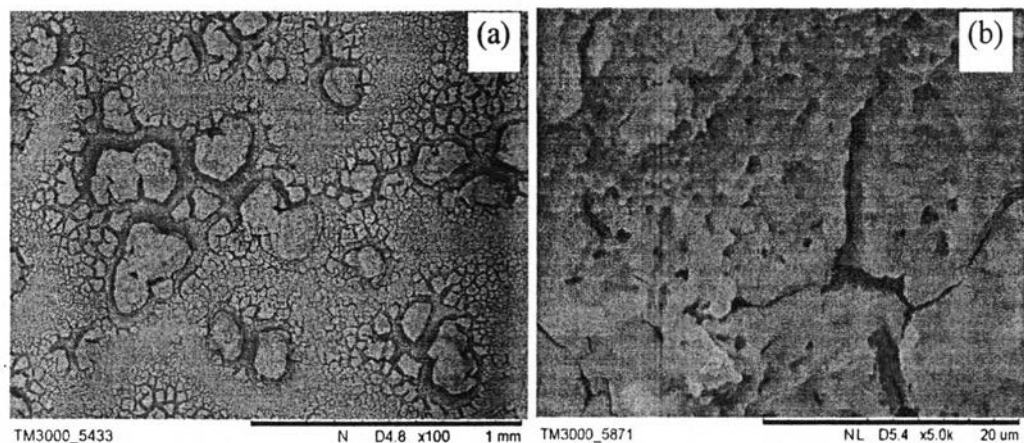


Figure 4.3 SEM micrographs of V_2O_5/TiO_2 film (a) 100X and (b) 5,000X magnification, respectively.

4.1.2 Point of Zero Charge Analysis

To study the charge on the surface of ZnO/TiO_2 film, the $300ZnO/TiO_2$, $500V_2O_5/TiO_2$ and TiO_2 films were subjected to a Zetasizer (Model ZS). Figures 4.4 shows the zeta potential of TiO_2 , $300ZnO/TiO_2$, $500V_2O_5/TiO_2$ and, respectively. The point of zero charge (PZC) is at the X-intercept, which is around 6.4, 8.5, and 4.3 for TiO_2 , $300ZnO/TiO_2$, and $500V_2O_5/TiO_2$ respectively. The charge of the films in the AO7 solution attains a negative charge at pH above the PZC and a positive charge at pH below the PZC (Muthirulan *et al.*, 2014). The charge affects the photocatalytic degradation of AO7. Although the AO7 degradation is highest at pH 3, the ZnO/TiO_2 film catalyst cannot be studied at that condition because the ZnO layer would leach out from the glass slide substrate (Rauf *et al.*, 2011).

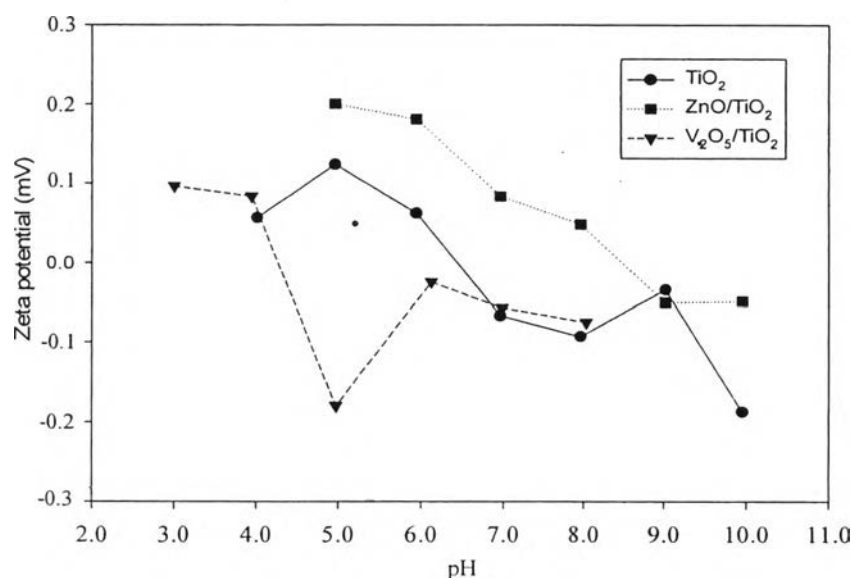


Figure 4.4 Zeta potential of TiO₂, ZnO/TiO₂, and V₂O₅/TiO₂ films.

4.2 Photocatalytic Activity

ZnO/TiO₂ and V₂O₅/TiO₂ were used as a bilayer film catalyst for the photocatalytic degradation of AO7. The first layer was coated by TiO₂, and then it was covered by the second layer, a mixture of ZnO and TiO₂ or V₂O₅ and TiO₂. To control the adsorption effect that could influence for the photocatalytic reaction, the bilayer film was immersed in the AO7 solution for 10 hr. The reactor was blocked from any interference from other light sources by using a black box. The conditions for the photocatalytic reaction were 30 °C, 300 rpm of stirrer speed, 5 lamps of UV-A light, 200 ml of 20 ppm AO7 solution. During the 8 hr reaction time, the UV-illumination was on for the first two hours (2 hr operating time). After that, the illumination was off for two hours (4 hr operating time). Before turning it on for two more hours (6 hr operating time) and off for the last two hours.

4.2.1 Photocatalytic Activity of 300ZnO/TiO₂ Film

Figure 4.5 shows the degradation of AO7 under the UV-A illumination for 8 hr. The result shows that the degradation of AO7 increases with the operating time. The highest photodegradation activity is 97.5%. When the bilayer

film is exposed to the UV radiation, the photogeneration of e^-/h^+ pairs takes place on the surface of the film. The p-n junction of ZnO/TiO₂ produces O₂[•] and OH[•] radicals. The OH[•] and O₂[•] radicals can easily react with AO7 molecules to form other species (Shifu *et al.*, 2008).

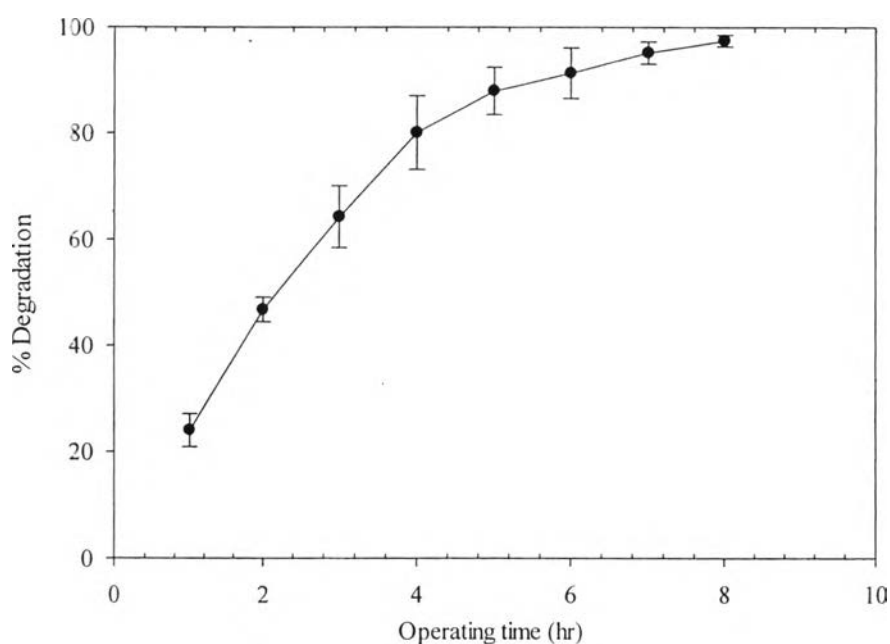


Figure 4.5 Photocatalytic degradation of acid orange 7 by the 300ZnO/TiO₂ bilayer film with the UV-A illumination for 8 hr.

4.2.2 TiO₂ Film on the Oxidation Energy Storage

In order to study the performance of oxidation energy storage on the bilayer films, the TiO₂ film was first tested. The TiO₂ film was calcined at 400 °C. The photocatalytic reaction were carried out at 30 °C, 300 rpm of stirrer speed, 5 lamps of UV-A light, 200 ml of 20 ppm AO7 solution. The UV-A light was turned on for 2 hr and turned off for 2 hr for the total of 8 hr operating time. Figure 6.6 shows the result from the photocatalytic degradation of AO7. The results indicate that the degradation of AO7 is about 6.7% after the first illumination and 4.6% after the second illumination. The reduction in the degradation is caused by the low activity of TiO₂. Moreover, the high recombination rate between electron and hole

prevents the electron and hole to produce OH^\bullet and O_2^\bullet radicals that can degrade the dye molecule. For this reason, the degradation of TiO_2 shows low photocatalytic activity even the photocatalytic system is under illumination (Jaiswal *et al.*, 2012). When there is on illumination, the highest degradation is about 0.3%. The result indicates that the degradation of AO7 is almost zero. It means that it is likely that there is no photocatalytic activity on the TiO_2 film in the dark condition. Moreover, in Figure 4.6, the result also shows a negative value about -0.1%. Because, during no illumination, there is the desorption of dye molecule from the TiO_2 film. The n-type TiO_2 alone cannot form the p-n catalyst so the degradation does not happen in the dark condition.

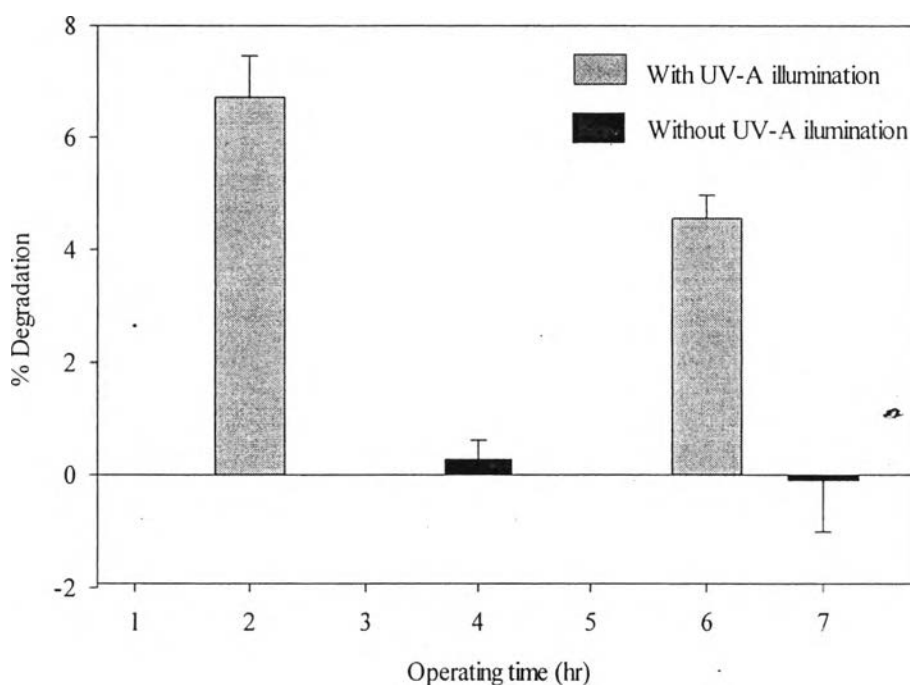


Figure 4.6 Photocatalytic degradation of acid orange -7 by the TiO_2 film with and without the UV-A illumination.

4.2.3 ZnO/ TiO_2 Bilayer Film on the Oxidation Energy Storage

The ZnO/ TiO_2 bilayer film was used as a catalyst to study the effect of oxidation energy storage on the photocatalytic activity with and without UV-A

illumination. In order to investigate the optimum reaction of oxidation energy storage, ZnO particles were calcined at 300, 400, and 500 °C, denoted as 300ZnO/TiO₂, 400ZnO/TiO₂, and 500ZnO/TiO₂, respectively. Figures 4.7 - 4.9 show the photocatalytic degradation of AO7 with the tested catalyst. Under the UV-A illumination, the results show that the degradation with the 500ZnO/TiO₂ film is about 42%, which is close to that of 400ZnO/TiO₂ film. Both 500ZnO/TiO₂ and 400ZnO/TiO₂ films have higher degradation than the 300ZnO/TiO₂ film. This may be because the energy band gap (E_g) is decreased at the high calcination temperature. The minimum energy required to excite the electron/hole pairs is decreased leading to the improvement of the separation efficiency of photogenerated charge (Ivonavo *et al.*, 2011). The p-n ZnO/TiO₂ bilayer film absorbs a small amount of energy and readily shifts the electron to the conduction band of TiO₂. At the same time, the hole will move in the opposite direction to the valence band of p-ZnO. The conduction band electron further reacts with dissolved oxygen to form O₂[•], whereas the hole reacts with water molecule to produce OH[•]. As a result, the active radicals are efficiently produced that can degrade the dye molecule and then achieve a high photocatalytic activity.

Another interesting effect of the 300ZnO/TiO₂ film, when there is no illumination, is the slight degradation of the dye molecule. It means that 300ZnO/TiO₂ can store the oxidation energy on their surface during the UV-A light. Takahashi and Tatsuma (2005) proposed that the p-type semiconductor can be combined with the n-type TiO₂ to form p-n junction. The hole is separated from electron and transferred into the bulk of p-type semiconductor for oxidation energy storage. Shifu *et al.* (2008) supported that, according to the energy band position, the valence band of ZnO is higher than that of TiO₂. The above position will attract the hole to flow into ZnO. Therefore, when there is no illumination, the trapped hole can react with water and generated OH[•] to decompose the dye molecule.

Furthermore, the result is compared with the TiO₂ film in Figure 4.6. It confirms that the degradation reaction taking place in the dark condition is the result from the formation of p-n junction of TiO₂/ZnO. However, after 4 hr, the UV-A light is turned on and turned off again, the results show in Figures 4.7 – 4.8. They indicate that the degradation decreases due to the loss of activity during the

photocatalytic reaction resulting in the decrease in the photocatalytic activity (Shifu *et al.*, 2008).

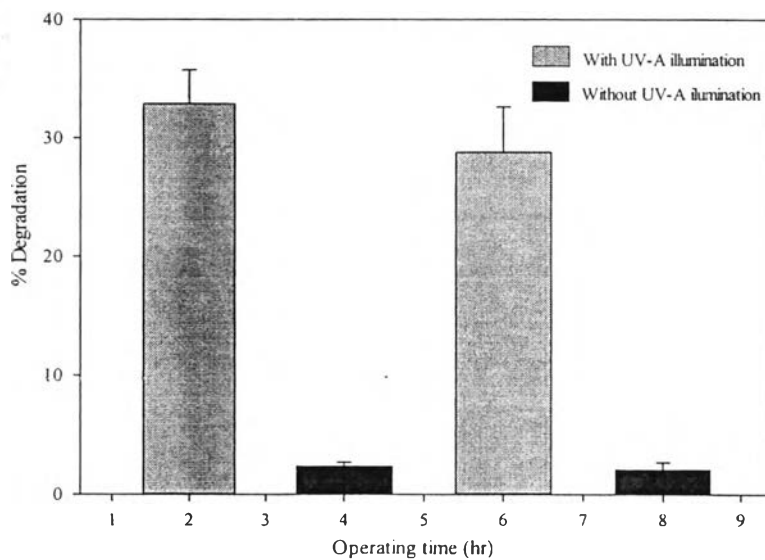


Figure 4.7 Photocatalytic degradation of acid orange 7 by the 300ZnO/TiO₂ film with and without the UV-A illumination.

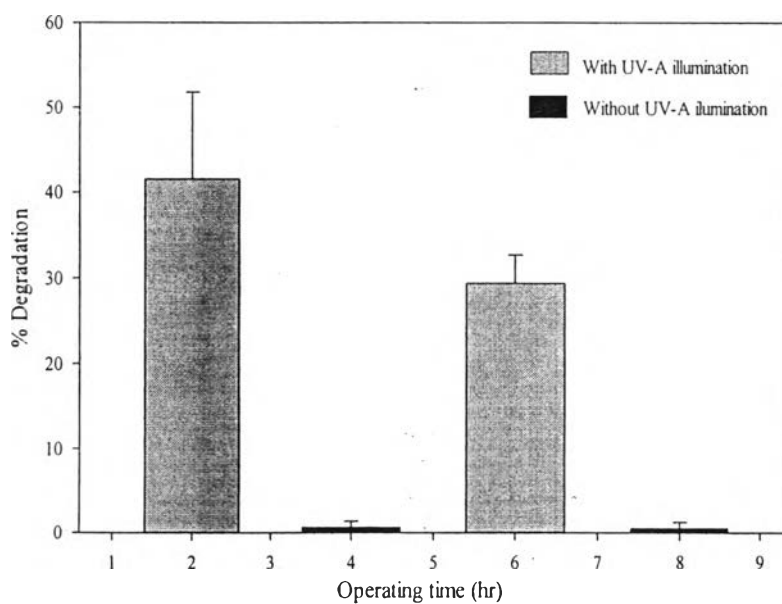


Figure 4.8 Photocatalytic degradation of acid orange 7 by the 400ZnO/TiO₂ film with and without the UV-A illumination.

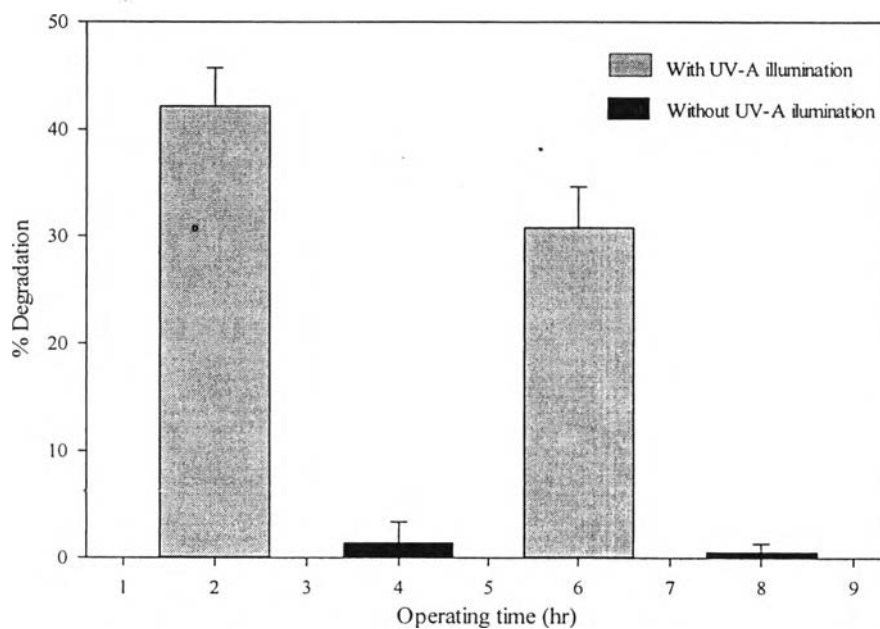


Figure 4.9 Photocatalytic degradation of acid orange 7 by the 500ZnO/TiO₂ film with and without UV-A illumination.

4.2.4 Effects of ZnO Loading of the 300ZnO/TiO₂ Bilayer Film on the Oxidation Energy Storage

In order to investigate the effect of ZnO loading on the 300ZnO/TiO₂ bilayer films, ZnO/TiO₂ was prepared at 50wt%, 75wt%, and 98 wt%. Figures 4.10 - 4.12 show the photocatalytic degradation of AO7 with the tested catalysts. The results show that the degradation of AO7 with and without illumination is also increased with the increase in the ZnO loading. Rauf *et al.* (2011) concluded that the increase in the catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the number of active radicals, leading to the discoloration of dye solution. In this research, it could be that the increase in p-ZnO can enhance the separation of photoexcited electron-hole pairs. The holes easily flow to the valence band of ZnO, whereas a high number of electrons move to the conduction band of TiO₂. The electrons and holes further combine with dissolved oxygen and water molecules to produce a high amount of O₂[•] and OH[•], so there is an increase in the active radicals to react with the AO7 molecules. Moreover, the high amount of ZnO helps to reduce the rate of e⁻/h⁺ recombination and resulting

in the high photocatalytic activity (Ku *et al.*, 2011). Table 4.1 shows the AO7 degradation by the ZnO/TiO₂ films. The effect of ZnO calcination temperature shows that the 300ZnO/TiO₂ has the highest photocatalytic activity, and the oxidation energy storage is achieved, whereas the 400ZnO/TiO₂ and 500ZnO/TiO₂ only show the AO7 degradation with UV-A illumination. From the effect of ZnO loading, the photocatalytic activity is enhanced by the increase in the ZnO loading and maximized at 98 wt%.

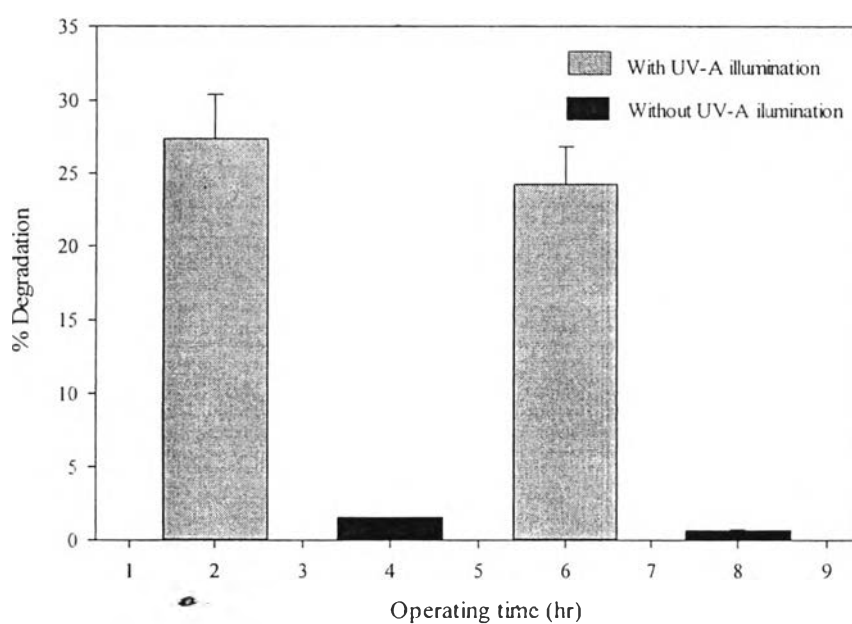


Figure 4.10 Photocatalytic degradation of acid orange 7 by the 300ZnO/TiO₂ film, 50wt% of ZnO, with and without UV-A illumination.

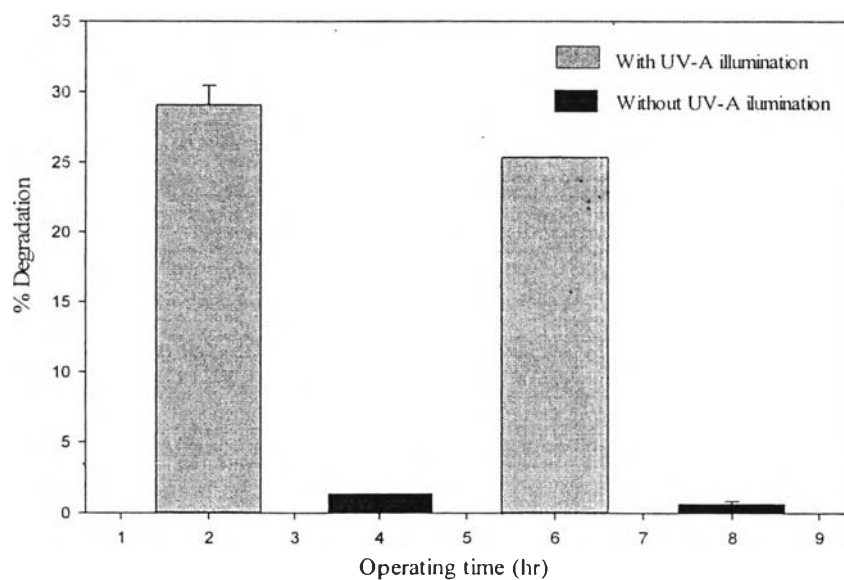


Figure 4.11 Photocatalytic degradation of acid orange 7 by the 300ZnO/TiO₂ film, 75 wt% of ZnO, with and without UV-A illumination.

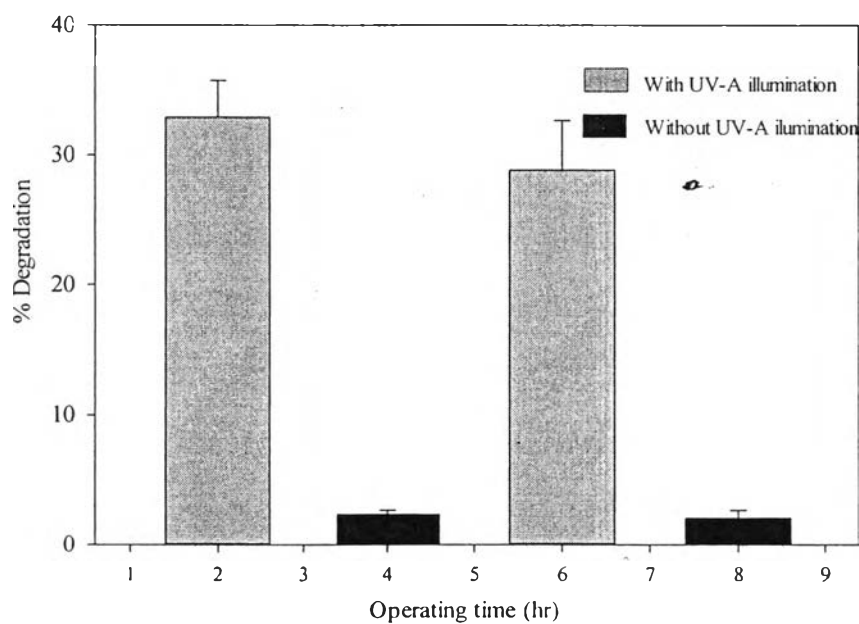


Figure 4.12 Photocatalytic degradation of acid orange 7 by the 300ZnO/TiO₂ film, 98 wt% of ZnO, with and without UV-A illumination.

Table 4.1 Acid orange 7 degradation from different ZnO/TiO₂ bilayer films

| | % AO7 degradation | | | |
|-------------------------------|----------------------|------|-------|------|
| | Operating time (hr)* | | | |
| | 2 | 4 | 6 | 8 |
| TiO₂ | 6.71 | 0.27 | 4.55 | 0.00 |
| 300ZnO/TiO₂ | 32.90 | 2.39 | 28.84 | 2.11 |
| 400ZnO/TiO₂ | 41.53 | 0.65 | 29.38 | 0.48 |
| 500ZnO/TiO₂ | 42.19 | 1.38 | 30.82 | 0.56 |
| 98 wt% ZnO | 32.90 | 2.39 | 28.84 | 2.11 |
| 50 wt% ZnO | 29.08 | 1.35 | 25.36 | 0.65 |
| 45 wt% ZnO | 27.38 | 1.56 | 24.25 | 0.67 |

* The UV-illumination was on for the first two hours (2 hr operating time). After that, the illumination was off for two hours (4 hr operating time). Before turning it on for two more hours (6 hr operating time) and off for the last two hours (8 hr operating time).

4.2.5 Reaction Rates of ZnO/TiO₂ Bilayer Film on the Oxidation Energy Storage

The rate of photocatalytic oxidation over TiO₂ can be expressed by Eq (4.1).

$$r = \frac{dC}{dt} \quad (4.1)$$

Where r is the oxidation rate of reactant (mol/l.s), C is the AO7 concentration (mol/l), t is the operating time (s) (Konstantinou and Albanis, 2004). Table 4.2 shows the reaction rates that during the UV-A illumination and no illumination. It can be clearly seen that the reaction rate with the illumination is higher than the rate without UV-A illumination. From the effect of ZnO calcination temperature, with UV-A

illumination, the 500ZnO/TiO₂ shows the highest reaction rate, followed by the 400ZnO/TiO₂ and 300ZnO/TiO₂ films. As explained before, it could be that the p-n junction between ZnO and TiO₂ can enhance the separation of e⁻/h⁺ pairs. The large number of radicals is produced by the efficient separation of e⁻/h⁺ pairs resulting in the high rate of AO7 degradation. In contrast, the result without illumination shows that the reaction rate of 300ZnO/TiO₂ is higher than the others. Due to the ability of the oxidation energy storage, the 300ZnO/TiO₂ can degrade the AO7 molecules resulting in the maximization of degradation rate (Rauf *et al.*, 2011).

The reaction rate increases continuously with the increase in the ZnO loading. At 98 wt% ZnO, the ZnO/TiO₂ bilayer film shows the maximum reaction rate with and without the UV-A illumination. It can be proposed that the high loading of ZnO actually contains the high number of active sites on the catalyst surface leading to the increase in the number of O[•] and OH[•] radicals. The increase in the radicals can induce the AO7 degradation and exhibits the high reaction rate. Pozen and Kambur (2011) suggested that a high loading of ZnO can increase the generation rate of e⁻/h⁺ pairs to enhance the degradation rate. Therefore, the maximum rate at 98 wt% of ZnO could be attributed to the high number of active site on the ZnO particles, which can increase the high number of radicals and increase the separation of e⁻/h⁺ pairs.

Table 4.2 Photocatalytic of AO7 degradation of reaction rates with and without UV-A illumination

| | Reaction rate ($\times 10^{10}$ mol/l.s) | | | |
|--------------------------|--|------|------|------|
| | Operating time (hr)* | | | |
| | 2 | 4 | 6 | 8 |
| 300 ZnO/TiO ₂ | 6.47 | 0.40 | 5.35 | 0.32 |
| 400ZnO/TiO ₂ | 7.58 | 0.29 | 6.38 | 0.05 |
| 500ZnO/TiO ₂ | 8.02 | 0.27 | 5.84 | 0.04 |
| 98 wt% ZnO | 6.47 | 0.40 | 5.35 | 0.32 |
| 50 wt% ZnO | 4.23 | 0.29 | 3.68 | 0.23 |
| 45 wt% ZnO | 3.63 | 0.37 | 3.15 | 0.27 |

* The UV-illumination was on for the first two hours (2 hr operating time). After that, the illumination was off for two hours (4 hr operating time). Before turning it on for two more hours (6 hr operating time) and off for the last two hours (8 hr operating time).

4.2.6 Stability of ZnO/TiO₂ Bilayer Film on the Oxidation Energy Storage

The stability of the 300ZnO/TiO₂ film was also studied by the 3-cycle photocatalytic reaction with and without UV-A illumination. The 1-cycle denotes that the 300ZnO/TiO₂ film is exposed under illumination for two hours, and then the illumination is turned off for two hours. For the illumination, the degradation is decreased from 42.80% to 13.67% when the operating time is increased at 2, 6, and 10 hr, respectively, as shown in Figure 4.13. Similarly, without illumination, the degradation is decreased from 2.29% to 0.91% at the operating time of 4, 8, and 12 hr. A possible reason could be explained that the active position on the ZnO/TiO₂ disappears during the reaction resulting in the decrease of photocatalytic activity (Shifu *et al.*, 2008).

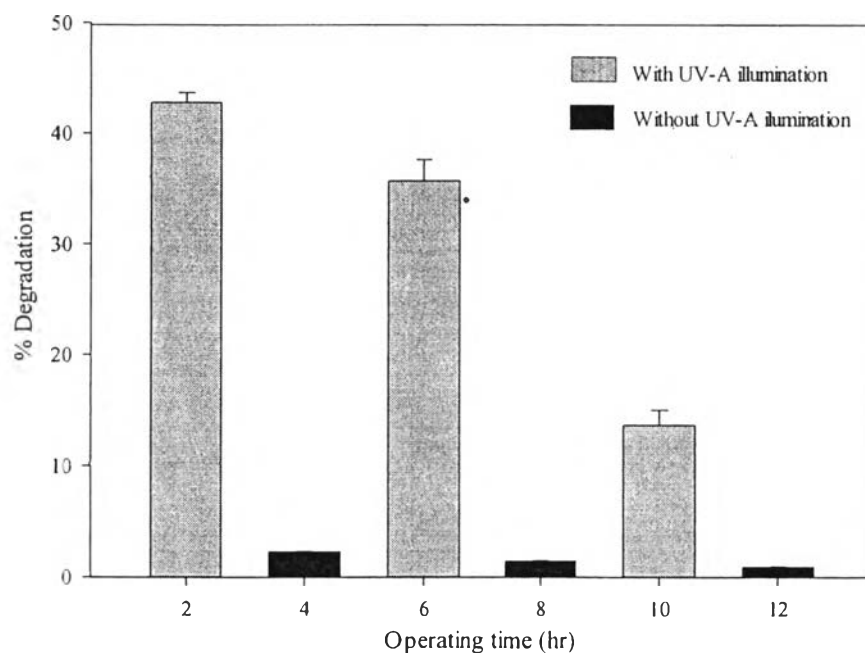


Figure 4.13 Stability of the 300ZnO/TiO₂ film on the photocatalytic degradation with and without UV-A illumination.

4.2.7 Effects of V₂O₅/TiO₂ Bilayer Film on the Photocatalytic Reaction

The V₂O₅ particles were calcined at 300 °C, 400 °C, and 500 °C and denoted as 300V₂O₅/TiO₂, 400V₂O₅/TiO₂, and 500V₂O₅/TiO₂, respectively, to study the calcined temperature effect of V₂O₅ particles on the photocatalytic reaction. Figure 4.14 shows the degradation of AO7 under UV-A illumination for 8 hr that the AO7 concentration does not change during the photocatalytic reaction at any given calcined temperature. It indicates that the preparation of V₂O₅/TiO₂ may not be suitable to form the catalyst film. The scanning electron microscopy (SEM) results show that the porosity of the V₂O₅/TiO₂ is lower than that of ZnO because PEG may not be suitable to form the porous structure of V₂O₅ particles. As explained before, the small porosity on the surface of V₂O₅/TiO₂ would prevent the light penetration into the TiO₂ layer. Therefore, the separation of e⁻/h⁺ could not completely be generated so the electrons and holes could not react with dissolved oxygen and water molecules to form O₂[•] and OH[•] resulting in low photocatalytic activity.

The degradation of AO7 with the 500V₂O₅/TiO₂ shows that the concentration of AO7 gradually decreases from 1 hr to 4 hr and increases beyond 4 hr, as shown in Figure 4.14. Nesic *et al.* (2013) suggested that at a high enough temperature, the heat force can raise electrons inside a solid particle and mobile to surface of particle. The high temperature is called Tammann temperature, which is 209 °C for V₂O₅ particle. Therefore, at 500 °C, electron diffusion can be easily driven toward V₂O₅ surface. The electrons on the V₂O₅ surface are moved to conduction band of TiO₂ and react with dissolved oxygen molecules to form O₂[•], whereas the holes transfer to the valance band of V₂O₅, then combining with the water molecules to form OH[•]. These radicals further degrade with AO7 dye molecules and decrease the AO7 concentration in 4hr. However, the concentration of AO7 is increased when the operating time is increased after 4 hr, which could be due to the effect of AO7 molecule desorption.

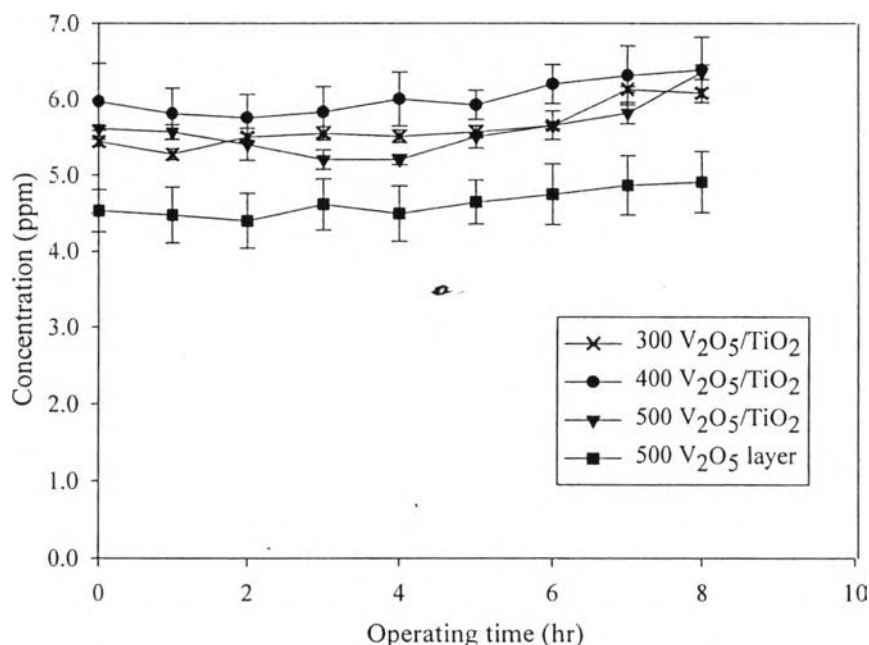


Figure 4.14 Photocatalytic degradation of acid orange 7 by the 300, 400, and 500V₂O₅/TiO₂ films with UV-A illumination.

4.2.8 Effects of V₂O₅ Loading on the V₂O₅/TiO₂ Bilayer Film on the Photocatalytic Reaction

The V₂O₅ loading was also studied in order to show its effect on the TiO₂ film photocatalytic. The 500V₂O₅/TiO₂ was prepared with 90.0 wt%, 45.0 wt%, 14.3 wt%, and 2.2 wt% V₂O₅. Figure 4.15 shows that all tested catalysts do not change the AO7 concentration during 8 hr. It may be because the loadings are too high even at 14.3 wt%, so that the V₂O₅ layer carries a high amount of V₂O₅ particles, which trend to agglomerate. It prevents the separation of e⁻/h⁺ pair. The electrons are trapped by other holes inside the bulk of V₂O₅ particles before transferring to the conduction band of TiO₂ layer. The increase in the V₂O₅ loading promotes fast recombination of e⁻/h⁺ pairs instead of the separation of e⁻/h⁺ pair. Therefore, the high e⁻/h⁺ recombination at the high V₂O₅ loading causes the reduction of photocatalytic activity (Chang *et al.*, 2011).

To avoid the fast recombination at the high V₂O₅ loadings, the photocatalytic activity of the V₂O₅/TiO₂ film was also prepared with a small amount of 2.2 wt% V₂O₅. Surprisingly, Figure 4.15 shows the opposite trend of the AO7 concentration during the photocatalytic degradation with the 2.2 wt% V₂O₅/TiO₂ film. The AO7 concentration for its degradation experiment with the 2.2 wt% V₂O₅/TiO₂ gradually decreases, while that with the other loadings are unchanged. The photocatalytic reaction was studied with the 2.2 wt% of V₂O₅ film with and without the TiO₂ layer at the same condition to confirm the effect of 2.2 wt% V₂O₅ loading. The experimental result with and without TiO₂ layer is clearly seen on Figure 4.16 that the AO7 concentration decreases by the V₂O₅/TiO₂ whereas the V₂O₅ film could not degrade the AO7 molecules resulting in the increase of AO7 concentration. Therefore, the decrease in the AO7 concentration is caused from the presence of the TiO₂ layer. Despite the presence of V₂O₅ layer, it is still unable to destroy the AO7 molecules. This is because during the preparation of the 2.2 wt% V₂O₅/TiO₂, the bilayer film barely contains V₂O₅. When the reaction is carried out with this bilayer film, only TiO₂ plays a major role on the photocatalytic process similar to the result of the TiO₂ film. The result proves that the AO7 concentration is diminished by the V₂O₅/TiO₂ bilayer film is the result from the presence of TiO₂ layer.

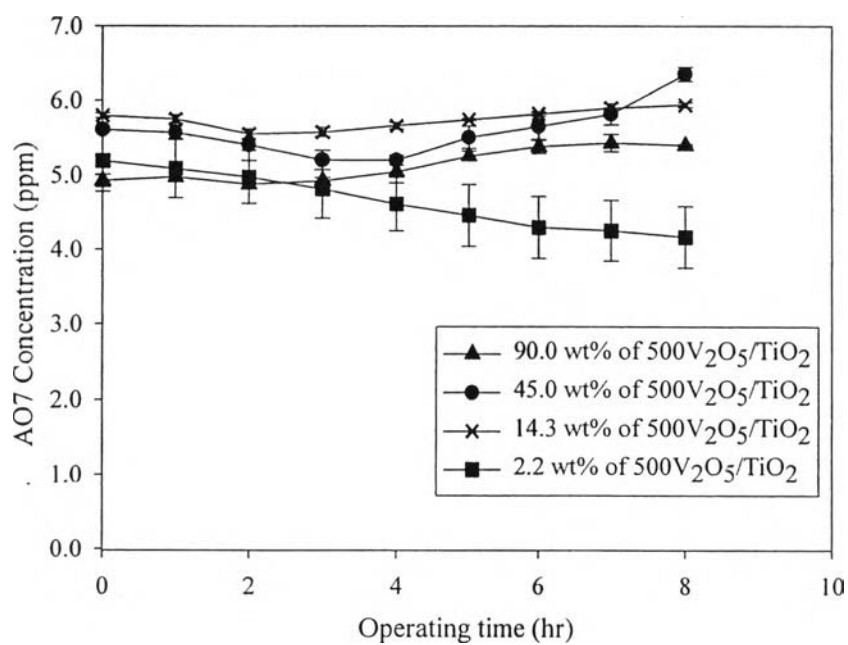


Figure 4.15 Photocatalytic degradation of acid orange 7 by 90.0 wt%, 45.0 wt%, 14.3 wt%, and 2.2 wt% of 500V₂O₅/TiO₂ film with the UV-A illumination.

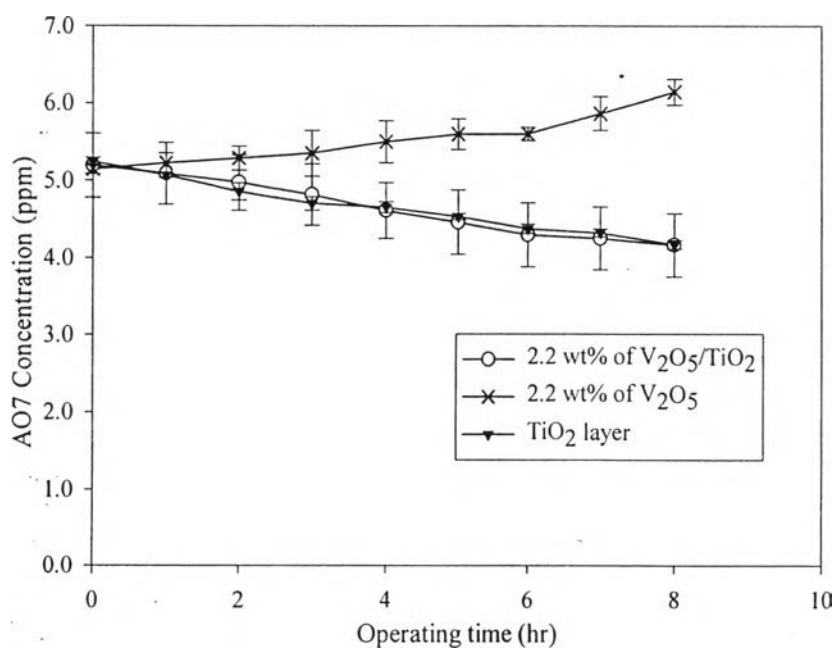


Figure 4.16 Photocatalytic degradation of acid orange 7 by 2.2 wt% of 500V₂O₅/TiO₂ film with the UV-A illumination.

4.2.9 pH Effects on the V₂O₅/TiO₂ Bilayer Film Activity on the Photocatalytic Reaction

Figure 4.4 shows that the PZC of V₂O₅/TiO₂ is about 4.5. Mutrirulan *et al.* (2014) concluded that at pH below PZC, the film catalyst is positively charged on its surface and adsorbed the negatively charged AO7 molecules. Moreover, the highest AO7 degradation was reported at pH 3. Therefore, the 500V₂O₅/TiO₂ was carried out at pH 3 to investigate whether the pH adjustment could increase the catalytic activity of V₂O₅/TiO₂.

Before the photocatalytic reaction, the 500V₂O₅/TiO₂ is allowed to adsorb AO7 for 10 hr. The results show that the initial AO7 concentration at pH 3 is lower than that at pH 7. It is because, at pH 3, the surface of 500V₂O₅/TiO₂ is positively charged and adsorbs the negatively charged AO7 molecules resulting in the low initial AO7 concentration, whereas, at pH 7, the surface is negatively charged leading to the low adsorption of AO7 molecules. Figure 4.17 shows that, at pH 3, the AO7 concentration is gradually increased with the operating time. It is contributed by the desorption of the AO7 molecules during the irradiation. Therefore, the adjustment at pH 3 helps to decrease the AO7 concentration during AO7 adsorption only, not the degradation.

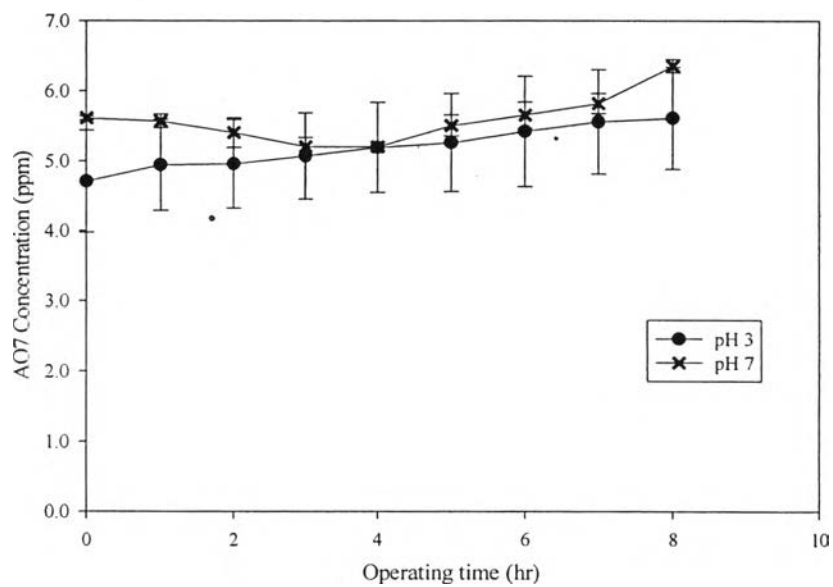


Figure 4.17 pH effect of 500V₂O₅/TiO₂ film on the photocatalytic degradation of AO7 with the UV-A illumination.