

## Chapter 4

### Discussion

#### 4.1 Syntheses and characterizations of Immo-TiO<sub>2</sub> films

##### 4.1.1 Syntheses of Immo-TiO<sub>2</sub> films

In this work, the Immo-TiO<sub>2</sub> films were prepared by direct mixing of commercial TiO<sub>2</sub> powder with latex and distilled water. The effect of parameters such as the amount of distilled water, the amount of latex, and the amount of commercial TiO<sub>2</sub> powder were studied to optimize the preparation of Immo-TiO<sub>2</sub> film for the maximum photocatalytic degradation of MB organic dye aqueous solution under UV light irradiation. The surface morphology of each Immo-TiO<sub>2</sub> film sample was governed by the amount of distilled water, latex, and commercial TiO<sub>2</sub> powder, which appeared as more or less dense of the TiO<sub>2</sub> particles on the surface of film causing the surface morphology and roughness of each film sample to be different. The different of the surface morphology and roughness of each film sample were influenced by (a) the viscosity of mixture, (b) the period of time for drying the film, and (c) the morphology of TiO<sub>2</sub> particles powder. The viscosity of mixture depends on the amount of distilled water, latex, and TiO<sub>2</sub>, decreased with increasing amount of distilled water resulting in fast deposition of TiO<sub>2</sub> particles to bottom of the mixture and finally increasing the TiO<sub>2</sub> particles on the bottom surface of the dried film. However, the opposite effect was observed when increasing amount of latex or TiO<sub>2</sub> as this would cause the viscosity of mixture to increase with the increasing amount of latex and TiO<sub>2</sub>. Therefore, in the case of using large amount of distilled water on the preparation of film would result in high surface morphology and roughness of film sample. The effect of varying the amount of distilled water on the viscosity of the mixture, and hence on the surface morphology and roughness of film sample, was more than the effect of varying the amount of latex and the amount of TiO<sub>2</sub>.

The period of time for drying of Immo-TiO<sub>2</sub> film at room temperature also depended on the amount of distilled water, latex, and TiO<sub>2</sub>. On increasing the amount of distilled water and the amount of latex the drying period was also increased

which resulting prolong deposition of TiO<sub>2</sub> particles to bottom of the mixture and finally increasing the TiO<sub>2</sub> particles on the bottom surface of the dried film. However, increasing the amount of TiO<sub>2</sub> showed opposite effect as the drying period decreased. The effect of varying amount of distilled water strongly influenced the drying period of Immo-TiO<sub>2</sub> film at room temperature than the effect of varying amount of latex and amount of TiO<sub>2</sub>.

The morphology of TiO<sub>2</sub> powders from various sources is different and this will affect the characteristic of the films. If the morphology of TiO<sub>2</sub> particles with high agglomerates is used the resulting film will have high surface morphology and roughness, and the opposite would result with low agglomerates. This result can be explained that the high agglomerates TiO<sub>2</sub> particles can deposit to the bottom of the mixture faster than the low agglomerates TiO<sub>2</sub> particles. Therefore, the effect of TiO<sub>2</sub> powders strongly influences the surface morphology and roughness of the films.

#### 4.1.2 Characterizations of Immo-TiO<sub>2</sub> films

##### 4.1.2.1 Scanning electron microscopy (SEM)

The SEM study gives the information about the surface morphology of all Immo-TiO<sub>2</sub> film samples on the rubber substrate. The difference in the surface morphology and roughness of each Immo-TiO<sub>2</sub> film sample can be revealed by this technique. The photographs and SEM images of TiO<sub>2</sub> anatase (Carlo Erba) and Degussa P25 are shown in Figures 11 and 12, respectively. It can be seen that the TiO<sub>2</sub> anatase powder showed a dense and highly agglomerates of TiO<sub>2</sub> particles more than Degussa P25. The particles of Degussa P25 are swelled and dispersed powder. The SEM images and cross section of Immo-TiO<sub>2</sub> anatase film samples prepared by varying the amount of distilled water, latex, and TiO<sub>2</sub> anatase are shown in Figures 13 and 14, respectively. Figures 13a show the surface morphology and roughness of Immo-TiO<sub>2</sub> anatase film samples prepared by varying the amount of distilled water. The surface morphology and roughness of Immo-TiO<sub>2</sub> anatase film samples increased with increasing amount of distilled water. This result can be explained as due to the large amount of distilled water caused the viscosity of the mixture to be low and prolonged the period of time for drying of Immo-TiO<sub>2</sub> anatase film at room temperature resulting, the TiO<sub>2</sub> particles to sink to bottom of the mixture faster than

when less amount of distilled water was used. As a result, more  $\text{TiO}_2$  particles appeared on the surface of the dried film on the reverse side, therefore, high the surface morphology and roughness of film sample. However, if much larger amount of distilled water (5 ml) was used, (Figure 13(5a)), some of  $\text{TiO}_2$  particles could be lost from the surface of film causing the film unstable. Figures 13b show the surface morphology and roughness of Immo- $\text{TiO}_2$  anatase film samples prepared by varying the amount of latex. The surface morphology and roughness of Immo- $\text{TiO}_2$  anatase film samples decreased with the increasing amount of latex. This result can be explained as due to the large amount of latex caused the viscosity of the mixture to increase and gave opposite result to that of water. The large amount of latex also prolonged the drying time for Immo- $\text{TiO}_2$  anatase film at room temperature but the effect was so minor to the surface texture. Therefore, the large amount of latex on the preparation of film gave low surface morphology and roughness of film sample. Figure 13c shows the surface morphology and roughness of Immo- $\text{TiO}_2$  anatase film samples prepared by varying the amount of commercial  $\text{TiO}_2$  anatase. The surface morphology and roughness of Immo- $\text{TiO}_2$  anatase film samples increased with the increasing amount of commercial  $\text{TiO}_2$  anatase. Generally, large amount of  $\text{TiO}_2$  should raise the viscosity of the mixture and lessen the drying time for Immo- $\text{TiO}_2$  film sample at room temperature. But due to the characteristic of the morphology of commercial  $\text{TiO}_2$  powder having dense and high agglomerate of particles, which exhibited its effect more pronounce than the effects of the viscosity of mixture and the drying time for Immo- $\text{TiO}_2$  anatase film at room temperature. Therefore, the final result was the large amount of commercial  $\text{TiO}_2$  anatase on the preparation of film yielded high surface morphology and roughness of film sample.

The corresponding SEM cross section of each Immo- $\text{TiO}_2$  anatase film sample is shown in Figure 14. The SEM cross section images clearly show the separation of  $\text{TiO}_2$  layer from the rubber layer when increasing amount of distilled water were used for the preparation of Immo- $\text{TiO}_2$  anatase films (Figure 14 (2a), (3a), (4a), and (5a)). These separations were not observed in the other samples indicating better mixture between the particles of  $\text{TiO}_2$  and the rubber latex.

The SEM images and cross section of Immo- $\text{TiO}_2$  Degussa P25 film samples prepared by varying the amount of distilled water, the amount of latex, and the

amount of TiO<sub>2</sub> anatase are shown in Figures 15 and 16, respectively. Figure 15a shows the surface morphology and roughness of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared by varying the amount of distilled water. The surface morphology and roughness of Immo-TiO<sub>2</sub> Degussa P25 film samples increased with the increasing amount of distilled water. This result can be explained as due to large amount of distilled water caused the viscosity of the mixture to be low and prolonged the drying time for Immo-TiO<sub>2</sub> Degussa P25 film at room temperature. The TiO<sub>2</sub> particles can sink to the bottom of the mixture faster than with less amount of distilled water resulting in more TiO<sub>2</sub> particles on the surface of the dried film (the reverse side). However, if much larger amount of distilled water (7 ml) was used, (Figure 15(5a)), some of TiO<sub>2</sub> particles could be lost from the surface of film causing the film unstable. Figure 15b shows the surface morphology and roughness of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared by varying the amount of latex. The surface morphology and roughness of Immo-TiO<sub>2</sub> Degussa P25 film samples increased with increasing amount of latex. This result can be explained as due to large amount of latex caused drying time for the TiO<sub>2</sub> particles deposition to the bottom of the mixture increase. The large amount of latex also high viscosity of the mixture but the effect was so minor to the surface texture. Therefore, the large amount of latex on the preparation of film gave high surface morphology and roughness of film sample. Figures 15c show the surface morphology and roughness of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared by varying the amount of commercial TiO<sub>2</sub> Degussa P25. The surface morphology and roughness of Immo-TiO<sub>2</sub> Degussa P25 film samples decreased with increasing amount of commercial TiO<sub>2</sub> Degussa P25. This result can be explained as due to large amount of commercial TiO<sub>2</sub> Degussa P25 raised the viscosity of mixture and lessen the drying time for Immo-TiO<sub>2</sub> Degussa P25 film samples at room temperature. The TiO<sub>2</sub> particles slowly sink to the bottom of the mixture and finally resulting low the TiO<sub>2</sub> particles on the surface of the dried film. Therefore, the large amount of commercial TiO<sub>2</sub> Degussa P25 on the preparation of film gave low surface morphology and roughness of film sample.

The corresponding SEM cross section of each Immo-TiO<sub>2</sub> Degussa P25 film samples are shown in Figure 16. The SEM cross section images clearly show the separation of TiO<sub>2</sub> layer from the rubber layer when increasing amount of distilled

water were used for the preparation of Immo-TiO<sub>2</sub> anatase films (Figures 16 (2a), (3a), (4a), and (5a)). These separations were not observed in the other samples indicating better mixing between the particles of TiO<sub>2</sub> and the rubber latex.

#### 4.1.2.2 X-ray powder diffraction (XRD)

The XRD peaks at  $2\theta = 25.50$  (101) and  $48.0^\circ$  in the spectrum of titanium dioxide are easily identified as the crystal of anatase form whereas the peaks at  $2\theta = 27.50$  (110) and  $54.5^\circ$  arise from the crystal of rutile form (Yoshio, et al., 1998). The XRD intensities of the anatase (101) and the rutile (110) peaks were also analyzed. The diffraction peaks for the anatase and rutile phase have been marked with 'A' and 'R', respectively, with the corresponding diffraction planes given in parenthesis. From Figure 18, A well-crystallized anatase form has been found for the Immo-TiO<sub>2</sub> anatase as shown in Figure 18c, which corresponds well with the commercial pure anatase powder as shown in Figure 18a. The same result was observed for the Immo-TiO<sub>2</sub> Degussa P25 as shown in Figures 18d and 18b, respectively. In addition, the other peak (the broad peak) of both Immo-TiO<sub>2</sub> thin films corresponding to the amorphous form of the rubber substrate is present in the diffractograms as evident from Figure 18e. The broad peak of Immo-TiO<sub>2</sub> anatase is observed at a much lower intensity than the broad peak of Immo-TiO<sub>2</sub> Degussa P25, indicating that the Immo-TiO<sub>2</sub> anatase has high content of TiO<sub>2</sub> particle on the surface (dense and coverage) of film than the Immo-TiO<sub>2</sub> Degussa P25, corresponding to the result from the SEM technique. The surface with high content of TiO<sub>2</sub> particles can decrease X-ray penetrate into the rubber substrate, therefore, the broad peak of the Immo-TiO<sub>2</sub> anatase showed a much lower intensity than that of the Immo-TiO<sub>2</sub> Degussa P25 and of the rubber substrate as shown in Figures 18c, 18d and 18e, respectively.

## 4.2 Photocatalytic activities of methylene blue (MB) by Immo-TiO<sub>2</sub> films

### 4.2.1 Photocatalytic degradation of methylene blue (MB) by Immo-TiO<sub>2</sub> films

The photocatalytic activities of these film samples were to be evaluated using methylene blue (MB) as a model organic dye compound. The photocatalytic

activities of film samples are studied in the degradation of methylene blue aqueous solution under UV irradiation. In the case of the simple photocatalytic reaction under UV-light irradiation, the degradation of MB should go through the interaction with the electron-hole pair ( $e_{CB}^- - h_{VB}^+$ ) as usual. The proposed MB degradation mechanism for the irradiated  $TiO_2$  system is summarized in equations 1-8 (Houas, et al., 2001).

1.  $TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}^+$
2.  $(O_2)_{ads} + e_{CB}^- \rightarrow O_2^{\bullet-}$
3.  $(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h_{VB}^+ \rightarrow H^+ + OH^{\bullet}$
4.  $O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$
5.  $2 HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
6.  $H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^-$
7.  $R_{(ads)} + OH^{\bullet} \rightarrow \text{degradation products}$
8.  $R_{(ads)} + h_{VB}^+ \rightarrow \text{degradation products}$

In step (2),  $(O_2)_{ads}$  comes from the  $O_2$  that was present in the system and was adsorbed onto the surface of the catalyst. In the degrading of MB, step (7)  $R = MB$  and since MB has a cationic configuration it should be favorably adsorbed to the negative sites of the as-prepared  $TiO_2$  surface, e.g.,  $Ti-O^{(-)}$  and subsequently attacked by the very active  $OH^{\bullet}$ , leading to the destruction of the MB molecule.

In generally, the photocatalytic reaction on the  $TiO_2$  surface is very sensitive to its surface structure because the photocatalytic is a surface reaction. The larger the surface area (high surface morphology and roughness), the more the photocatalytic reaction takes place. The photocatalytic activities of Immo- $TiO_2$  anatase

film samples prepared with varying amount of distilled water, amount of latex, and amount of commercial  $\text{TiO}_2$  anatase are summarized in Table 3. The photocatalytic activities of Immo- $\text{TiO}_2$  anatase film samples prepared with varying amount of distilled water at 1 ml, 2 ml, and 3 ml showed very similar and good performances. The Immo- $\text{TiO}_2$  anatase film sample prepared with 3 ml of distilled water showed slightly better photocatalytic activities than the other two films. The order of activities of Immo- $\text{TiO}_2$  anatase film is 3 ml > 2 ml > 1 ml in varying amount of distilled water due to the surface morphology and roughness of the film increased with the increasing amount of distilled water. The efficiencies of photocatalytic degradation of MB as a function of times of Immo- $\text{TiO}_2$  anatase film samples prepared with varying amount of distilled water are shown in Figure 56.

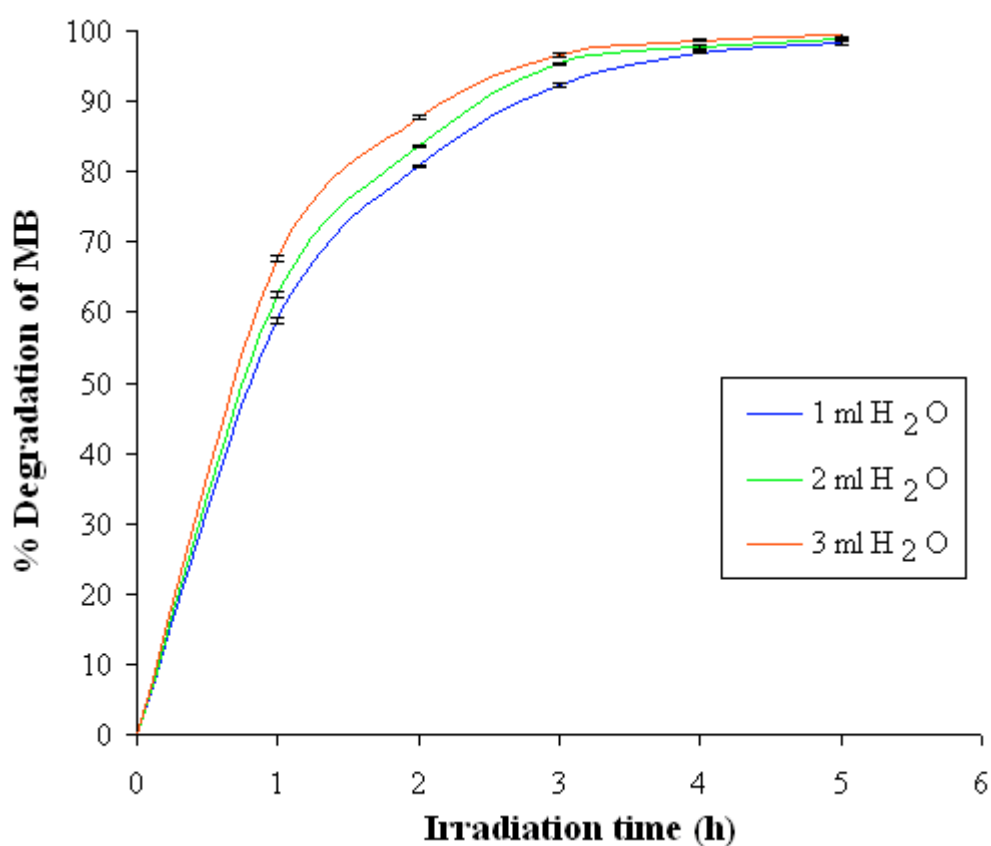


Figure 56 The efficiencies of photocatalytic degradation of MB as a function of times of Immo- $\text{TiO}_2$  anatase film samples prepared with varying amount of distilled water (including adsorption)

The photocatalytic activities of Immo-TiO<sub>2</sub> anatase film samples prepared with varying amount of latex at 3 ml, 5 ml, 7 ml, and 9 ml showed very similar and good performances. The Immo-TiO<sub>2</sub> anatase film sample prepared with 3 ml of latex showed slightly better photocatalytic activities than the other films. The order of activities of Immo-TiO<sub>2</sub> anatase film is 3 ml > 5 ml > 7 ml > 9 ml in varying amount of latex due to the surface morphology and roughness of the film decreased with the increasing amount of latex. The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> anatase film samples prepared with varying amount of latex are shown in Figure 57.

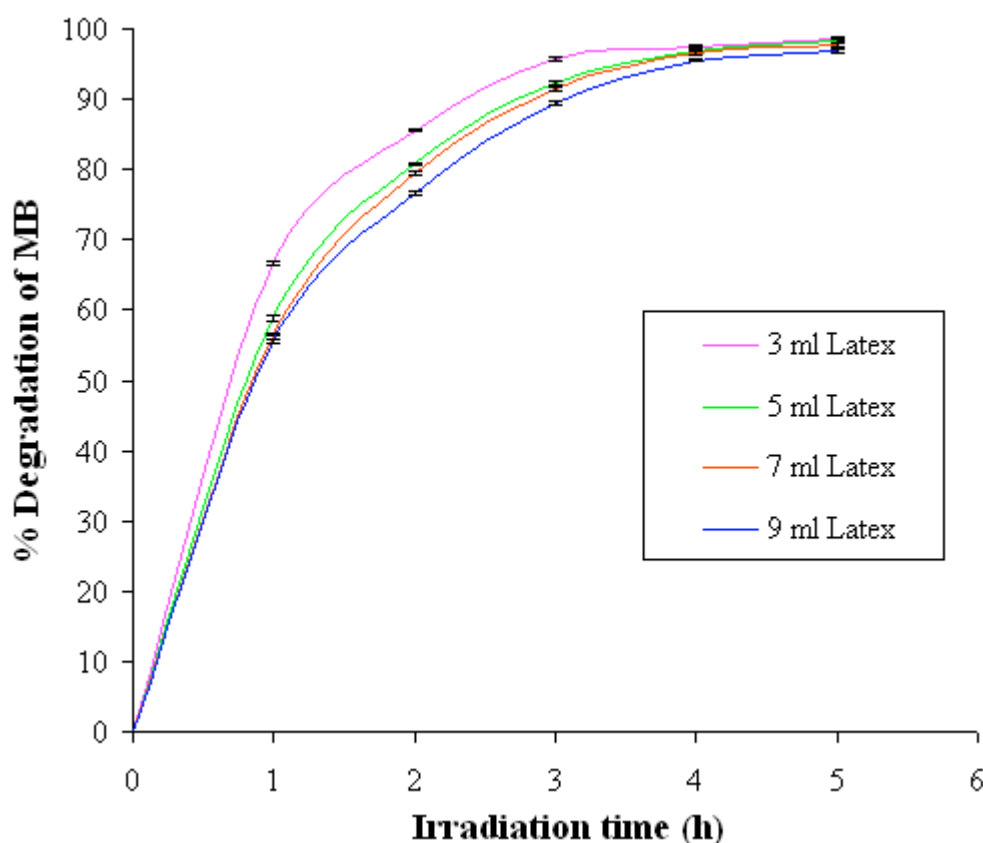


Figure 57 The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> anatase film samples prepared with varying amount of latex (including adsorption)



The photocatalytic activities of Immo-TiO<sub>2</sub> anatase film samples prepared with varying amount of commercial TiO<sub>2</sub> anatase at 0.1 g, 0.2 g, and 0.3 g showed very similar and good performances except the Immo-TiO<sub>2</sub> anatase film sample prepared with 0.05 g of commercial TiO<sub>2</sub> anatase. The Immo-TiO<sub>2</sub> anatase film sample prepared with 0.3 g of latex showed slightly better photocatalytic activities than the other films. The order of activities of Immo-TiO<sub>2</sub> anatase film is 0.3 g > 0.2 g > 0.1 g > 0.05 g in varying amount of commercial TiO<sub>2</sub> anatase due to the surface morphology and roughness of the film increased with the increasing amount of commercial TiO<sub>2</sub> anatase. The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> anatase film samples prepared with varying amount of commercial TiO<sub>2</sub> anatase are shown in Figure 58.

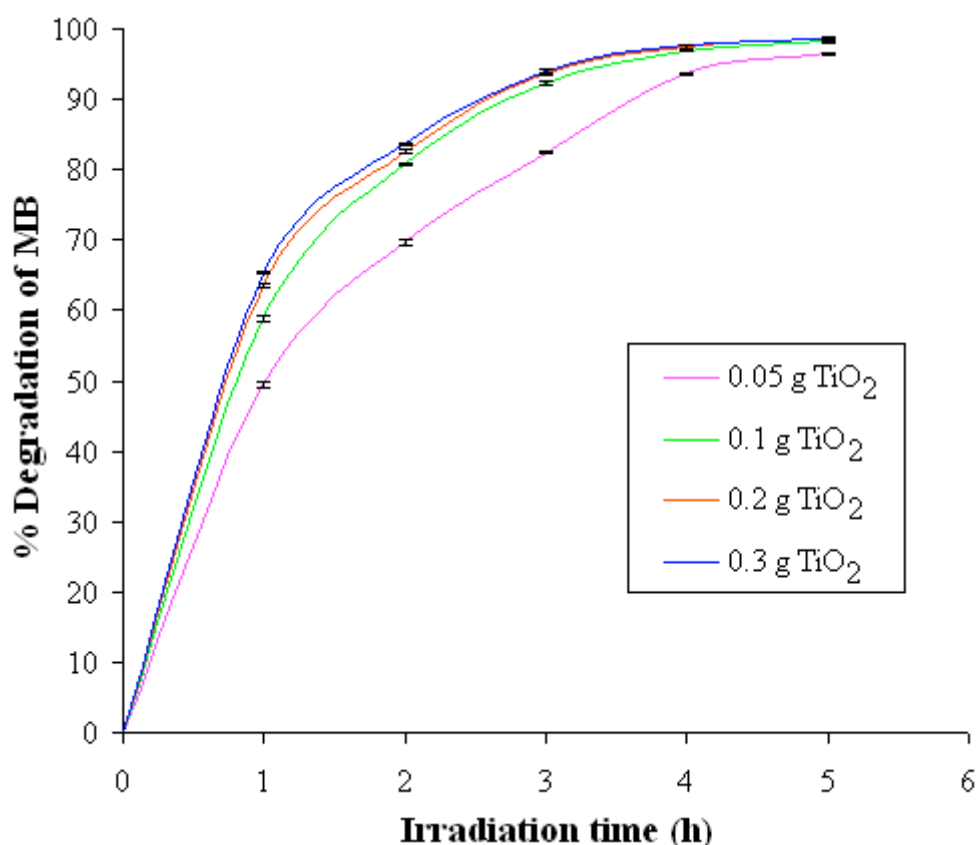


Figure 58 The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> anatase film samples prepared with varying amount of commercial TiO<sub>2</sub> anatase (including adsorption)

For the photocatalytic activities of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of distilled water, amount of latex, and amount of commercial TiO<sub>2</sub> Degussa P25 are summarized in Table 4. The photocatalytic activities of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of distilled water at 1 ml, 3 ml, and 5 ml exhibited different efficiencies on the photocatalytic degradation of MB. The Immo-TiO<sub>2</sub> Degussa P25 film sample prepared with 5 ml of distilled water showed better photocatalytic activities than the other films. The order of activities of Immo-TiO<sub>2</sub> Degussa P25 film is 5 ml > 3 ml > 1 ml in varying amount of distilled water due to the surface morphology and roughness of the film increased with the increasing amount of distilled water. The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of distilled water are shown in Figure 59.

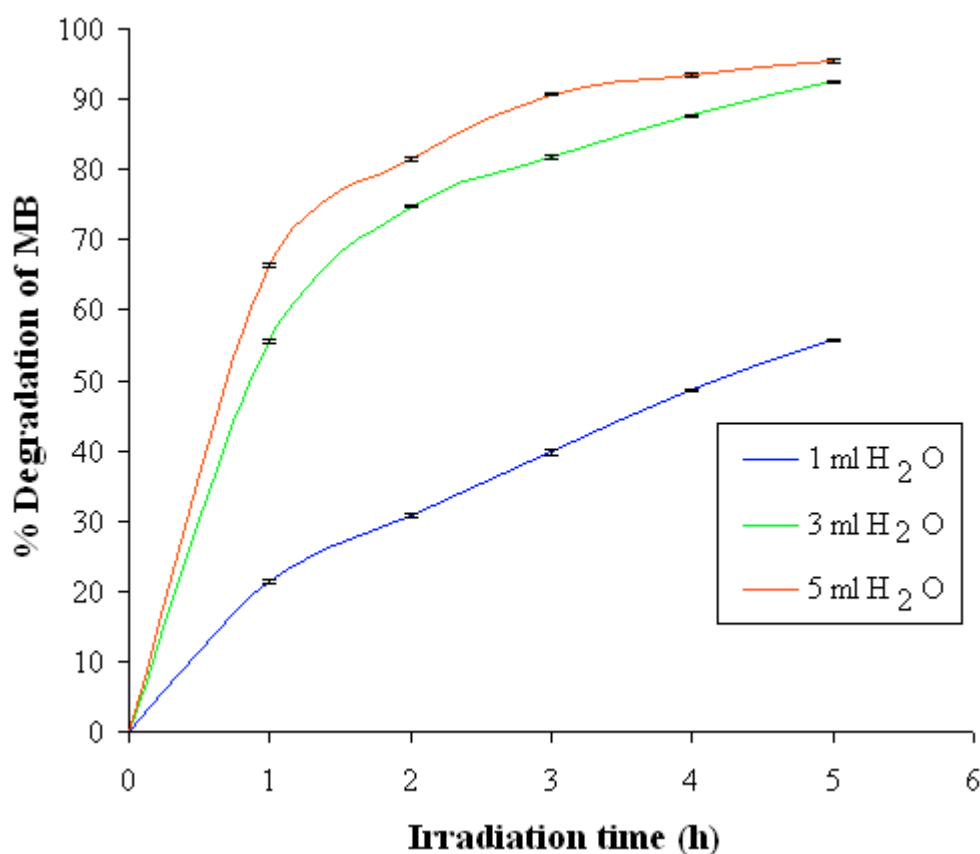


Figure 59 The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of distilled water (including adsorption)

The photocatalytic activities of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of latex at 3 ml, 5 ml, 7 ml, and 9 ml exhibited different efficiencies on the photocatalytic degradation of MB. The Immo-TiO<sub>2</sub> Degussa P25 film sample prepared with 9 ml of latex showed better photocatalytic activities than the other films. The order of activities of Immo-TiO<sub>2</sub> Degussa P25 film is 9 ml > 7 ml > 5 ml > 3 ml in varying amount of latex due to the surface morphology and roughness of the film increased with the increasing amount of latex. The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of latex are shown in Figure 60.

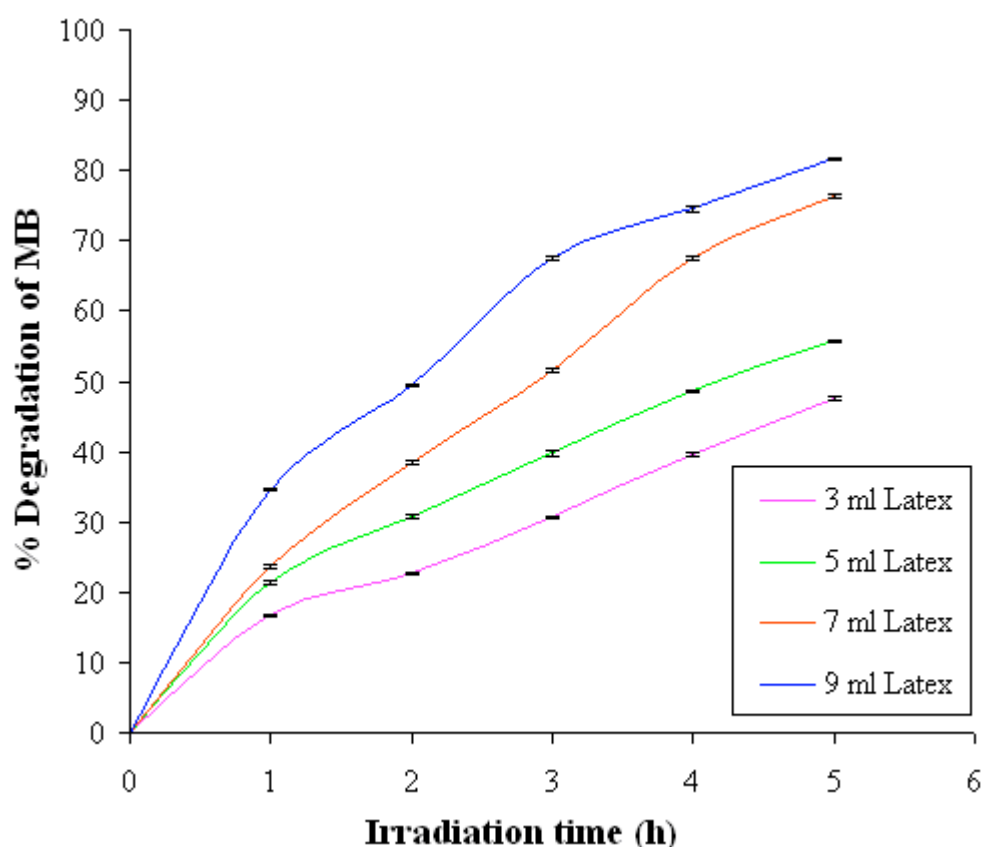


Figure 60 The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of latex (including adsorption)

The photocatalytic activities of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of commercial TiO<sub>2</sub> Degussa P25 at 0.05 g, 0.1 g, and 0.2 g exhibited different efficiencies on the photocatalytic degradation of MB. The Immo-TiO<sub>2</sub> Degussa P25 film sample prepared with 0.05 g of commercial TiO<sub>2</sub> Degussa P25 showed better photocatalytic activities than the other films. The order of activities of Immo-TiO<sub>2</sub> Degussa P25 film is 0.05 g > 0.1 g > 0.2 g in varying amount of commercial TiO<sub>2</sub> anatase due to the surface morphology and roughness of the film decreased with the increasing amount of commercial TiO<sub>2</sub> Degussa P25. The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of commercial TiO<sub>2</sub> Degussa P25 are shown in Figure 61.

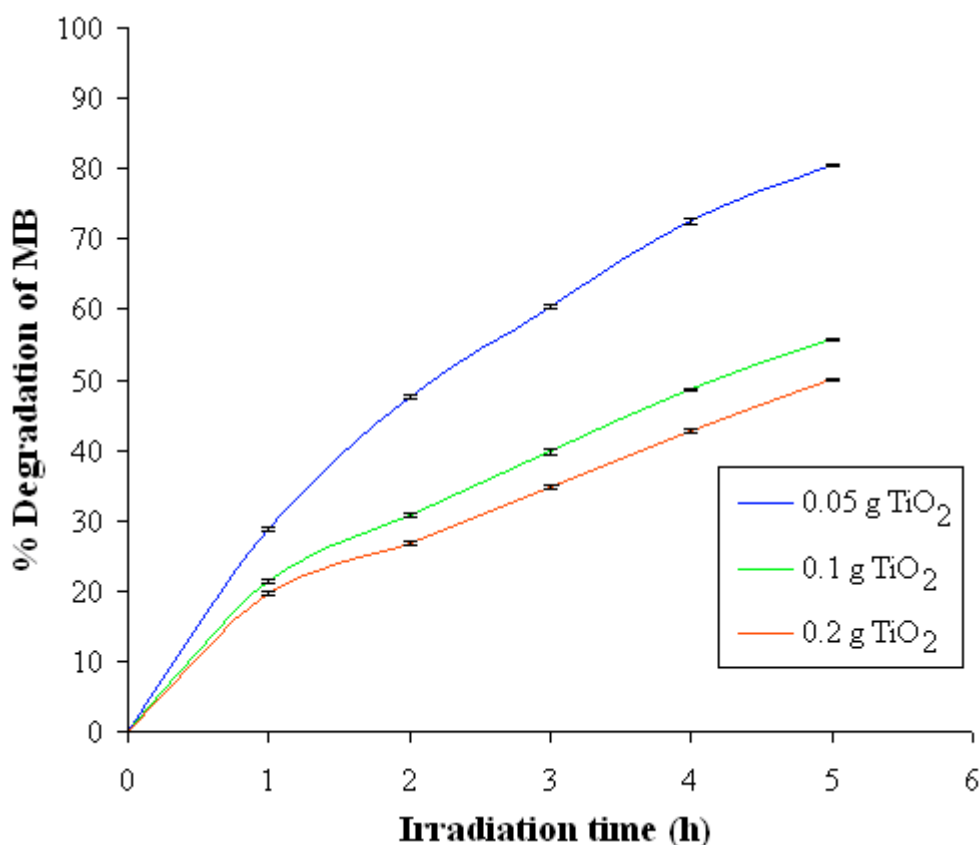


Figure 61 The efficiencies of photocatalytic degradation of MB as a function of times of Immo-TiO<sub>2</sub> Degussa P25 film samples prepared with varying amount of commercial TiO<sub>2</sub> Degussa P25 (including adsorption)

The highest of photocatalytic activities of the Immo-TiO<sub>2</sub> anatase and the Immo-TiO<sub>2</sub> Degussa P25 film samples are selected in comparative studies with the commercial TiO<sub>2</sub> samples in powder form; anatase (Carlo Erba) and Degussa P25. Both commercial TiO<sub>2</sub> samples in powder form showed higher photocatalytic activities than in the film form. This could be higher number of TiO<sub>2</sub> particles (of powder) in contact with MB molecules in the solution. The order of activities is Degussa P25 > Anatase (Carlo Erba) > Immo-TiO<sub>2</sub> anatase > Immo-TiO<sub>2</sub> Degussa P25. The higher photocatalytic activities of Degussa P25 compared with Anatase (Carlo Erba) due to the slow recombination of electron-hole pair and larger surface area of the former. The high photocatalytic activities of the Immo-TiO<sub>2</sub> anatase film than that of the Immo-TiO<sub>2</sub> Degussa P25 film is due to the high surface morphology and roughness of the former. The efficiencies of photocatalytic degradation of MB under irradiation times by Degussa P25, Anatase (Carlo Erba), Immo-TiO<sub>2</sub> anatase film, and Immo-TiO<sub>2</sub> Degussa P25 film are shown in Figure 62.

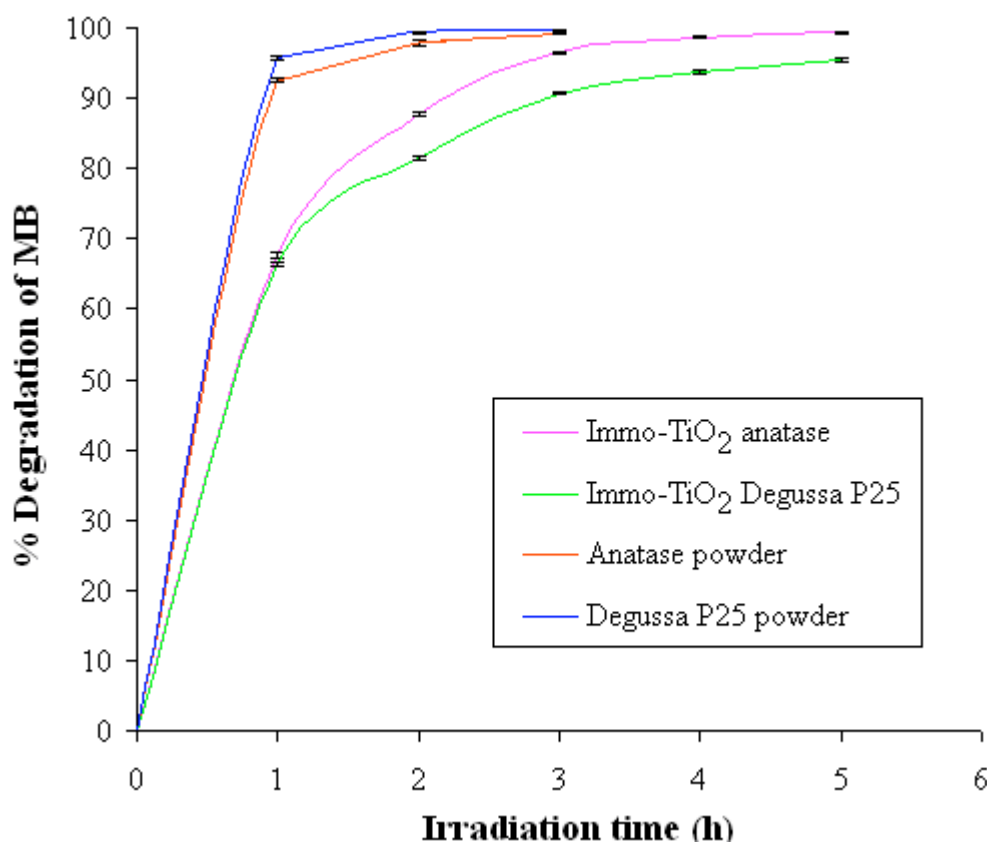


Figure 62 The efficiencies of photocatalytic degradation of MB under irradiation times by Degussa P25, Anatase (Carlo Erba), Immo-TiO<sub>2</sub> anatase film, and Immo-TiO<sub>2</sub> Degussa P25 film (including adsorption)

The optimal conditions for preparation of the Immo-TiO<sub>2</sub> anatase film were: 3 ml of distilled water, 5 ml of latex, and amount 0.1 g of commercial TiO<sub>2</sub> anatase whereas the Immo-TiO<sub>2</sub> Degussa P25 film were: 5ml of distilled water, 5 ml of latex, and amount 0.1 g of commercial TiO<sub>2</sub> Degussa P25. They showed the highest photocatalytic activities in the degradation of MB. This recipe was then used to prepare the film for the rest of the following experiments.

#### 4.2.2 The effect of UV light intensity on the photocatalytic degradation of Immo-TiO<sub>2</sub> films

The effect of UV light intensity on the photocatalytic degradation of Immo-TiO<sub>2</sub> anatase film and Immo-TiO<sub>2</sub> Degussa P25 film were investigated by increasing light sources: 1 tube, 3 tubes, and 5 tubes. The photocatalytic activities of Immo-TiO<sub>2</sub> anatase film and Immo-TiO<sub>2</sub> Degussa P25 film are shown in Tables 5 and 6, respectively. It is found that increasing of the light source increases the photocatalytic activities of MB solution due to the higher UV light intensity. The high UV light intensity increases photon influx entering into the MB dye solution and consequently excites the TiO<sub>2</sub> particles in the film resulting, the OH<sup>•</sup> radicals formed at the surface of film increases. As the reactive number of OH<sup>•</sup> radicals attacking the dye molecules increases, the photodegradation efficiencies also increases. The order of activities is 5 tubes > 3 tubes > 1 tube. The effect of UV light intensity on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film and Immo-TiO<sub>2</sub> Degussa P25 film are shown in Figures 63 and 64, respectively.

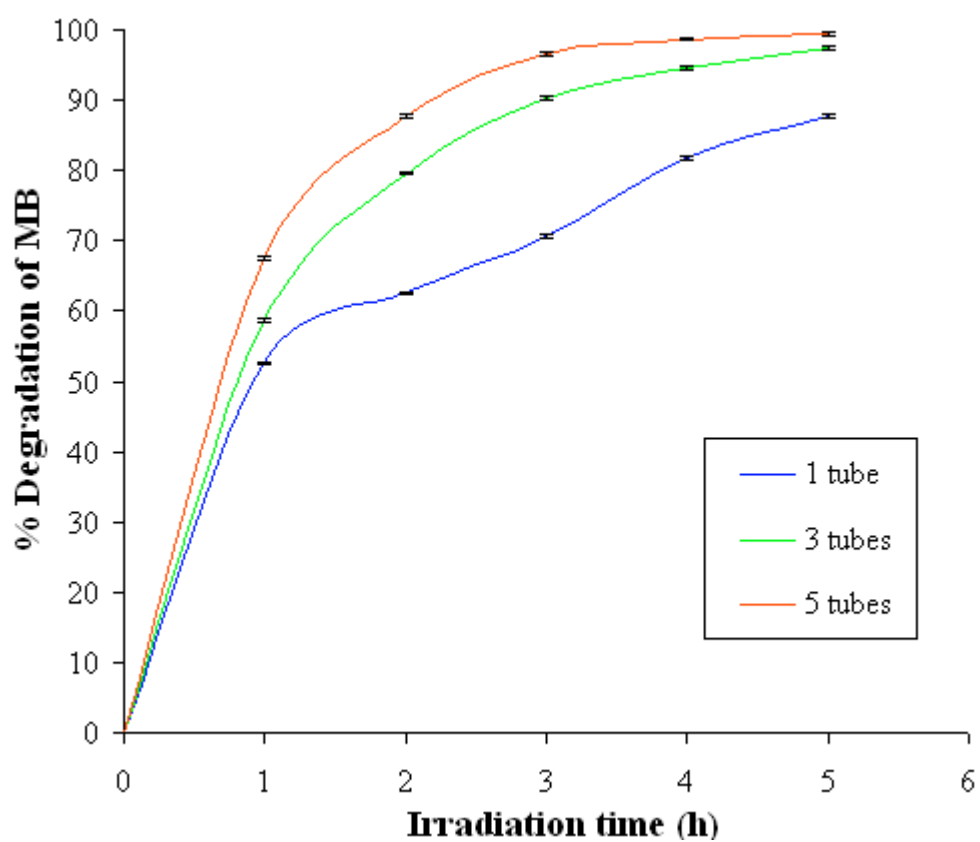


Figure 63 The effect of UV light intensity on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film (including adsorption)

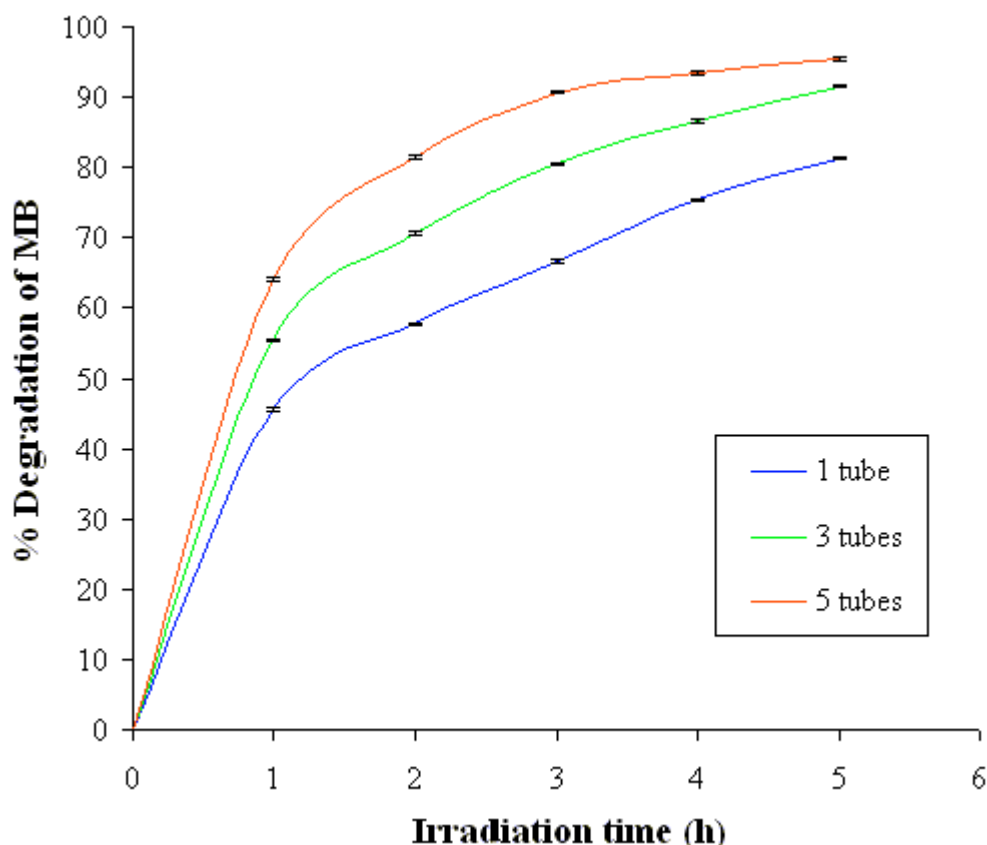


Figure 64 The effect of UV light intensity on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> Degussa P25 film (including adsorption)

#### 4.2.3 The effect of initial concentration of MB on the photocatalytic degradation of Immo-TiO<sub>2</sub> films

The effect of initial concentration of MB on the photocatalytic degradation of Immo-TiO<sub>2</sub> anatase film and Immo-TiO<sub>2</sub> Degussa P25 film were investigated under the concentration of MB solution at  $1.0 \times 10^{-5}$  M,  $2.0 \times 10^{-5}$  M and  $3.0 \times 10^{-5}$  M with the results shown in Tables 5 and 6, respectively. It is found that increasing the dye concentration decreases the photocatalytic activities of MB solution under UV light irradiation. When the dye concentration was increased, the amount of dye molecules adsorbed on the film surface was also increased but the intensity of UV light and illumination time were constant. Therefore, the increase in the dye concentration would decrease the path length of photon entering into the dye solution. Another factor is that at high dye concentration, the deeper colored solution would be



less transparent to the UV light and the dye molecules may absorb a significant amount of UV light causing less light reaching the catalyst resulting the  $\text{OH}^\bullet$  radicals formed on the surface of film to decrease, the reactive number of  $\text{OH}^\bullet$  radicals attacking the dye molecules decreases and thus photodegradation efficiencies decreases (Toor, et al., 2006). The effect of initial concentration of MB on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film and Immo-TiO<sub>2</sub> Degussa P25 film are shown in Figures 65 and 66, respectively.

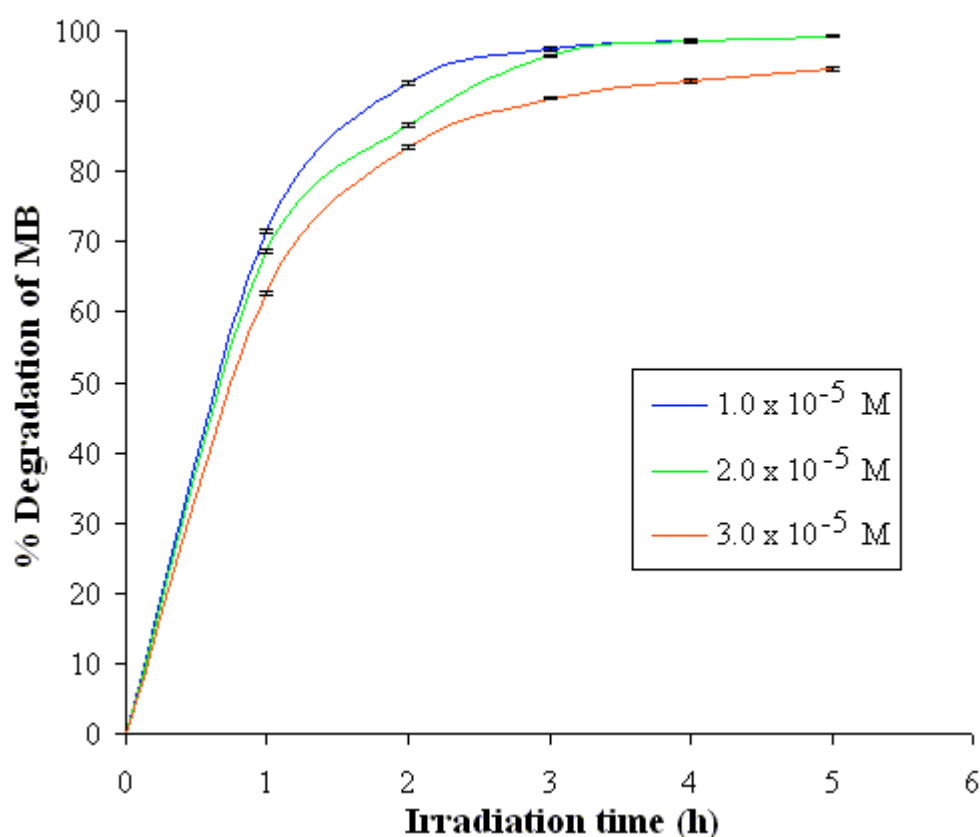


Figure 65 The effect of initial concentration of MB on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film (including adsorption)

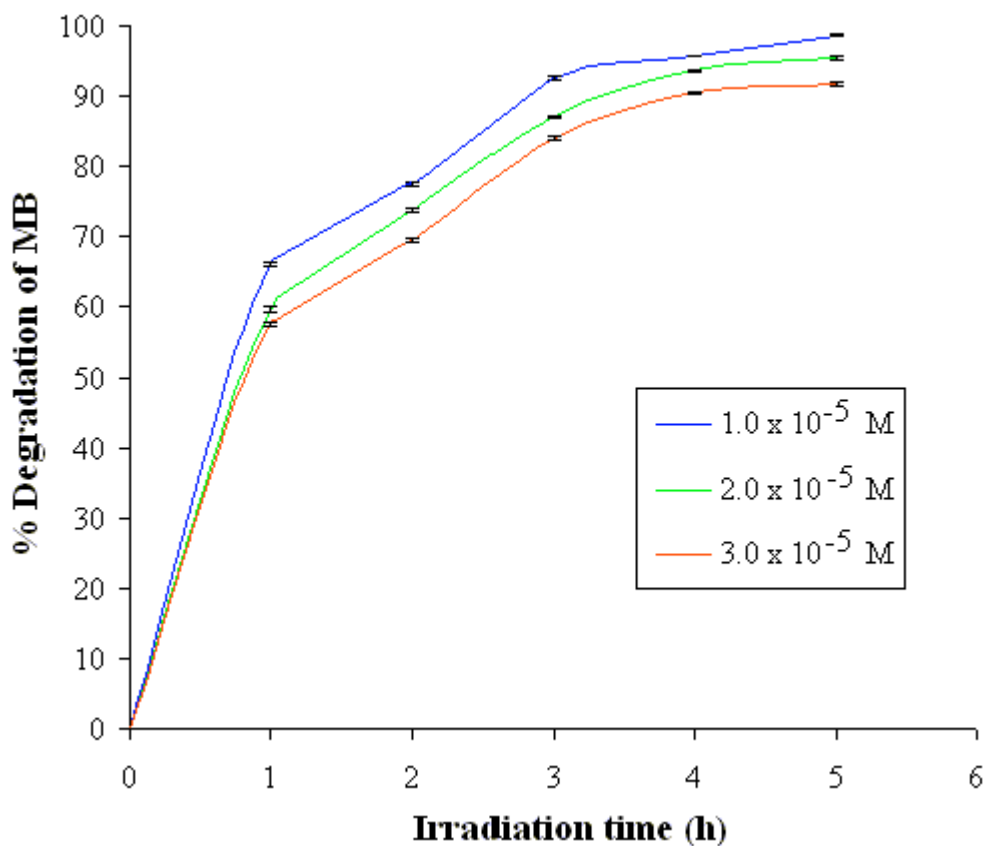
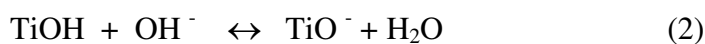
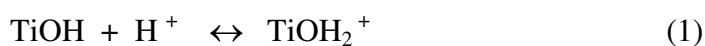


Figure 66 The effect of initial concentration of MB on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> Degussa P25 film (including adsorption)

#### 4.2.4 The effect of pH on the photocatalytic degradation of Immo-TiO<sub>2</sub> films

The effect of pH on the photocatalytic degradation of Immo-TiO<sub>2</sub> anatase film and Immo-TiO<sub>2</sub> Degussa P25 film were investigated under the pH of MB dye solution in the range of 3 to 9 with the results shown in Tables 5 and 6, respectively. The results of both films showed that the photocatalytic degradation of MB increased with the increasing pH of MB solution. It is known that the metal oxide particles in water exhibits amphoteric behavior and readily reacts with dye which can be described by the following chemical equilibrium equations (Silva, et al., 2006):



Generally, for charged surface of  $\text{TiO}_2$  particles, a significant dependency of the photocatalytic efficiency on the pH value was observed, since the overall surface charge and hence the adsorptive properties of  $\text{TiO}_2$  particles depend strongly on the solution pH. It is expected that at pH below 6.86, the surface of  $\text{TiO}_2$  film acquires a positive charge and hence the electrostatic repulsion between the surface of  $\text{TiO}_2$  film and dye cation retards the photodegradation activities. On the other hand, at pH above 6.86, electrostatic interaction between the negative surface of  $\text{TiO}_2$  film and dye cation leads to strong adsorption with a corresponding high photodegradation activities and reaches a maximum at pH 8. If the pH of MB solution was above 8, the films would be unstable. The order of activities is  $\text{pH } 8 > \text{pH } 6.86 > \text{pH } 5 > \text{pH } 3$ . The effect of pH on the photocatalytic efficiencies of Immo- $\text{TiO}_2$  anatase film and Immo- $\text{TiO}_2$  Degussa P25 film are shown in Figures 67 and 68, respectively.

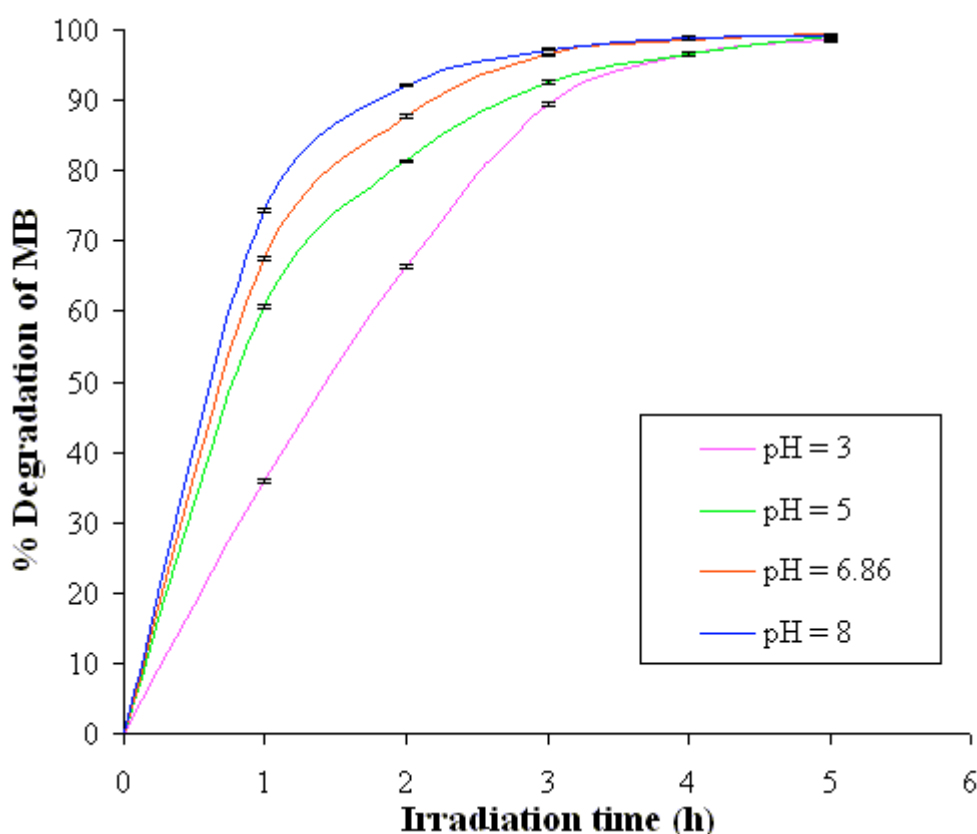


Figure 67 The effect of pH of MB on the photocatalytic efficiencies of Immo- $\text{TiO}_2$  anatase film (including adsorption)

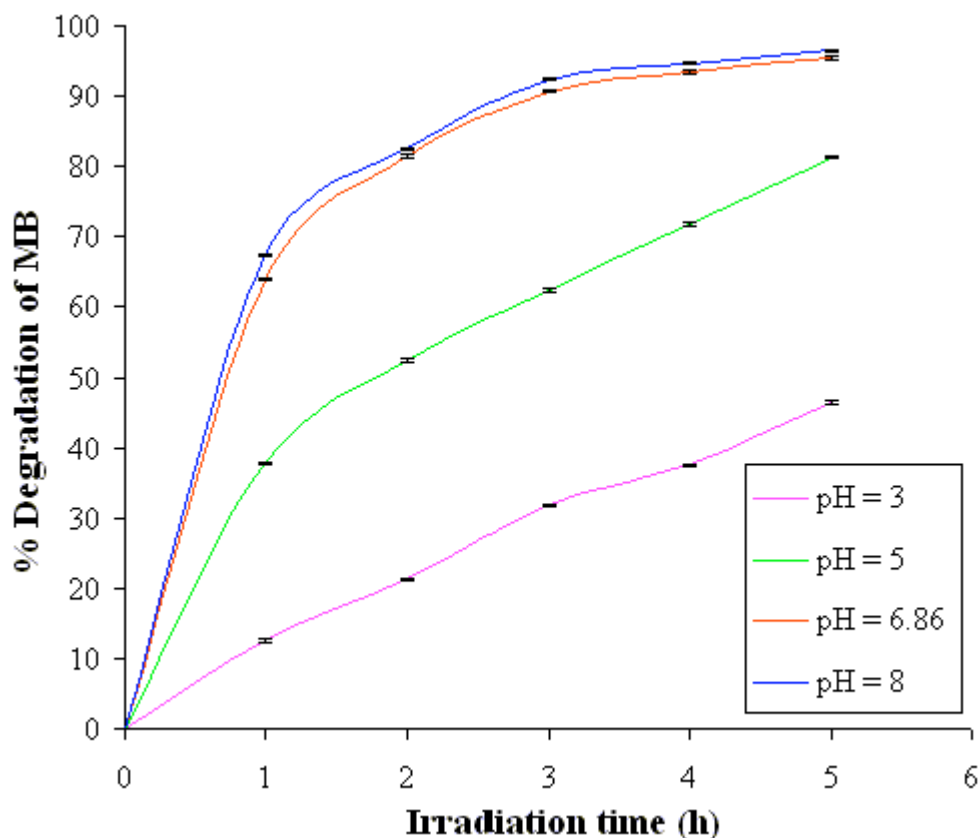


Figure 68 The effect of pH of MB on the photocatalytic efficiencies of Immo-TiO<sub>2</sub> Degussa P25 film (including adsorption)

#### 4.2.5 Study of the reused of Immo-TiO<sub>2</sub> film on the photocatalytic degradation of MB aqueous solution

Only the Immo-TiO<sub>2</sub> anatase film can be used repeatedly on the photocatalytic degradation of MB solution because the surface of film can be “self-cleaning” after used. The photocatalytic activities of Immo-TiO<sub>2</sub> anatase film on the continuous use is shown in Tables 7. It is found that the photocatalytic activities decreased with the number of repeated uses except in the second use that showed highest photocatalytic activities. This may result from the accumulation of MB molecules on the surface of the film and block the UV light to reach the TiO<sub>2</sub> particles in the film, hence, lowering the photocatalytic activities of the film. For the case of the second use that showed highest photocatalytic activities, this may result from the fact

that traces of impurities remained on the rubber surface during the preparation was destroyed in the first photodegradation. The photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film from the four repeating uses are shown in Figure 69.

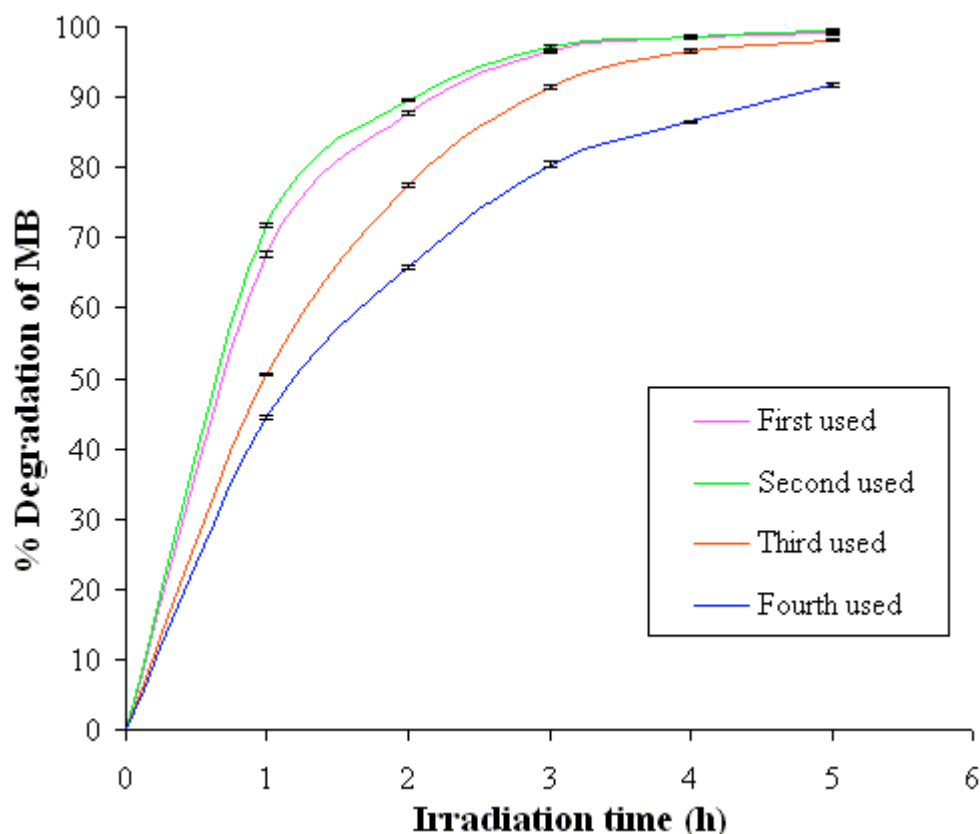


Figure 69 The photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film from the four repeating uses (including adsorption)

The surface that became dirty after uses could be cleaned easily by submerging film in the water and illuminating with UV light for 10 h. After the “self-cleaning” the film surface became white as new film again. The photocatalytic activities of Immo-TiO<sub>2</sub> anatase film with self-cleaning are shown in Tables 7. In the repeated uses, after each self-cleaning the photodegradation efficiencies could be restored to the almost like-new performances. The photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film on the repeated uses with self-cleaning are shown in Figure 70.

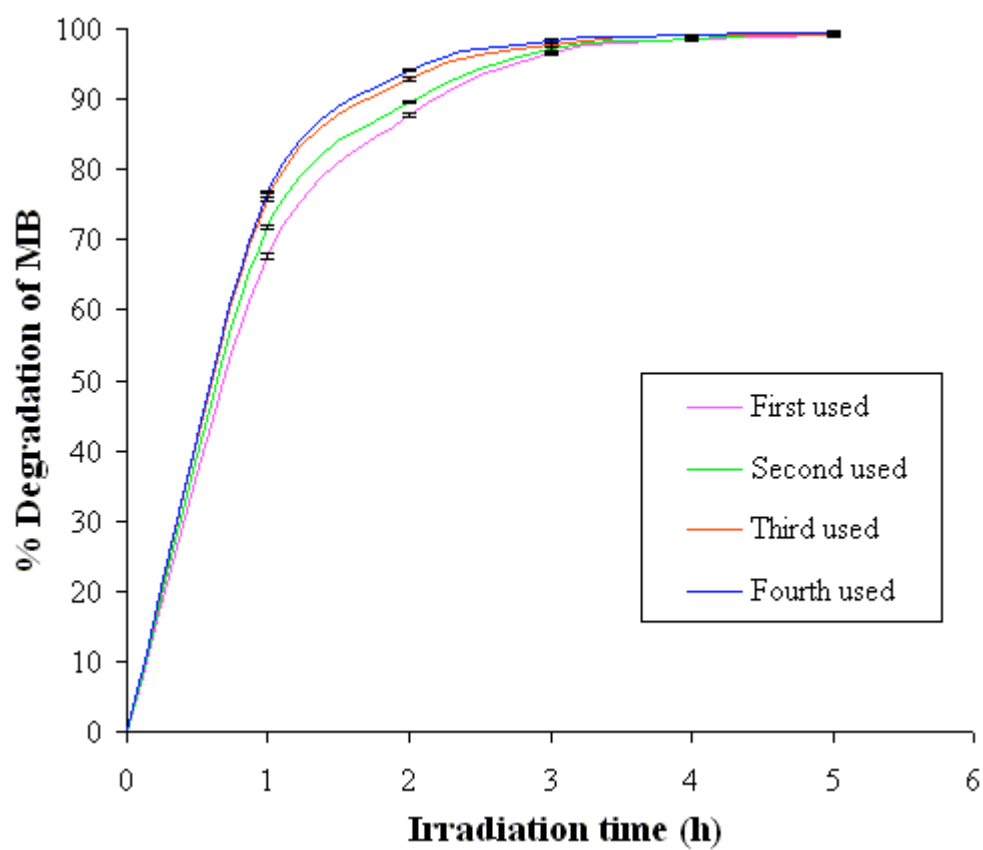


Figure 70 The photocatalytic efficiencies of Immo-TiO<sub>2</sub> anatase film on the repeated uses with self-cleaning (including adsorption)