Chapter 3

Results

3.1 Syntheses and characterizations of Immo-TiO$_2$ films

3.1.1 Syntheses of Immo-TiO$_2$ films

In the present study, the Immo-TiO$_2$ films were prepared by direct mixing of commercial TiO$_2$ powder with latex and distilled water. The Immo-TiO$_2$ film samples on the rubber substrate are shown in Figure 10.

![Figure 10](image)

Figure 10  The photographs of Immo-TiO$_2$ film samples (left: front view ; right : back view)

The effect of various parameters such as amount of distilled water, amount of latex, and amount of commercial TiO$_2$ were studied to optimize the preparation of Immo-TiO$_2$ films for maximum photocatalytic degradation of MB aqueous solution under UV light irradiation. In the case of Immo-TiO$_2$ anatase film, these samples were further studied for various parameters such as the amount of distilled water (1 ml, 2 ml, 3 ml, 4 ml, and 5 ml), amount of latex (3 ml, 5 ml, 7 ml, and 9 ml) and amount of commercial TiO$_2$ anatase (0.05 g, 0.1 g, 0.2 g, and 0.3 g). For Immo-TiO$_2$ Degussa P25 film, these samples were further studied for various parameters such as the amount of distilled water (1 ml, 3 ml, 5 ml, 6 ml, and 7 ml), amount of latex (3 ml, 5 ml, 7 ml, and 9 ml) and amount of commercial TiO$_2$ Degussa P25 (0.05 g, 0.1 g, 0.2 g, and 0.3 g).
3.1.2 Characterizations of Immo-TiO$_2$ films

3.1.2.1 Scanning electron microscopy (SEM)

Scanning electron microscopy is a technique used to investigate the surface morphology and cross section of all Immo-TiO$_2$ film samples. The photographs and SEM images of commercial TiO$_2$ anatase powder and commercial TiO$_2$ Degussa P25 powder are shown in Figures 11 and 12, respectively. The SEM images of Immo-TiO$_2$ anatase and cross sections of each film are shown in Figures 13 and 14, respectively, whereas the SEM images of Immo-TiO$_2$ Degussa P25 and cross sections of each film are shown in Figures 15 and 16, respectively.

![Figure 11](image1.png)  Left: the photograph of commercial TiO$_2$ anatase powder (0.1 g) and right: the SEM image of commercial TiO$_2$ anatase powder

![Figure 12](image2.png)  Left: the photograph of commercial TiO$_2$ Degussa P25 powder (0.1 g) and right: the SEM image of commercial TiO$_2$ Degussa P25 powder
Immo-TiO$_2$ anatase films

a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO$_2$)

1a) 1 ml

2a) 2 ml

3a) 3 ml
b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO$_2$)

1b) 3 ml
2b) 5 ml

3b) 7 ml

4b) 9 ml
c) Varying amount of TiO$_2$ anatase (Fixed; 1ml distilled water and 5ml latex)

1c) 0.05 g

2c) 0.1 g

3c) 0.2 g
Figure 13  SEM surface images of Immo-TiO$_2$ anatase films

Immo-TiO$_2$ anatase films

a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO$_2$)

1a) 1 ml
2a) 2 ml

3a) 3 ml

4a) 4 ml
5a) 5 ml

b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO₂)

1b) 3 ml
2b) 5 ml

3b) 7 ml

4b) 9 ml
c) Varying amount of TiO$_2$ anatase (Fixed; 1ml distilled water and 5ml latex)

1c) 0.05 g

2c) 0.1 g

3c) 0.2 g
Figure 13 shows the SEM micrographs of Immo-TiO$_2$ anatase film samples prepared by varying amount of distilled water (Figure 13a), the amount of latex (Figure 13b), and the amount of commercial TiO$_2$ anatase (Figure 13c). In Figure 13a, the surface morphology and roughness of Immo-TiO$_2$ anatase film samples increased with increasing amount of distilled water as shown in Figures 13(1a), (2a), (3a) and (4a), respectively. When larger amount of distilled water (5 ml) was used, (Figure 13(5a)), some of TiO$_2$ particles were lost from the surface of film causing the film unstable. The surface morphology and roughness of Immo-TiO$_2$ anatase film samples decreased with increasing amount of latex as shown in Figures 13(1b), (2b), (3b) and (4b), respectively. When varying amount of TiO$_2$, Figure 13c, the surface morphology and roughness of Immo-TiO$_2$ anatase film samples increased with increasing amount of commercial TiO$_2$ anatase as shown in Figures 13(1c), (2c), (3c) and (4c), respectively.

The corresponding SEM cross sections of each Immo-TiO$_2$ anatase film samples are shown in Figure 14. The SEM cross section images clearly show the separation of TiO$_2$ layer from the rubber layer when increasing amounts of distilled water were used for the preparation of Immo-TiO$_2$ anatase films (Figures 14(2a), (3a), (4a), and (5a)). These separations were not observed in other samples indicating better mixing between TiO$_2$ particles and the rubber latex.
Immo-TiO$_2$ Degussa P25 films

a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO$_2$)

1a) 1 ml

2a) 3 ml

3a) 5 ml
4a) 6 ml

5a) 7 ml

b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO$_2$)

1b) 3 ml
2b) 5 ml

3b) 7 ml

4b) 9 ml
c) Varying amount of TiO$_2$ Degussa P25 (Fixed; 1ml distilled water and 5ml latex)

1c) 0.05 g

2c) 0.1 g

3c) 0.2 g

Figure 15 SEM surface images of Immo-TiO$_2$ Degussa P25 films
Immo-TiO₂ Degussa P25 films

a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO₂)

1a) 1 ml

2a) 3 ml

3a) 5 ml
4a) 6 ml

5a) 7 ml

b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO$_2$)

1b) 3 ml
c) Varying amount of TiO$_2$ Degussa P25 (Fixed; 1ml distilled water and 5ml latex)

1c) 0.05 g

2c) 0.1 g

3c) 0.2 g

Figure 16  SEM cross section images of Immo-TiO$_2$ Degussa P25 films
Figure 15 shows the SEM micrographs of Immo-TiO\textsubscript{2} Degussa P25 film samples prepared by varying amount of distilled water (Figure 15a), the amount of latex (Figure 15b), and the amount of commercial TiO\textsubscript{2} Degussa P25 (Figure 15c). In Figure 15a, the surface morphology and roughness of Immo-TiO\textsubscript{2} Degussa P25 film samples increased with increasing amount of distilled water as shown in Figures 15(1a), (2a), (3a), and (4a), respectively. When larger amount of distilled water (7 ml) was used, (Figure 15(5a)), some of TiO\textsubscript{2} particles were lost from the surface of film causing the resulting film unstable. The surface morphology and roughness of Immo-TiO\textsubscript{2} Degussa P25 film samples increased with the increasing amount of latex as shown in Figures 15(1b), (2b), (3b), and (4b), respectively. When varying amount of commercial TiO\textsubscript{2} Degussa P25, Figure 15c, the surface morphology and roughness of Immo-TiO\textsubscript{2} Degussa P25 film samples decreased with increasing amount of commercial TiO\textsubscript{2} Degussa P25 as shown in Figures 15(1c), (2c) and (3c), respectively.

The corresponding SEM cross sections of each Immo-TiO\textsubscript{2} Degussa P25 film samples are shown in Figure 16. The SEM cross section images clearly show the separation of TiO\textsubscript{2} layer from the rubber layer when increasing amounts of distilled water were used for the preparation of Immo-TiO\textsubscript{2} Degussa P25 films (Figure 16(2a), (3a), (4a), and (5a)). These separations were not observed in other samples indicating better mixing between TiO\textsubscript{2} particles and the rubber latex. The SEM images of Immo-TiO\textsubscript{2} anatase films generally show higher surface morphology and roughness than Immo-TiO\textsubscript{2} Degussa P25 films. The SEM images of surface and cross section of rubber substrate are shown in Figure 17 for comparison.

![Figure 17](image_url)  
Figure 17  Left: the SEM image of rubber substrate surface; right: the SEM of cross section of rubber substrate
3.1.2.2 X-ray powder diffraction (XRD)

The XRD pattern at \( \theta = 25.50 \) (101) and 48.0° in the spectrum of titanium dioxide are easily identified as the crystal of anatase form whereas the peaks at \( \theta = 27.50 \) (110) and 54.5° 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 powder XRD patterns of the Immo-TiO\(_2\) anatase film, Immo-TiO\(_2\) Degussa P25 film, the original commercial TiO\(_2\) powders and the rubber substrate are shown in Figure 18. The XRD of rubber substrate is also shown in the same figure for comparison.

![XRD patterns of both commercial TiO\(_2\) powders](image)

Figure 18  XRD patterns of both commercial TiO\(_2\) powders; a) Anatase (Carlo Eaba), b) Degussa P25, c) Immo-TiO\(_2\) anatase film, d) Immo-TiO\(_2\) Degussa P25 film, and e) Rubber substrate
3.2 Photocatalytic activities of methylene blue (MB) by Immo-TiO$_2$ films

In this work, 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 these film samples, if present, would show up as the degradation of methylene blue aqueous solution under UV irradiation causing the blue color of methylene blue aqueous solution to disappear as shown in Figure 19.

![Figure 19](image)

Figure 19  The photocatalytic degradation of methylene blue aqueous solution by Immo-TiO$_2$ film under UV irradiation

3.2.1 Preparation of calibration standard solutions

Methylene blue concentrations were measured by using the standard calibration curve. In this work, the concentration of standard methylene blue solutions were prepared in the range $2.5 \times 10^{-6}$ M to $3.0 \times 10^{-5}$ M in order to construct reliable standard calibration curve of methylene blue. The absorbance of methylene blue solution was measured with SPECORD S100 spectrophotometer. The absorption spectra of methylene blue in this range are shown in Figure 20.
Figure 20  The absorption spectra of methylene blue solution in the range of 
2.5 x 10^{-6} M to 3.0 x 10^{-5} M

The standard calibration curve of methylene blue solution in the range 
of 2.5 x 10^{-6} M to 3.0 x 10^{-5} M is shown in Figure 21.

Figure 21  The standard calibration curve of methylene blue solution in the range 
of 2.5 x 10^{-6} M to 3.0 x 10^{-5} M
3.2.2 The experiment for photocatalytic degradation of methylene blue (MB) by Immo-TiO\(_2\) thin films

In the photocatalysis studies, the Immo-TiO\(_2\) thin film was settled in a petri dish containing 60 ml of MB aqueous solution (2.5 \times 10^{-5}M). The solution was then stirred for 1 h in the dark to reach the adsorption equilibrium in tightly closed wooden photoreactor compartment (0.9m X 0.9m X 0.9m) to avoid interference from ambient light. Then the irradiation began using UV-light and stirring (with magnetic bar) at 400 rpm. At given irradiation time intervals (every 1 h), 4 ml of MB solution was collected. The degradation of MB solution was analyzed by using UV-Vis spectrophotometer (Specord S100, Analytik Jena, Germany) from the changes in absorbance of the absorption maximum at 665 nm. The concentration of MB solution was determined quantitatively through the calibration graph, which was constructed in 3.2.1. The blank experiments were carried out under the same conditions by illuminating an aqueous solution of methylene blue alone (Figures 22) and solution of methylene blue with the rubber substrate (Figure 23).

![Figure 22](image)

Figure 22 The absorption spectra of methylene blue solution alone under UV irradiation
The results from the photocatalytic experiments of all Immo-TiO$_2$ anatase films and Immo-TiO$_2$ Degussa P25 films under UV irradiation as a function of times are shown in Figures 24 and 25, respectively. It can be seen that the absorption peak ($\lambda = 665$ nm) of MB solution will be slowly decreases with increasing irradiation time indicating the MB molecules are being degraded in the photocatalytic reaction by Immo-TiO$_2$ film samples.

a) Films prepared by varying amount of distilled water

1a) 1ml
b) Films prepared by varying amount of latex

1b) 3 ml
c) Films prepared by varying amount of TiO$_2$ anatase

**1c) 0.05 g**

**2c) 0.1 g**

**3c) 0.2 g**
4c) 0.3 g

Figure 24 The UV-Vis spectral change of methylene blue with Immo-TiO$_2$ anatase film samples under UV irradiation as a function of times

a) Films prepared by varying amount of distilled water

1a) 1 ml
2a) 3 ml

3a) 5 ml

b) Films prepared by varying amount of latex

1b) 3 ml
4b) 9 ml

c) Films prepared by varying amount of TiO$_2$ Degussa P25

1c) 0.05 g
Figure 25  The UV-Vis spectral change of methylene blue with Immo-TiO$_2$ Degussa P25 film samples under UV irradiation as a function of times

2c) 0.1 g

3c) 0.2 g
For a comparison, the UV-Vis spectral change of methylene blue solution by commercial TiO$_2$ powders under UV irradiation as a function of times are shown in Figures 26 and 27, respectively. It can be seen that the absorption peak ($\lambda = 665$ nm) of MB solution is quickly decreasing and disappear completely in 3 h of irradiation time as the MB molecules are degraded in the photocatalytic reaction of each commercial TiO$_2$ samples.

Figure 26  The UV-Vis spectral change of methylene blue by commercial TiO$_2$ anatase powder (Carlo Erba) under UV irradiation as a function of time

Figure 27  The UV-Vis spectral change of methylene blue by commercial TiO$_2$ Degussa P25 powder under UV irradiation as a function of times
The relative MB remained $C/C_0$ of Immo-TiO$_2$ anatase film samples prepared by varying amount of distilled water, amount of latex, and amount of commercial TiO$_2$ as a function of irradiation times are shown in Figures 28, 29, and 30, respectively. The relative remained $C/C_0$ graphs of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ anatase film samples.

Figure 28  The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film samples prepared by varying amount of distilled water as a function of irradiation times
Figure 29  The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film samples prepared by varying amount of latex as a function of irradiation times.
Figure 30  The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film samples prepared by varying amount of commercial TiO$_2$ as a function of irradiation times.
The relative MB remained $C/C_0$ of Immo-TiO$_2$ Degussa P25 film samples prepared by varying amount of distilled water, amount of latex, and amount of commercial TiO$_2$ as a function of irradiation times are shown in Figures 31, 32, and 33, respectively. The relative remained $C/C_0$ graphs of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction by Immo-TiO$_2$ Degussa P25 film samples.

Figure 31 The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ Degussa P25 film samples prepared by varying amount of distilled water as a function of irradiation times
Figure 32  The relative remained C/C₀ of methylene blue by Immo-TiO₂ Degussa P25 film samples prepared by varying amount of latex as a function of irradiation times.
Figure 33  The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ Degussa P25 film samples prepared by varying amount of commercial TiO$_2$ as a function of irradiation times
For the relative remained $C/C_0$ of methylene blue by commercial TiO$_2$ powders as a function of irradiation times are shown in Figures 34 and 35 respectively. The relative remained $C/C_0$ graphs of MB solution quickly decrease to near zero value with increased irradiation time (into 3 h) indicating the MB molecules are completely destroyed in the photocatalytic reaction of each commercial TiO$_2$ samples.

Figure 34  The relative remained $C/C_0$ of methylene blue by commercial TiO$_2$ anatase powder (Carlo Erba) as a function of irradiation times.
Figure 35  The relative remained $C/C_0$ of methylene blue by commercial TiO$_2$ Degussa P25 powder as a function of irradiation times

The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ anatase film samples, Immo-TiO$_2$ Degussa P25 film samples, commercial TiO$_2$ anatase powder, and commercial TiO$_2$ Degussa P25 powder can be calculated from Figure 28 to Figure 35 are shown in Tables 3 and 4, respectively.

Table 3  The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ anatase film samples as a function of irradiation times (including adsorption)
<table>
<thead>
<tr>
<th>Immo-TiO₂ anatase thin films</th>
<th>% Degradation of MB (average)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 h</td>
</tr>
<tr>
<td>Anatase powder</td>
<td>93.36±0.17</td>
</tr>
<tr>
<td>Degussa P25 powder</td>
<td>96.10±0.22</td>
</tr>
<tr>
<td>a) films prepared by</td>
<td></td>
</tr>
<tr>
<td>varying amount of distilled water</td>
<td></td>
</tr>
<tr>
<td>1 ml</td>
<td>58.90±0.37</td>
</tr>
<tr>
<td>2 ml</td>
<td>62.43±0.45</td>
</tr>
<tr>
<td>3 ml</td>
<td>68.63±0.45</td>
</tr>
<tr>
<td>4 ml **</td>
<td>-</td>
</tr>
<tr>
<td>5 ml **</td>
<td>-</td>
</tr>
<tr>
<td>b) films prepared by</td>
<td></td>
</tr>
<tr>
<td>varying amount of latex</td>
<td></td>
</tr>
<tr>
<td>3 ml</td>
<td>66.60±0.33</td>
</tr>
<tr>
<td>5 ml</td>
<td>58.90±0.37</td>
</tr>
<tr>
<td>7 ml</td>
<td>56.53±0.20</td>
</tr>
<tr>
<td>9 ml</td>
<td>55.57±0.25</td>
</tr>
<tr>
<td>c) films prepared by</td>
<td></td>
</tr>
<tr>
<td>varying amount of TiO₂</td>
<td></td>
</tr>
<tr>
<td>0.05 g</td>
<td>49.43±0.34</td>
</tr>
<tr>
<td>0.1 g</td>
<td>58.90±0.37</td>
</tr>
<tr>
<td>0.2 g</td>
<td>63.50±0.17</td>
</tr>
<tr>
<td>0.3 g</td>
<td>65.37±0.17</td>
</tr>
</tbody>
</table>

* n=3, average ± SD

** due to unstability of the films (as shown in Figure 13) these films were not investigated further

Table 4  The percentage degradation of methylene blue (MB) by Immo-TiO₂ Degussa P25 film samples as a function of irradiation times (including adsorption)
<table>
<thead>
<tr>
<th>Immo-TiO\textsubscript{2} Degussa P25 thin films</th>
<th>% Degradation of MB (average)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 h</td>
</tr>
<tr>
<td>Anatase powder</td>
<td>93.36±0.17</td>
</tr>
<tr>
<td>Degussa P25 powder</td>
<td>96.10±0.22</td>
</tr>
<tr>
<td>a) films prepared by varying amount of distilled water</td>
<td></td>
</tr>
<tr>
<td>1 ml</td>
<td>21.37±0.17</td>
</tr>
<tr>
<td>3 ml</td>
<td>55.57±0.31</td>
</tr>
<tr>
<td>5 ml</td>
<td>66.47±0.25</td>
</tr>
<tr>
<td>6 ml **</td>
<td>-</td>
</tr>
<tr>
<td>7 ml **</td>
<td>-</td>
</tr>
<tr>
<td>b) films prepared by varying amount of latex</td>
<td></td>
</tr>
<tr>
<td>3 ml</td>
<td>16.70±0.22</td>
</tr>
<tr>
<td>5 ml</td>
<td>21.37±0.17</td>
</tr>
<tr>
<td>7 ml</td>
<td>23.53±0.25</td>
</tr>
<tr>
<td>9 ml</td>
<td>34.60±0.22</td>
</tr>
<tr>
<td>c) films prepared by varying amount of TiO\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>0.05 g</td>
<td>28.70±0.23</td>
</tr>
<tr>
<td>0.1 g</td>
<td>21.37±0.17</td>
</tr>
<tr>
<td>0.2 g</td>
<td>19.57±0.17</td>
</tr>
</tbody>
</table>

* n=3, average ± SD

** due to unstability of the films (as shown in Figure 13) these films were not investigated further

The photocatalytic activities of Immo-TiO\textsubscript{2} anatase film samples prepared by varying amount of distilled water, amount of latex, amount of commercial...
$\text{TiO}_2\ \text{anatase}$ are summarized in Table 3 and compared with the commercial $\text{TiO}_2$ samples in powder form; anatase (Carlo Erba) and Degussa P25. In the series of varying amount of distilled water, the film sample prepared with 3 ml of distilled water showed higher photocatalytic activities than the other films, but lower than both commercial $\text{TiO}_2$ in powder form. The optimal conditions for preparation of Immo-$\text{TiO}_2\ \text{anatase}$ film were: 3 ml of distilled water, 5 ml of latex, and 0.1 g of commercial $\text{TiO}_2$ anatase. This recipe was then used to prepare the film for the rest of the following experiments.

The photocatalytic activities of Immo-$\text{TiO}_2$ Degussa P25 film samples prepared by varying amount of distilled water, amount of latex, amount of commercial $\text{TiO}_2$ Degussa P25 are summarized in Table 4 and compared with the commercial $\text{TiO}_2$ samples in powder form; anatase (Carlo Erba) and Degussa P25. In the series of varying amount of distilled water, the film sample prepared with 5 ml of distilled water showed higher photocatalytic activities than the other films, but lower than both commercial $\text{TiO}_2$ in powder form. The optimal conditions for preparation of Immo-$\text{TiO}_2$ Degussa P25 film were: 5 ml of distilled water, 5 ml of latex, and 0.1 g of commercial $\text{TiO}_2$ Degussa P25. This recipe was then used to prepare the film for the rest of the following experiments.

3.2.3 The effect of UV light intensity on the photocatalytic degradation of Immo-$\text{TiO}_2$ films

In this work, the effect of UV light intensity on the photocatalytic degradation of Immo-$\text{TiO}_2$ anatase film and Immo-$\text{TiO}_2$ Degussa P25 film were investigated by increasing light sources: 1 tube, 3 tubes, and 5 tubes. The absorption spectra of methylene blue solution by Immo-$\text{TiO}_2$ anatase film and Immo-$\text{TiO}_2$ Degussa P25 film as a function of irradiation times are shown in Figures 36 and 37, respectively. It can be seen that the absorption peak ($\lambda = 665 \text{ nm}$) of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-$\text{TiO}_2$ film samples.

Immo-$\text{TiO}_2$ anatase film
a) 1 tube

b) 3 tubes

c) 5 tubes
Figure 36  The UV-Vis spectral change of methylene blue by Immo-TiO\textsubscript{2} anatase film under various UV light intensity

Immo-TiO\textsubscript{2} Degussa P25 film

a) 1 tube

b) 3 tubes
c) 5 tubes

Figure 37  The UV-Vis spectral change of methylene blue by Immo-TiO\textsubscript{2} Degussa P25 film under various amount of UV light intensity

The relative remained C/C\textsubscript{0} of methylene blue by Immo-TiO\textsubscript{2} anatase film and Immo-TiO\textsubscript{2} Degussa P25 film under various UV light intensity as a function
of irradiation times are shown in Figures 38 and 39, respectively. The relative remained $C/C_0$ graphs of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO\textsubscript{2} film samples.

![Graph showing the relative remained $C/C_0$ of methylene blue by Immo-TiO\textsubscript{2} anatase film under various UV light intensity as a function of irradiation times]

Figure 38 The relative remained $C/C_0$ of methylene blue by Immo-TiO\textsubscript{2} anatase film under various UV light intensity as a function of irradiation times.
3.2.4 The effect of initial concentration of MB on the photocatalytic degradation of Immo-TiO$_2$ films

The effect of initial concentration of MB on the photocatalytic degradation of Immo-TiO$_2$ anatase film and Immo-TiO$_2$ Degussa P25 film were investigated under the concentration of MB solution at 1.0 x 10$^{-5}$ M, 2.0 x 10$^{-5}$ M and 3.0 x 10$^{-5}$ M. The absorption spectra of methylene blue solution by Immo-TiO$_2$ anatase film and Immo-TiO$_2$ Degussa P25 film as a function of irradiation times are shown in Figures 40 and 41, respectively. It can be seen that the absorption peak ($\lambda$ = 665 nm) of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ film samples.
Immo-TiO$_2$ anatase film

a) $1.0 \times 10^{-5}$M

b) $2.0 \times 10^{-5}$M

c) $3.0 \times 10^{-5}$M
Figure 40  The UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film under various initial concentration of MB as a function of irradiation times

Immo-TiO$_2$ Degussa P25 film

a)  $1.0 \times 10^{-5}$ M
Figure 41 The UV-Vis spectral change of methylene blue by Immo-TiO$_2$ Degussa P25 film under various initial concentration of MB as a function of irradiation times
The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film and Immo-TiO$_2$ Degussa P25 film under various initial concentrations of MB as a function of irradiation times are shown in Figures 42 and 43, respectively. The relative remained $C/C_0$ graphs of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ film samples.

![Figure 42](image)

Figure 42. The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film under various initial concentration of MB as a function of irradiation times
Figure 43  The relative remained C/C₀ of methylene blue by Immo-TiO₂ Degussa P25 film under various initial concentration of MB as a function of irradiation times

3.2.5  The effect of pH on the photocatalytic degradation of Immo-TiO₂ films

The effect of pH on the photocatalytic degradation of Immo-TiO₂ anatase film and Immo-TiO₂ Degussa P25 film were investigated under the pH of MB dye solution in the range of 3 to 9. The natural pH of MB aqueous solution in this work was 6.86. The pH of MB dye solution was adjusted by adding dilute aqueous solution of HCl and NaOH. The absorption spectra of methylene blue solutions by Immo-TiO₂ anatase film and Immo-TiO₂ Degussa P25 film as a function of irradiation times are shown in Figures 44 and 45, respectively. It can be seen that the absorption peak (λ = 665 nm) of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO₂ film samples.
Immo-TiO\textsubscript{2} anatase film

a) at pH = 3

![Absorbance vs. Wavelength graph for pH = 3](image)

b) at pH = 5

![Absorbance vs. Wavelength graph for pH = 5](image)
c) at pH = 6.86

![UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film under various pH of MB aqueous solution as a function of irradiation times](image1)

\[\text{Absorbance} \times 10^{-3} \times \text{MB} \]

\[\text{Wavelength (nm)} \]

\[\text{MB 2.5} \times 10^{-3} \text{ M}
\text{adsorption 1 h}
\text{irradiation 1 h}
\text{irradiation 2 h}
\text{irradiation 3 h}
\text{irradiation 4 h}
\text{irradiation 5 h}\]

d) at pH = 8

![UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film under various pH of MB aqueous solution as a function of irradiation times](image2)

\[\text{Absorbance} \times 10^{-3} \times \text{MB} \]

\[\text{Wavelength (nm)} \]

\[\text{MB 2.5} \times 10^{-3} \text{ M}
\text{adsorption 1 h}
\text{irradiation 1 h}
\text{irradiation 2 h}
\text{irradiation 3 h}
\text{irradiation 4 h}
\text{irradiation 5 h}\]

Figure 44 The UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film under various pH of MB aqueous solution as a function of irradiation times.
Immo-TiO\textsubscript{2} Degussa P25 film

a) at pH = 3

![Graph showing absorbance vs. wavelength for pH = 3](image)

b) at pH = 5

![Graph showing absorbance vs. wavelength for pH = 5](image)
c) at pH = 6.86

Figure 45  The UV-Vis spectral change of methylene blue by Immo-TiO$_2$ Degussa P25 film under various pH of MB aqueous solution as a function of irradiation times

d) at pH = 8
The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film and Immo-TiO$_2$ Degussa P25 film under various pHs as a function of irradiation times are shown in Figures 46 and 47, respectively. The relative remained $C/C_0$ graphs of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ anatase film samples.

![Figure 46](image)

*Figure 46* The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film under various pH of MB solution as a function of irradiation times
Figure 47 The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ Degussa P25 film under various pH of MB solution as a function of irradiation times.

The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ anatase film and Immo-TiO$_2$ Degussa P25 film under various intensity of UV light, initial concentrations of MB aqueous solution and pHs of MB solution can be calculated from Figures 38, 39, 42, 43, 46, and 47 are shown in Tables 5 and 6, respectively.
Table 5 The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ anatase film various UV light intensity, initial concentration of MB, and pH of MB solution as a function of irradiation times (including adsorption)

<table>
<thead>
<tr>
<th>Immo-TiO$_2$ anatase thin film</th>
<th>% Degradation of MB (average)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 h</td>
</tr>
<tr>
<td>a) UV light intensity (amount of blacklight)</td>
<td></td>
</tr>
<tr>
<td>1 tube</td>
<td>52.57±0.17</td>
</tr>
<tr>
<td>3 tubes</td>
<td>58.63±0.29</td>
</tr>
<tr>
<td>5 tubes</td>
<td>67.63±0.45</td>
</tr>
<tr>
<td>b) concentration of MB</td>
<td></td>
</tr>
<tr>
<td>1.0 x 10$^{-5}$ M</td>
<td>71.53±0.29</td>
</tr>
<tr>
<td>2.0 x 10$^{-5}$ M</td>
<td>68.63±0.20</td>
</tr>
<tr>
<td>3.0 x 10$^{-5}$ M</td>
<td>62.67±0.20</td>
</tr>
<tr>
<td>c) pH of MB solution</td>
<td></td>
</tr>
<tr>
<td>at = 3</td>
<td>35.90±0.22</td>
</tr>
<tr>
<td>at = 5</td>
<td>60.60±0.29</td>
</tr>
<tr>
<td>at = 6.86**</td>
<td>67.63±0.45</td>
</tr>
<tr>
<td>at = 8</td>
<td>74.37±0.17</td>
</tr>
</tbody>
</table>

* n=3, average ± SD

** natural pH of MB aqueous solution
Table 6 The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ Degussa P25 film under various UV light intensity, initial concentration of MB, and pH of MB solution as a function of irradiation times (including adsorption)

<table>
<thead>
<tr>
<th>Immo-TiO$_2$ Degussa P25 thin film</th>
<th>% Degradation of MB (average)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 h</td>
</tr>
<tr>
<td>a) UV light intensity</td>
<td></td>
</tr>
<tr>
<td>(amount of blacklight)</td>
<td></td>
</tr>
<tr>
<td>1 tube</td>
<td>45.67±0.29</td>
</tr>
<tr>
<td>3 tubes</td>
<td>55.43±0.20</td>
</tr>
<tr>
<td>5 tubes</td>
<td>64.06±0.34</td>
</tr>
<tr>
<td>b) concentration of MB</td>
<td></td>
</tr>
<tr>
<td>1.0 x 10$^{-5}$ M</td>
<td>66.13±0.20</td>
</tr>
<tr>
<td>2.0 x 10$^{-5}$ M</td>
<td>59.67±0.45</td>
</tr>
<tr>
<td>3.0 x 10$^{-5}$ M</td>
<td>57.50±0.22</td>
</tr>
<tr>
<td>c) pH of MB solution</td>
<td></td>
</tr>
<tr>
<td>at = 3</td>
<td>12.60±0.29</td>
</tr>
<tr>
<td>at = 5</td>
<td>37.77±0.20</td>
</tr>
<tr>
<td>at = 6.86**</td>
<td>64.06±0.34</td>
</tr>
<tr>
<td>at = 8</td>
<td>67.47±0.17</td>
</tr>
</tbody>
</table>

* n=3, average ± SD

** natural pH of MB aqueous solution

3.2.6 Study of the reused of Immo-TiO$_2$ film on the photocatalytic degradation of MB aqueous solution

The Immo-TiO$_2$ anatase film can be used repeatedly on the photocatalytic degradation of MB solution. The photographs of Immo-TiO$_2$ anatase film and Immo-TiO$_2$ Degussa P25 film before and after used are shown in Figures 48 and 49, respectively.
The absorption spectra of methylene blue solutions by Immo-TiO$_2$ anatase film in the repeated uses four times are shown in Figure 50. It can be seen that the absorption peak ($\lambda = 665 \text{ nm}$) of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ anatase film.
a) First use

![Graph](image1)

b) Second use

![Graph](image2)
c) Third use

![UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times](image1)

Figure 50  The UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times

d) Fourth use

![UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times](image2)
The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times as a function of irradiation times are shown in Figure 51. The relative remained $C/C_0$ graphs of MB solution gradually decreasing with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ anatase film.

![Figure 51](image)

Figure 51 The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times

After repeated uses twice, the surface of Immo-TiO$_2$ anatase film became “dirty” as it showed some bluish color due to accumulation of MB molecules and the photocatalytic activities of film decreased. However, this dirty surface could be cleaned easily by submerging film in water and illuminating with UV light (5 tubes) for 10 h. After the “self-cleaning”, the film surface became clean but not as white as the
new film. The photographs of the dirty film after the second use are shown in Figure 52 and after self-cleaning by UV illuminating in Figure 53.

a) before second use  

![Image of Immo-TiO\textsubscript{2} anatase film before second use](image1)

b) after second use  

![Image of Immo-TiO\textsubscript{2} anatase film after second use](image2)

Figure 52  The photographs of Immo-TiO\textsubscript{2} anatase film a) before second use  

b) after second use on the photocatalytic degradation of MB

a) before UV illuminating  

![Image of Immo-TiO\textsubscript{2} anatase film before UV illuminating](image3)

b) after UV illuminating  

![Image of Immo-TiO\textsubscript{2} anatase film after UV illuminating](image4)

Figure 53  The photographs of Immo-TiO\textsubscript{2} anatase film a) before cleaning  

b) after cleaning
The absorption spectra of methylene blue solution by Immo-TiO$_2$ anatase film in the repeated uses four times, with self-cleaning after second use, are shown in Figure 54. It can be seen that the absorption peak ($\lambda = 665$ nm) of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ film.

a) First use

![Absorption spectra for first use](image1)

b) Second use

![Absorption spectra for second use](image2)
c) Third use (cleaning before use)

![Graph](https://via.placeholder.com/150)

**Figure 54** The UV-Vis spectral change of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times (with self-cleaning after use)

d) Fourth use (cleaning before use)

![Graph](https://via.placeholder.com/150)
The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses four times (with “self-cleaning” after second use) as a function of irradiation times as shown in Figure 55. The relative remained $C/C_0$ graphs of MB solution gradually decrease with increased irradiation time as the MB molecules are degraded in the photocatalytic reaction of Immo-TiO$_2$ anatase film.

![Graph of relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film](image)

**Figure 55** The relative remained $C/C_0$ of methylene blue by Immo-TiO$_2$ anatase film in the repeated uses (with “self-cleaning” after use)

The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ anatase film under continuous use and cleaning before use can be calculated from Figures 51 and 55 are shown in Tables 7.
Table 7  The percentage degradation of methylene blue (MB) by Immo-TiO$_2$ anatase film under continuous use and cleaning before use as a function of irradiation times (including adsorption)

<table>
<thead>
<tr>
<th>Immo-TiO$_2$ anatase thin film</th>
<th>% Degradation of MB (average)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 h</td>
</tr>
<tr>
<td>a) continuous use</td>
<td></td>
</tr>
<tr>
<td>First use</td>
<td>67.63±0.45</td>
</tr>
<tr>
<td>Second use</td>
<td>71.73±0.20</td>
</tr>
<tr>
<td>Third use</td>
<td>50.57±0.25</td>
</tr>
<tr>
<td>Fourth use</td>
<td>44.47±0.20</td>
</tr>
<tr>
<td>b) cleaning before use</td>
<td></td>
</tr>
<tr>
<td>First use</td>
<td>67.63±0.45</td>
</tr>
<tr>
<td>Second use</td>
<td>71.73±0.20</td>
</tr>
<tr>
<td>Third used**</td>
<td>75.73±0.12</td>
</tr>
<tr>
<td>Fourth used***</td>
<td>76.67±0.17</td>
</tr>
</tbody>
</table>

* n=3, average ± SD
** cleaning before use (after second use)
*** cleaning before use (after third use)