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.

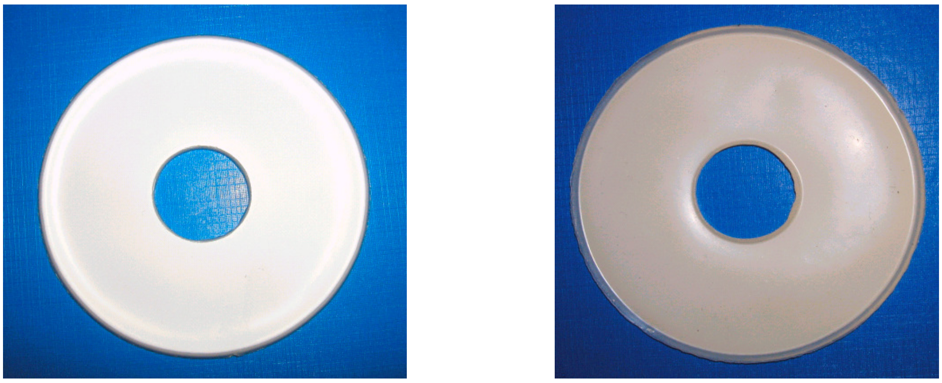


Figure 10 The photographs of Immo-TiO_2 film samples (left: front view ; right : back view)

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.

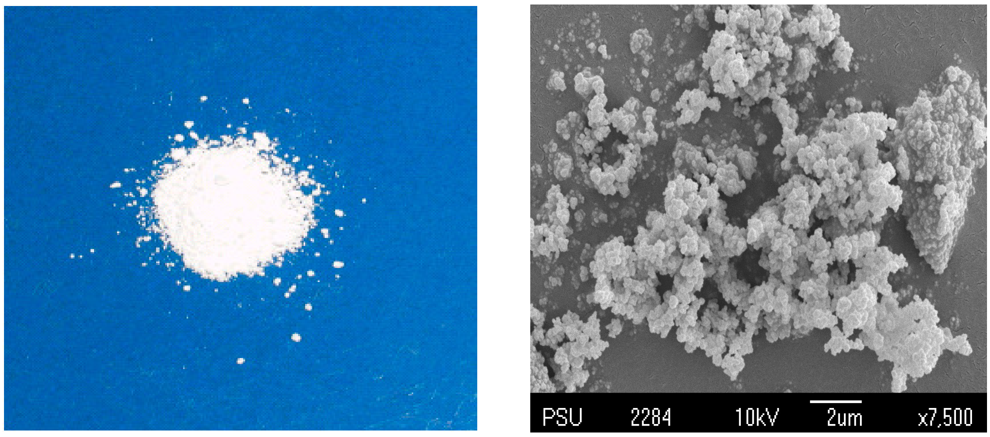


Figure 11 Left: the photograph of commercial TiO_2 anatase powder (0.1 g) and right: the SEM image of commercial TiO_2 anatase powder

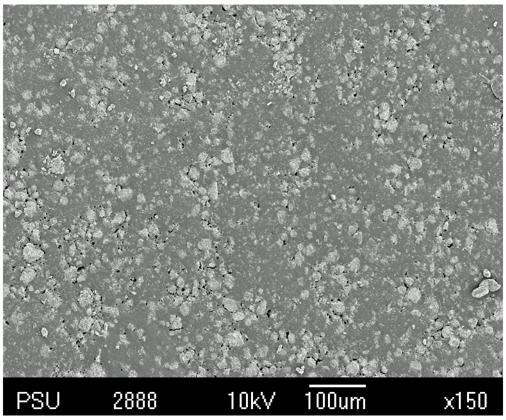
Figure 12 Left: the photograph of commercial TiO_2 Degussa P25 powder (0.1 g) and right: the SEM image of commercial TiO_2 Degussa P25 powder

Immo-TiO_2 anatase films

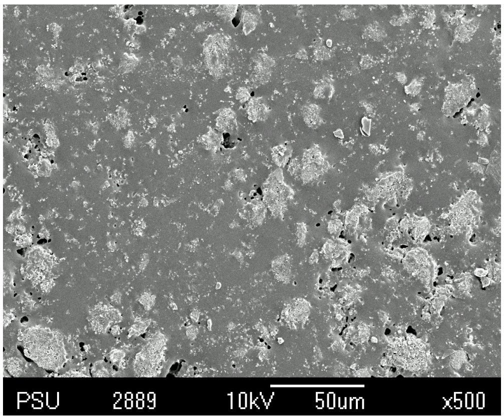
a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO_2)

1a) 1 ml

150×

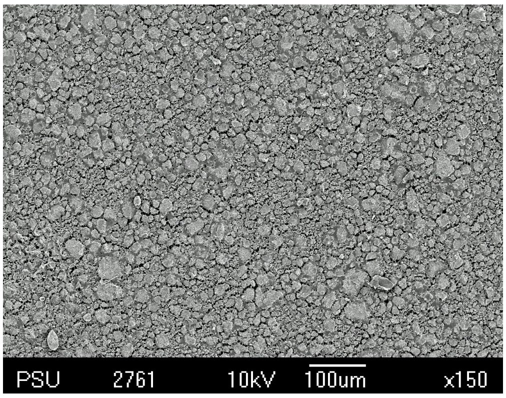


500×

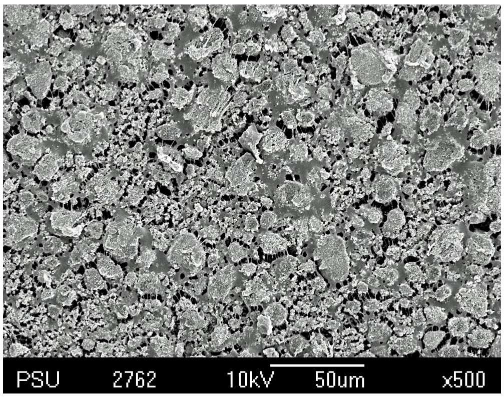


2a) 2 ml

150×

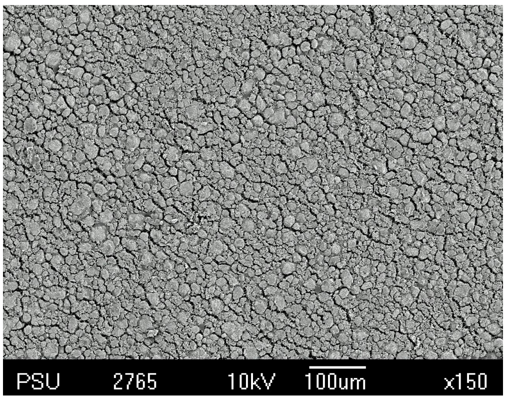


500×

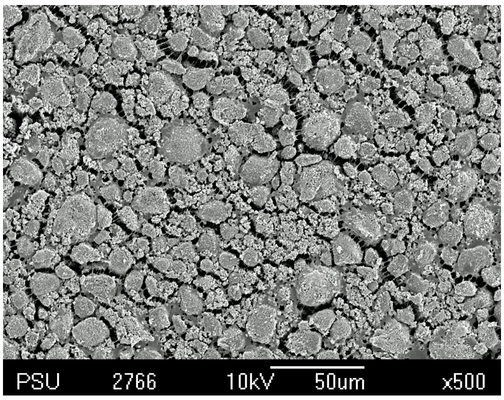


3a) 3 ml

150×

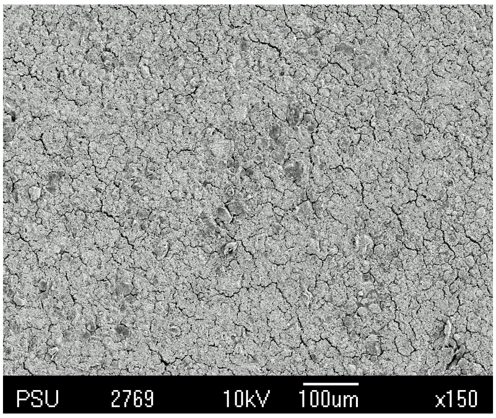


500×

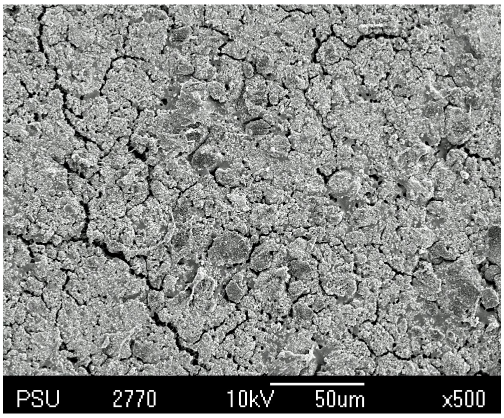


4a) 4 ml

150×

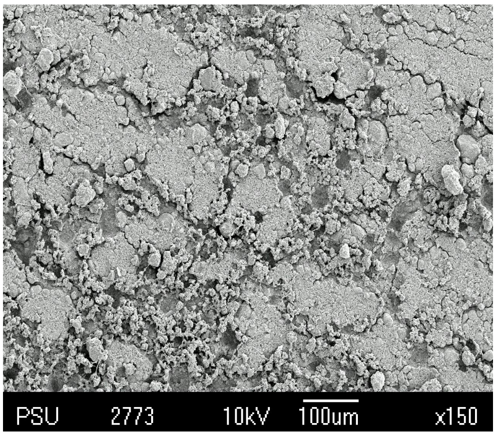


500×

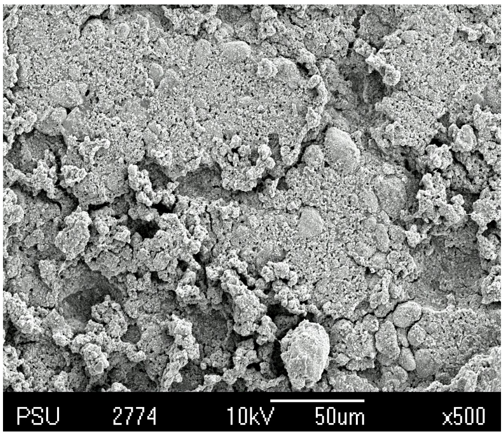


5a) 5 ml

150×



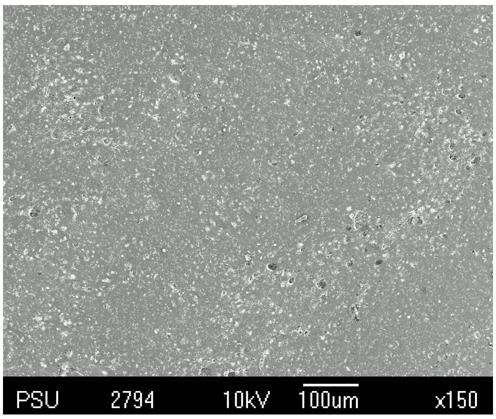
500×



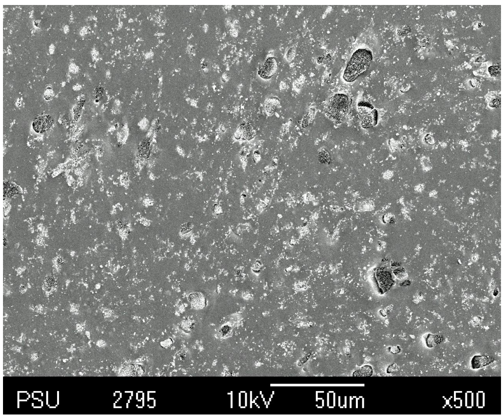
b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO_2)

1b) 3 ml

150×

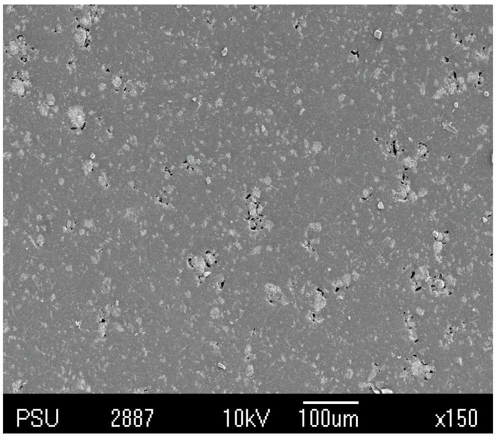


500×

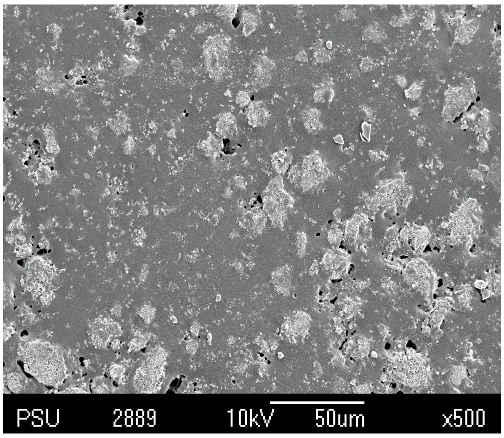


2b) 5 ml

150×

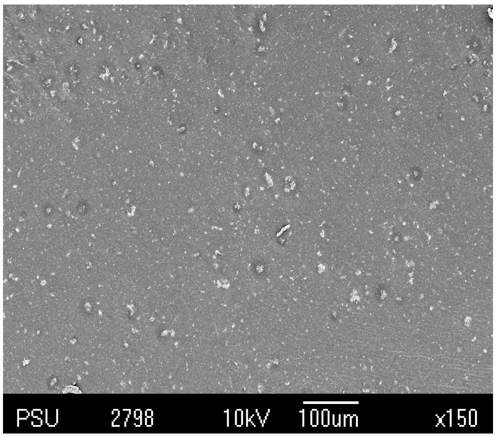


500×

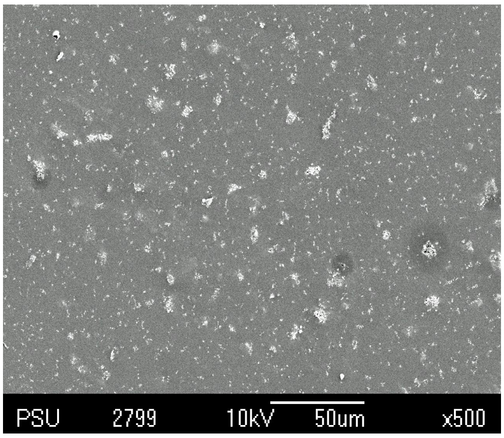


3b) 7 ml

150×

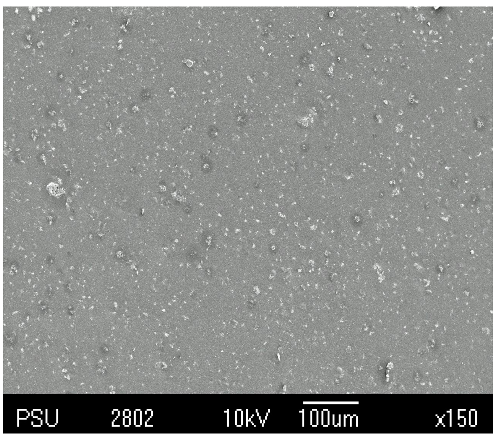


500×

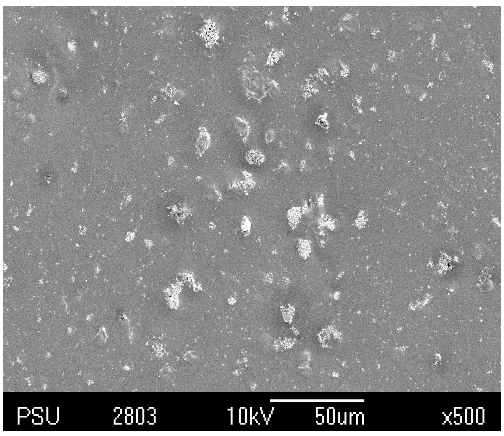


4b) 9 ml

150×



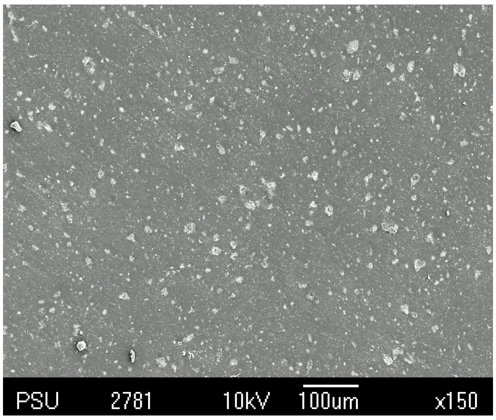
500×



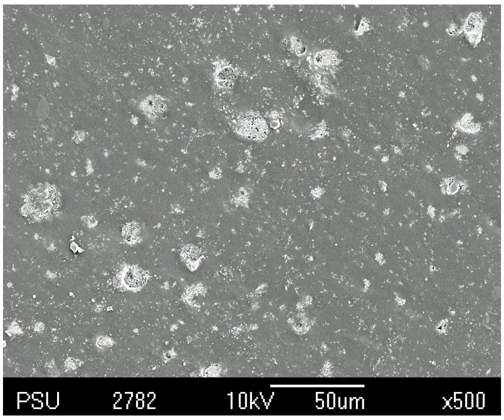
c) Varying amount of TiO_2 anatase (Fixed; 1ml distilled water and 5ml latex)

1c) 0.05 g

150×

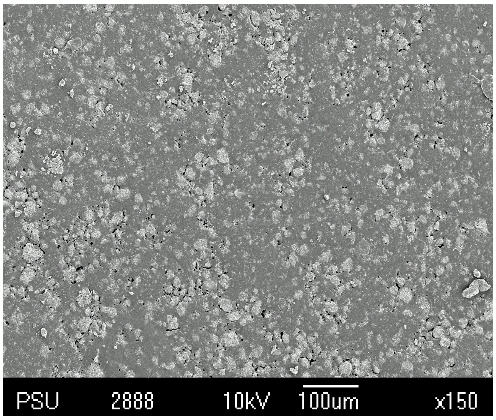


500×

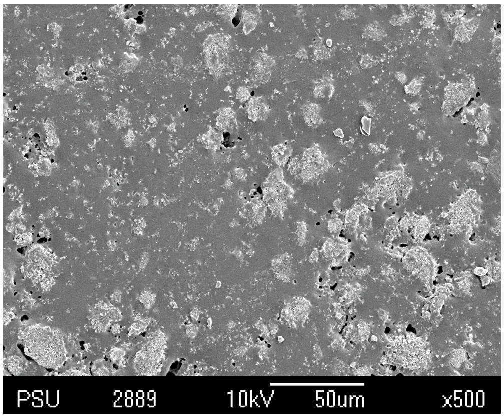


2c) 0.1 g

150×

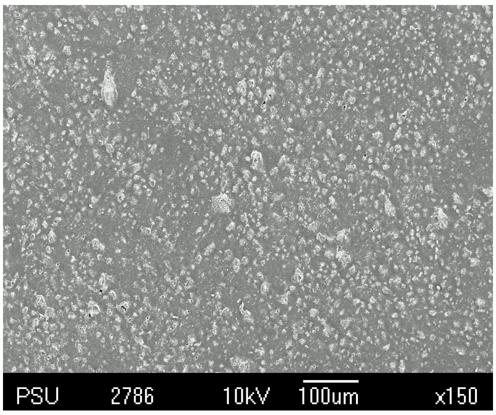


500×

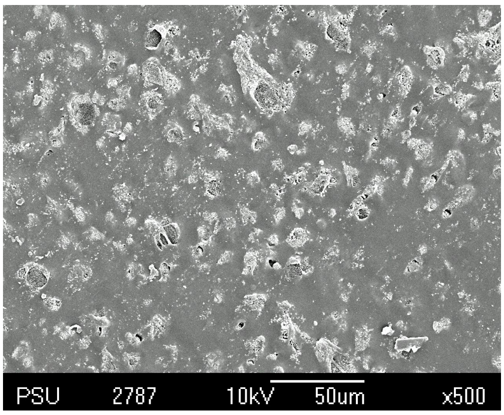


3c) 0.2 g

150×

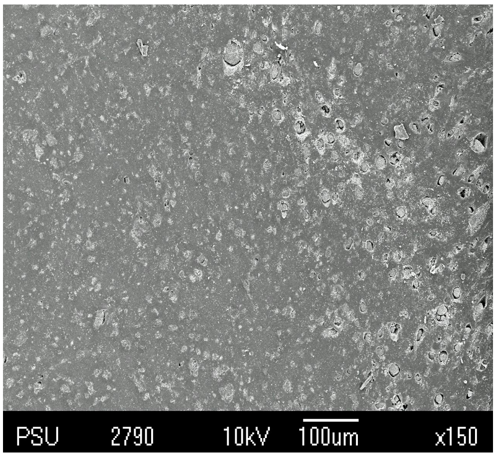


500×



4c) 0.3 g

150×



500×

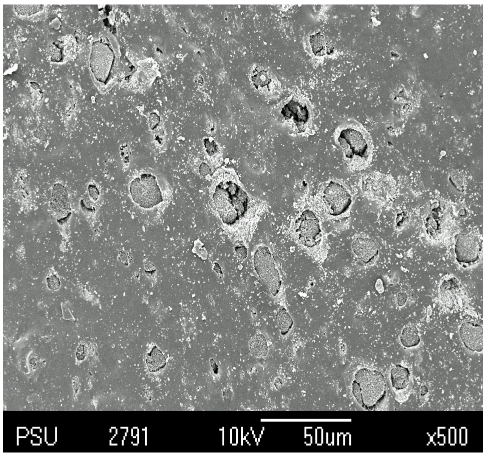


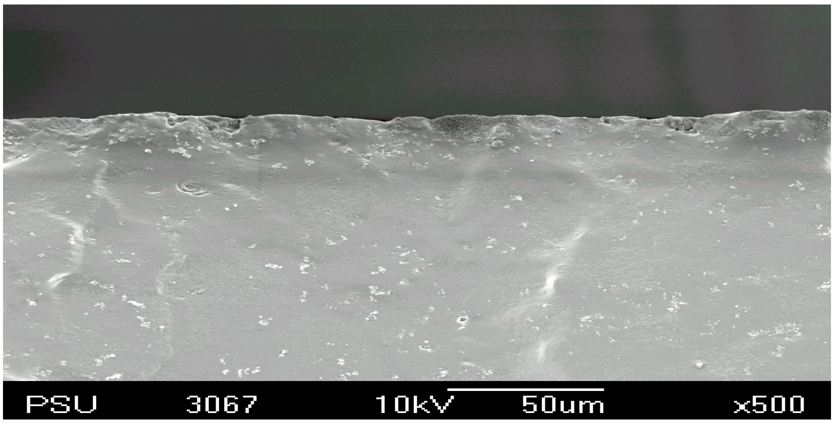
Figure 13 SEM surface images of Immo-TiO_2 anatase films

Immo-TiO_2 anatase films

a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO_2)

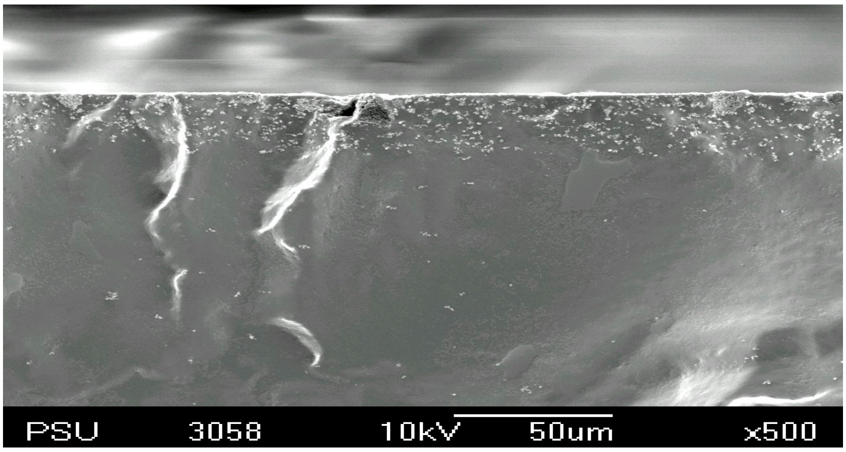
1a) 1 ml

500×



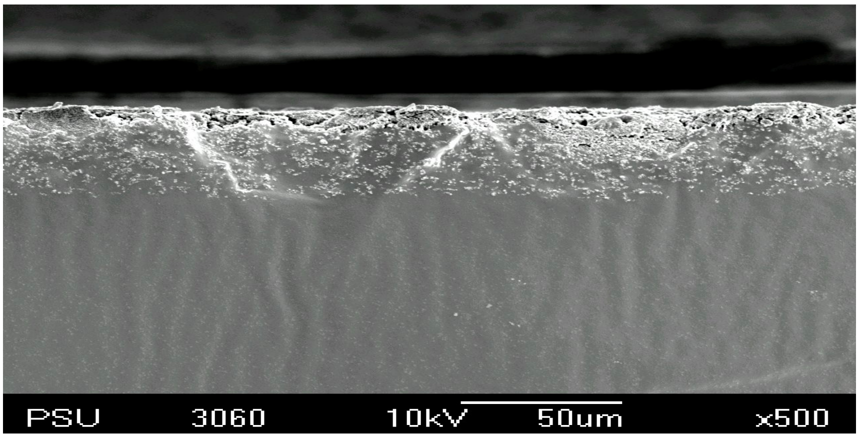
2a) 2 ml

500×



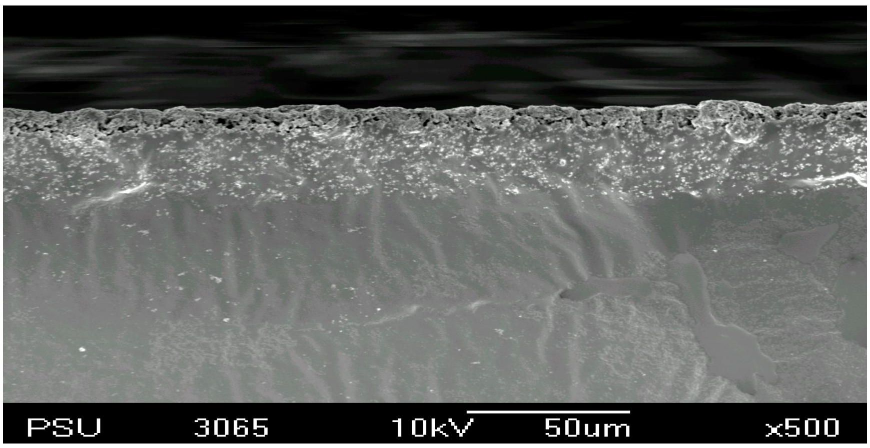
3a) 3 ml

500×



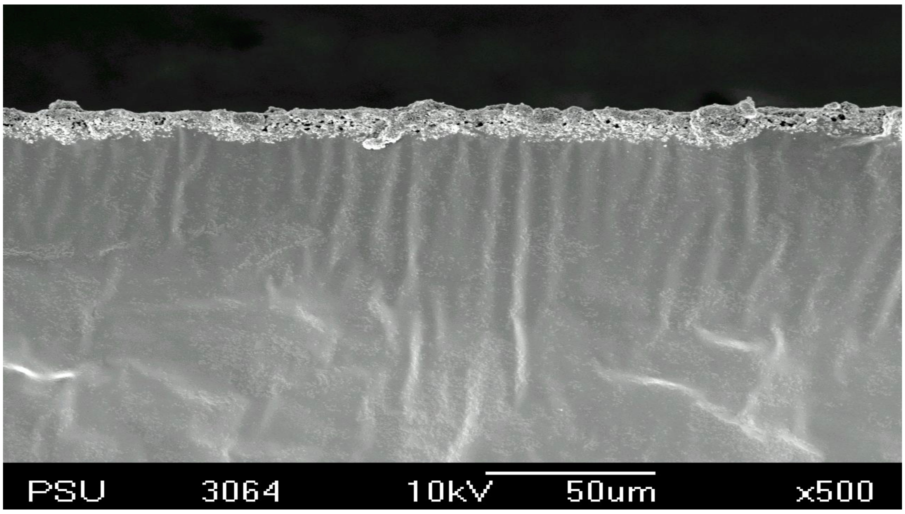
4a) 4 ml

500×



5a) 5 ml

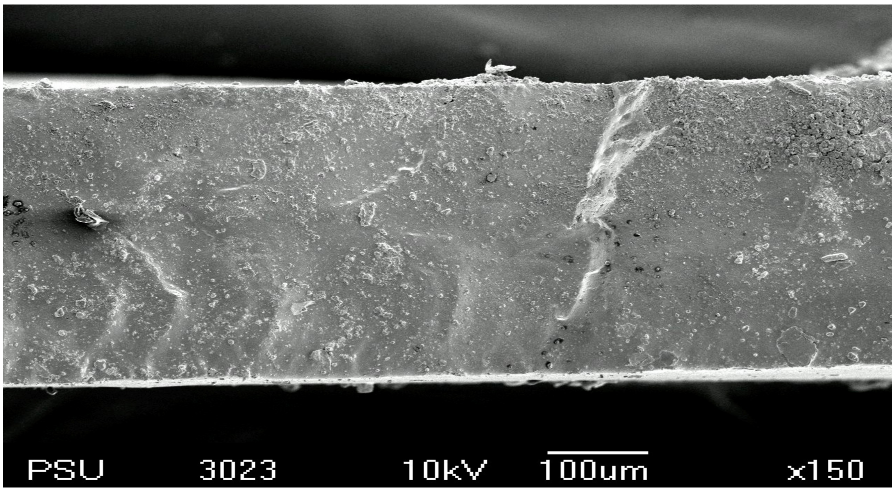
500×



b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO_2)

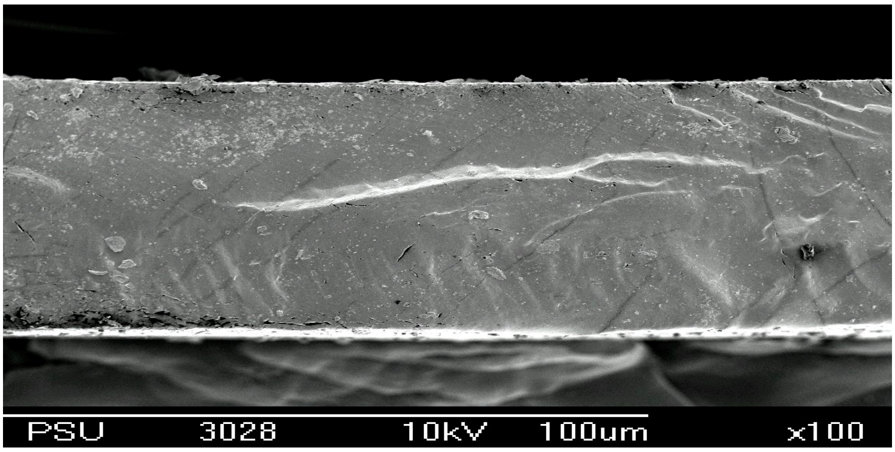
1b) 3 ml

150×



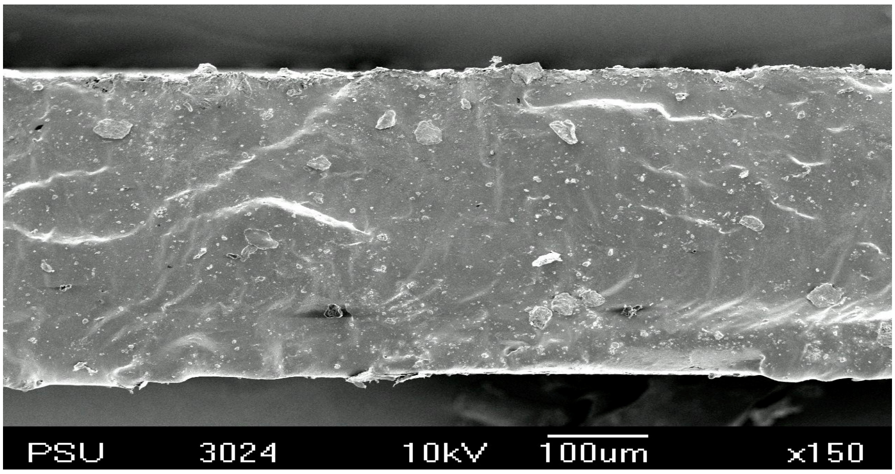
2b) 5 ml

100×



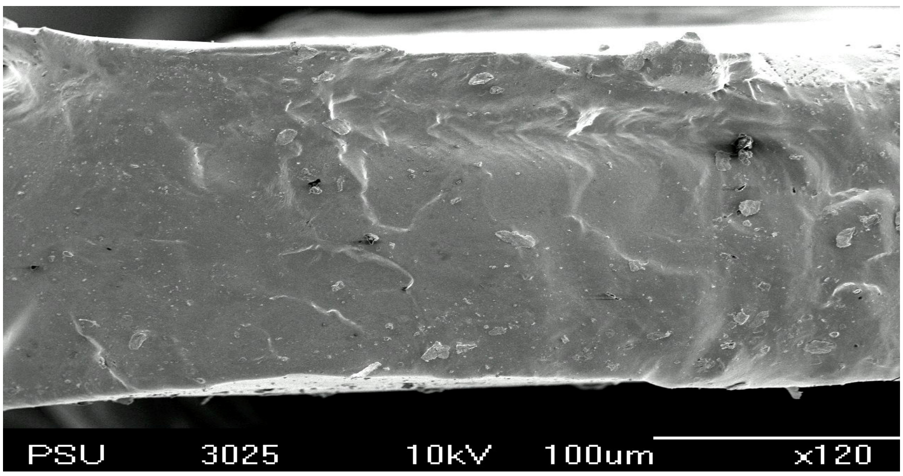
3b) 7 ml

150×



4b) 9 ml

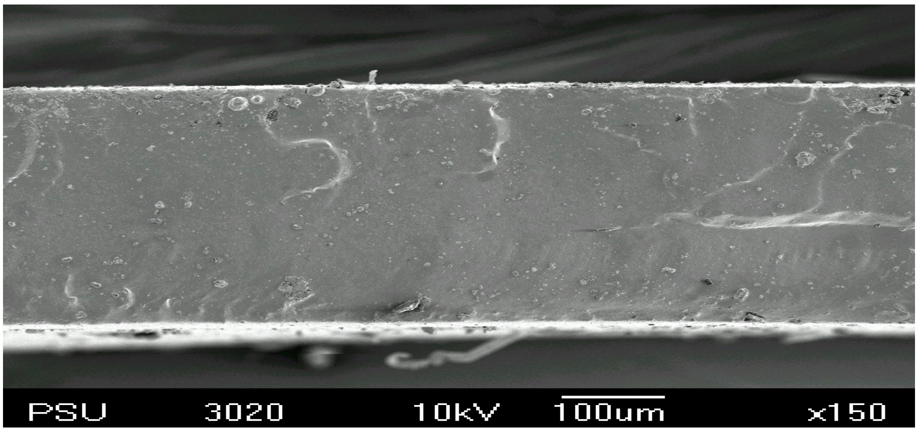
120×



c) Varying amount of TiO_2 anatase (Fixed; 1ml distilled water and 5ml latex)

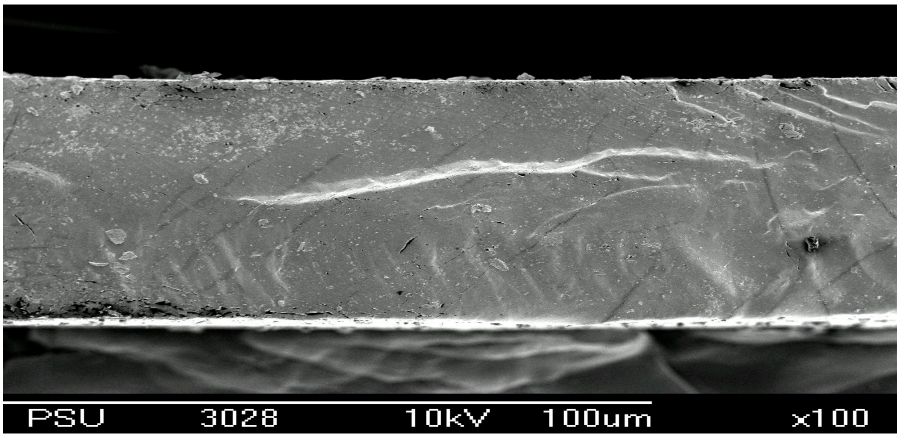
1c) 0.05 g

150×



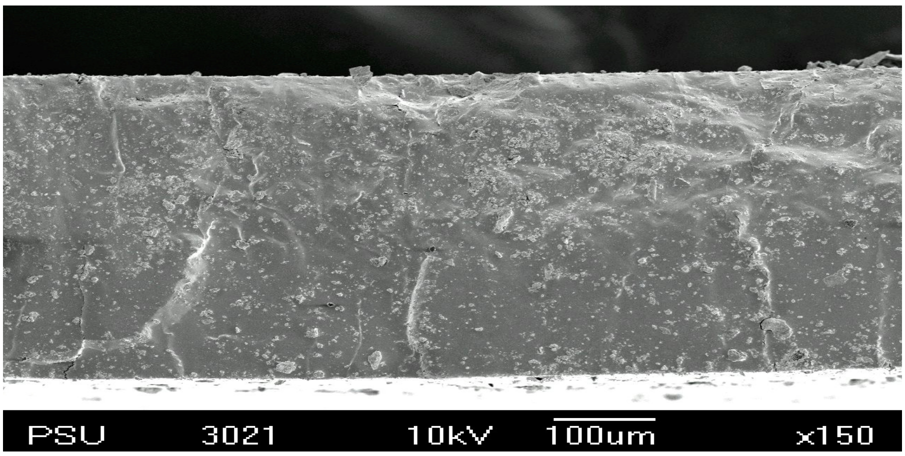
2c) 0.1 g

100×



3c) 0.2 g

150×



4c) 0.3 g

150×

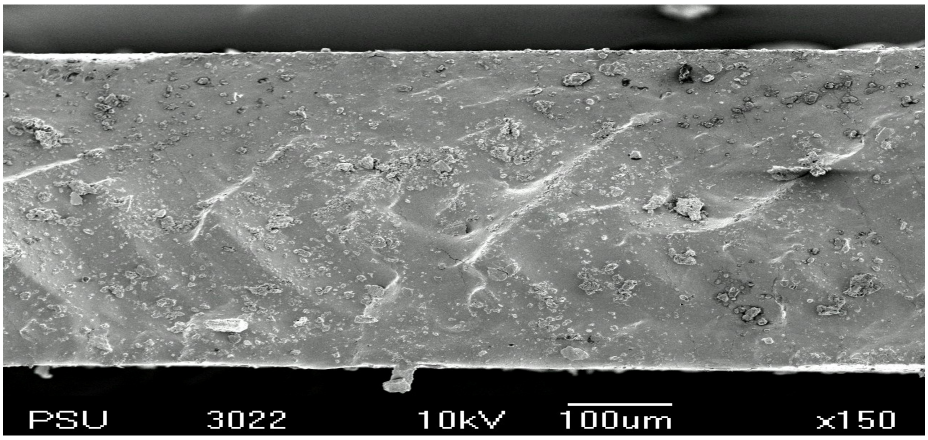


Figure 14 SEM cross section images of Immo-TiO_2 anatase films

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.

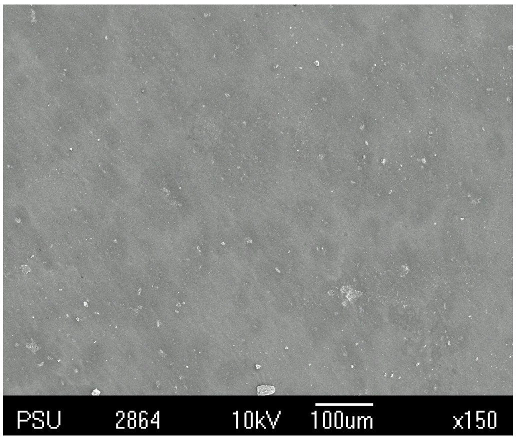
The corresponding SEM cross sections of each Immo-TiO_2 anatase film samples are shown in Figure 14. The SEM cross section images clearly show the separation of TiO_2 layer from the rubber layer when increasing amounts of distilled water were used for the preparation of Immo-TiO_2 anatase films (Figures 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

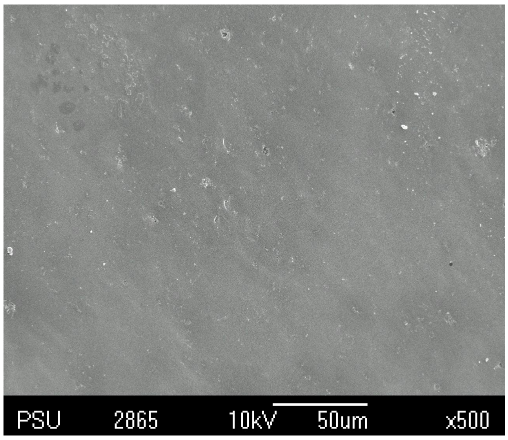
a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO_2)

1a) 1 ml

150×

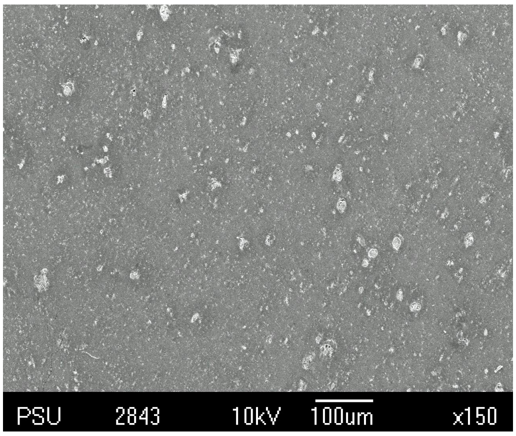


500×

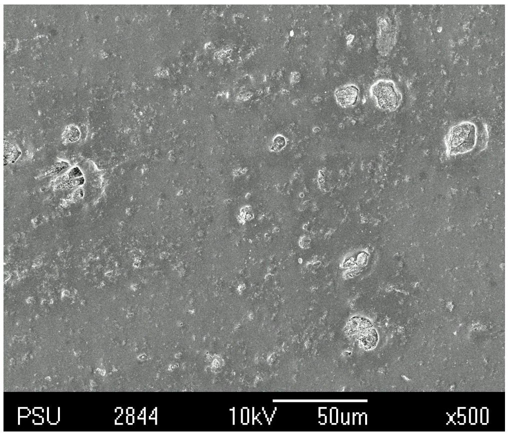


2a) 3 ml

150×

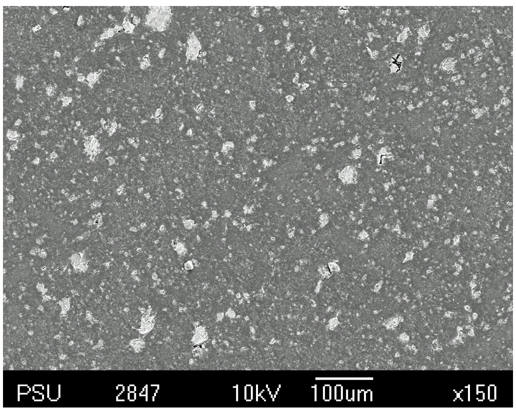


500×

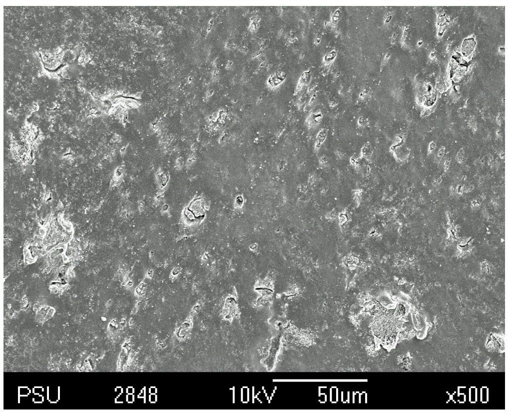


3a) 5 ml

150×

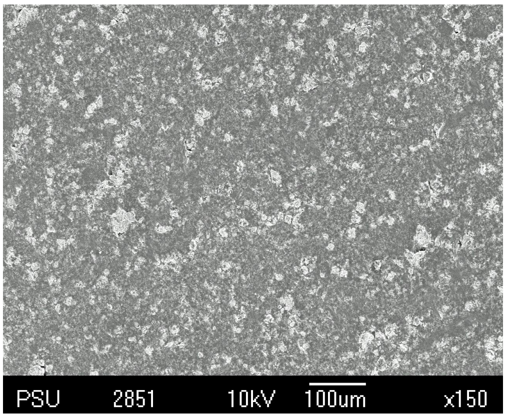


500×

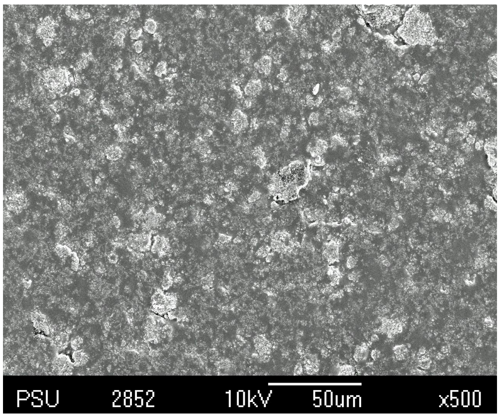


4a) 6 ml

150×

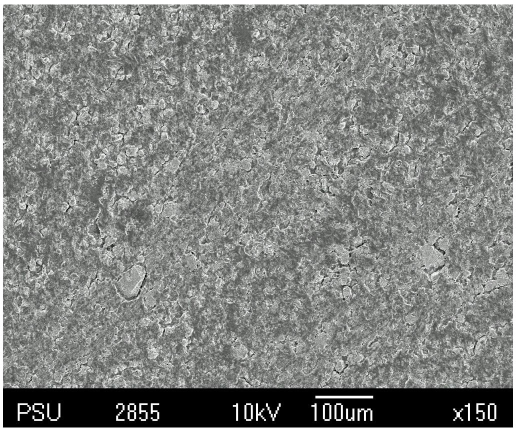


500×

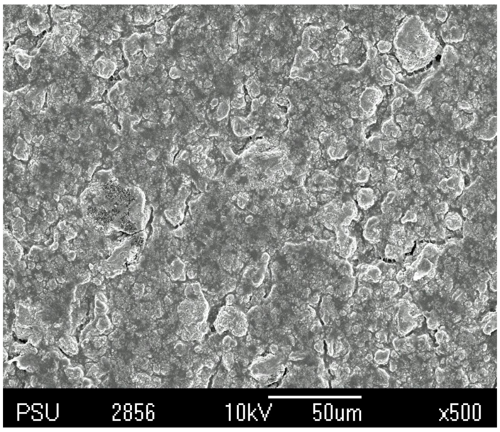


5a) 7 ml

150×



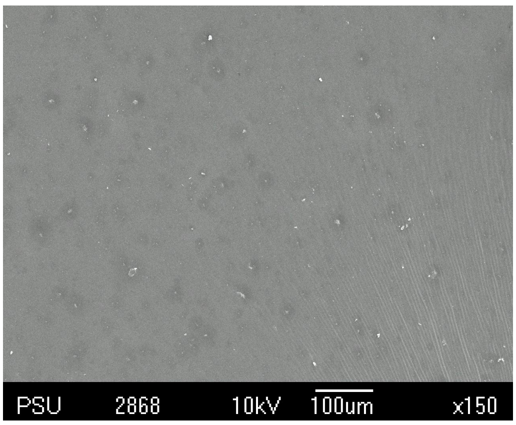
500×



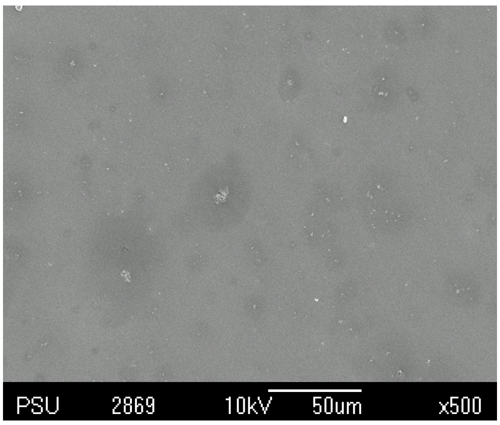
b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO_2)

1b) 3 ml

150×

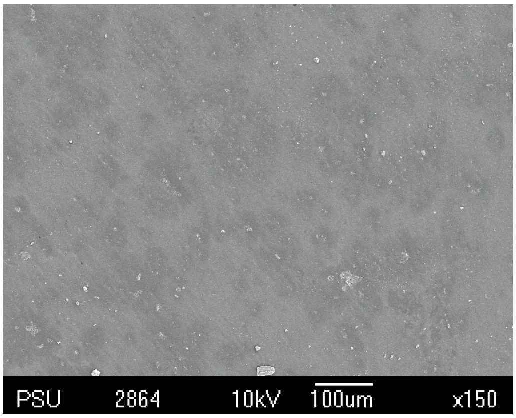


500×

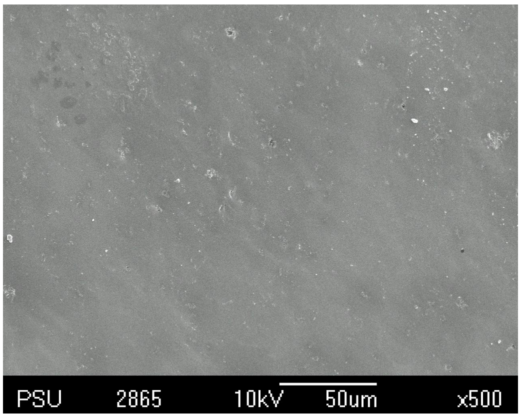


2b) 5 ml

150×

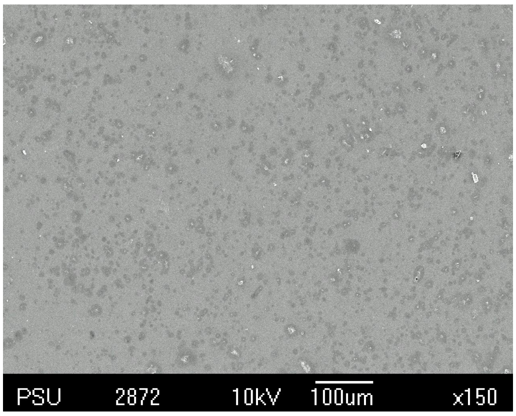


500×

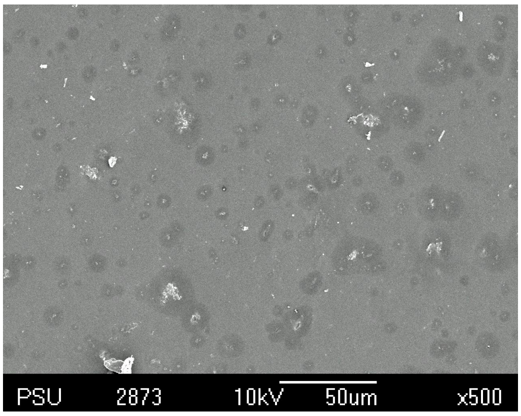


3b) 7 ml

150×

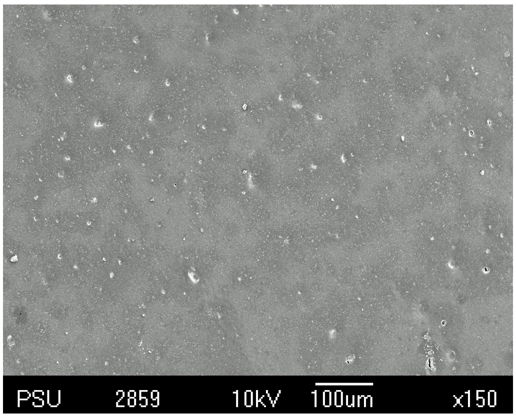


500×

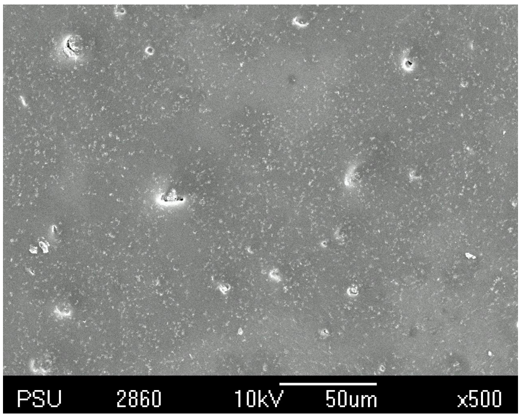


4b) 9 ml

150×



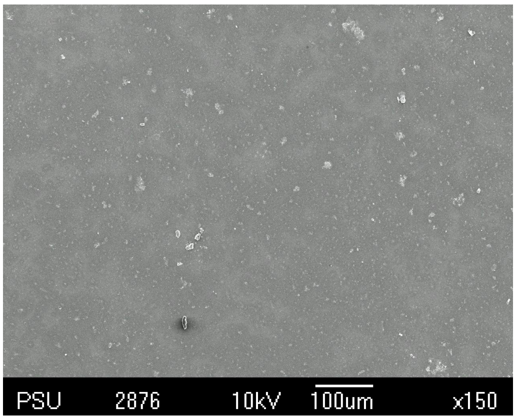
500×



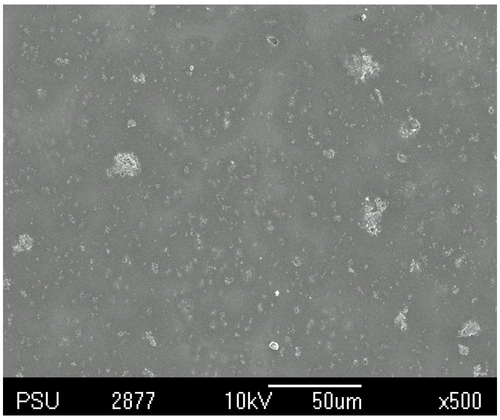
c) Varying amount of TiO_2 Degussa P25 (Fixed; 1ml distilled water and 5ml latex)

1c) 0.05 g

150×

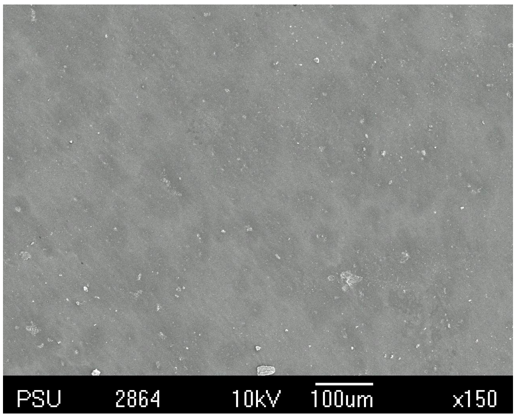


500×

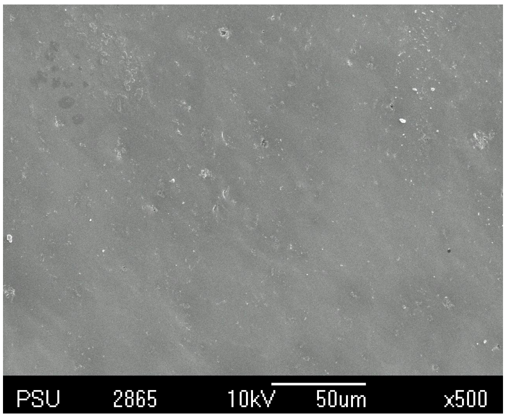


2c) 0.1 g

150×

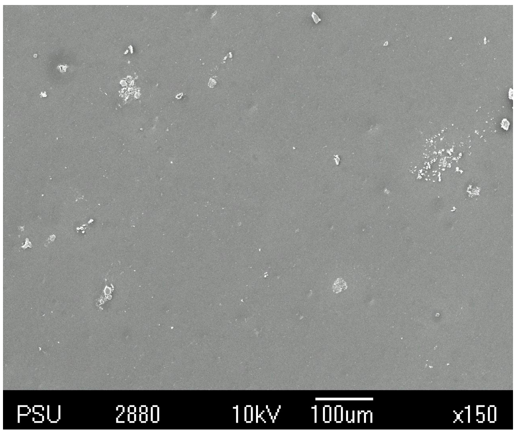


500×



3c) 0.2 g

150×



500×

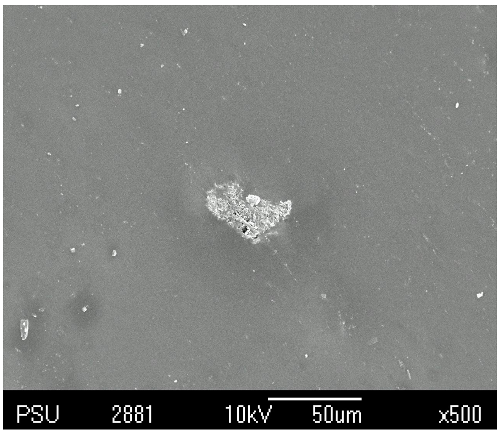


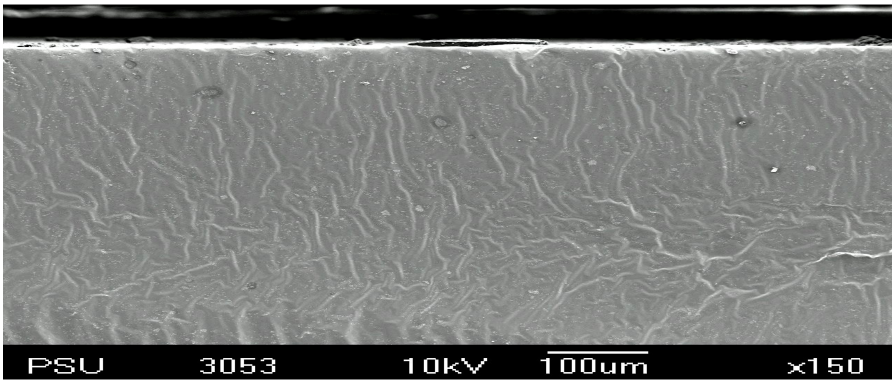
Figure 15 SEM surface images of Immo-TiO_2 Degussa P25 films

Immo-TiO_2 Degussa P25 films

a) Varying amount of distilled water (Fixed; 5ml latex and 0.1g TiO_2)

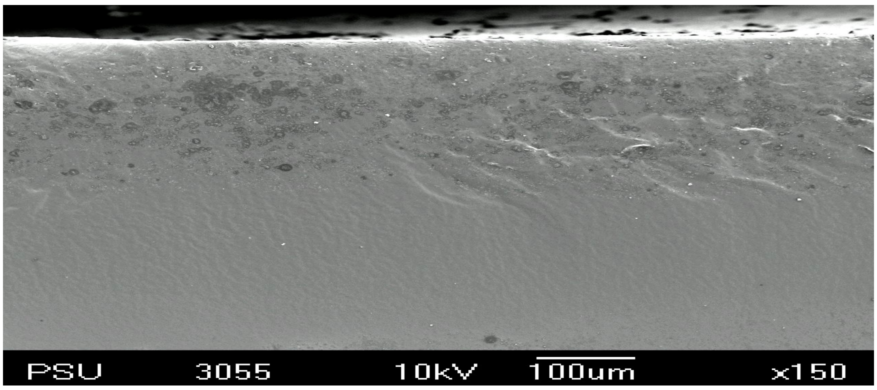
1a) 1 ml

150×



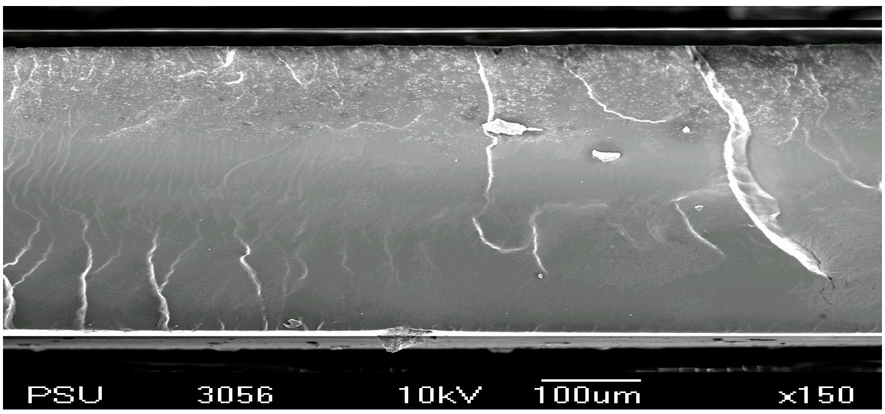
2a) 3 ml

150×



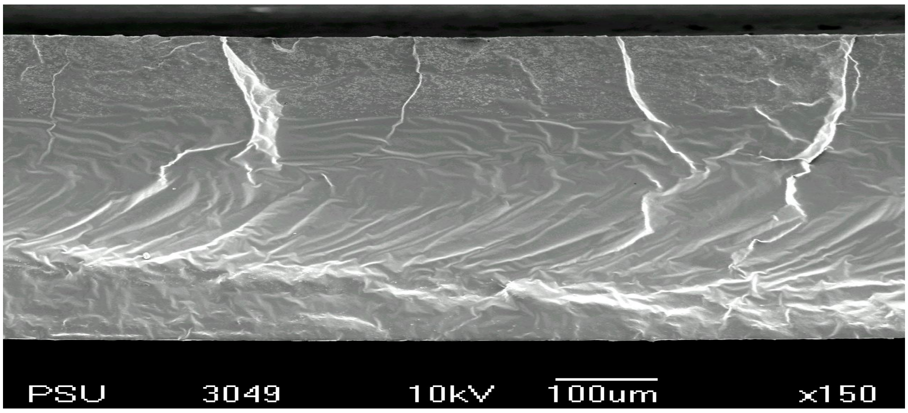
3a) 5 ml

150×



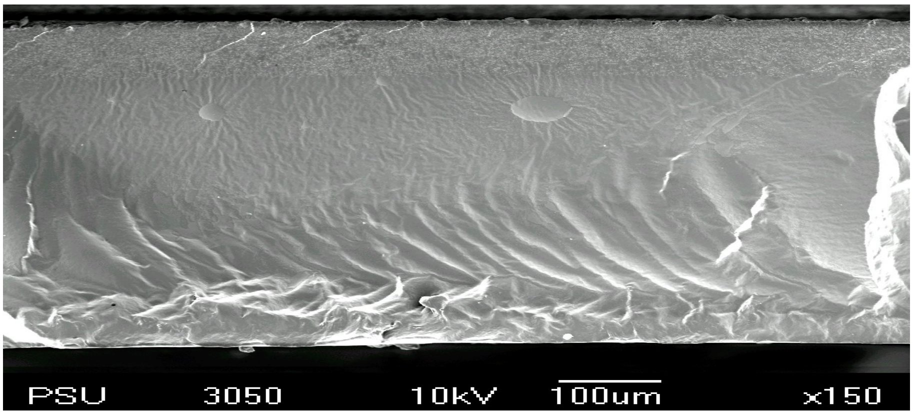
4a) 6 ml

150×



5a) 7 ml

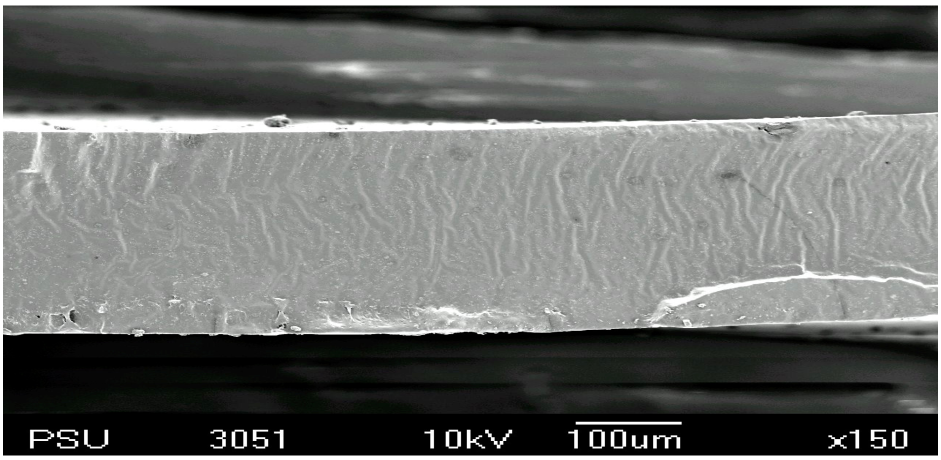
150×



b) Varying amount of latex (Fixed; 1ml distilled water and 0.1g TiO_2)

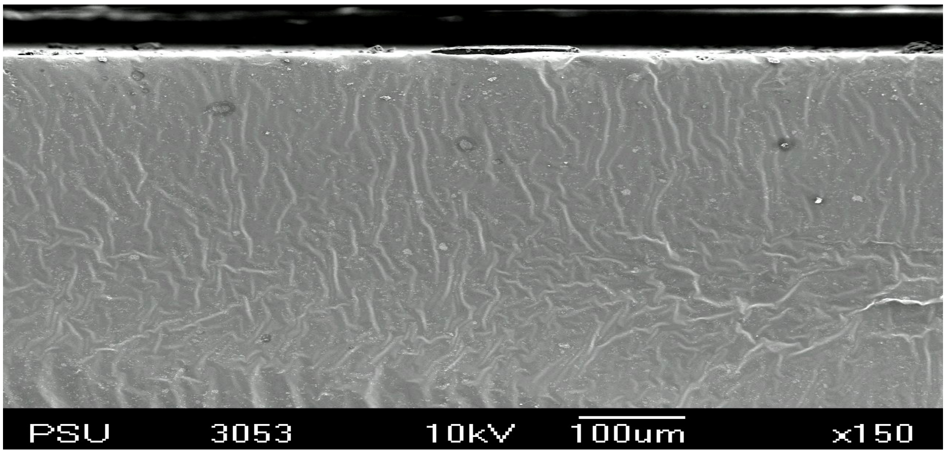
1b) 3 ml

150×



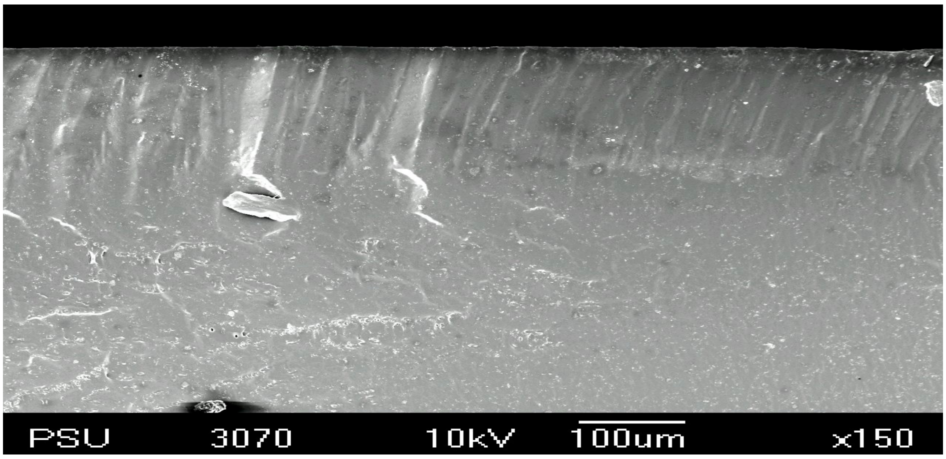
2b) 5 ml

150×



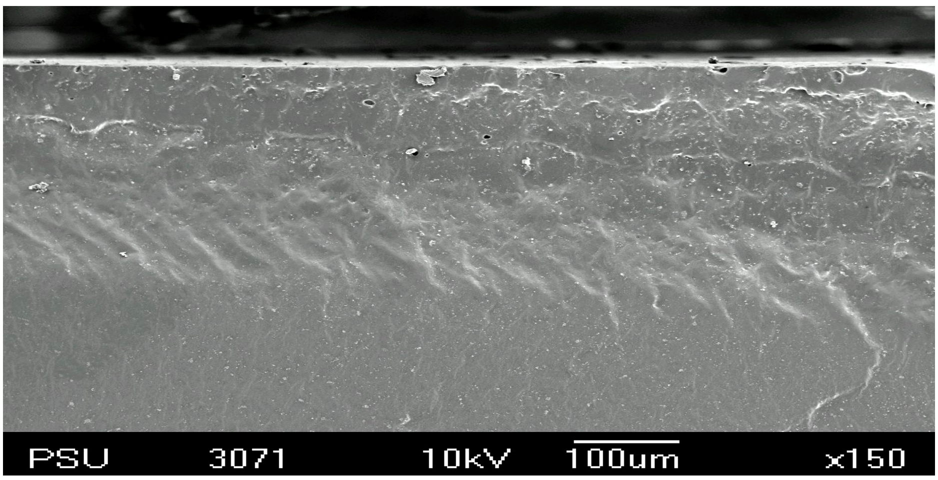
3b) 7 ml

150×



4b) 9 ml

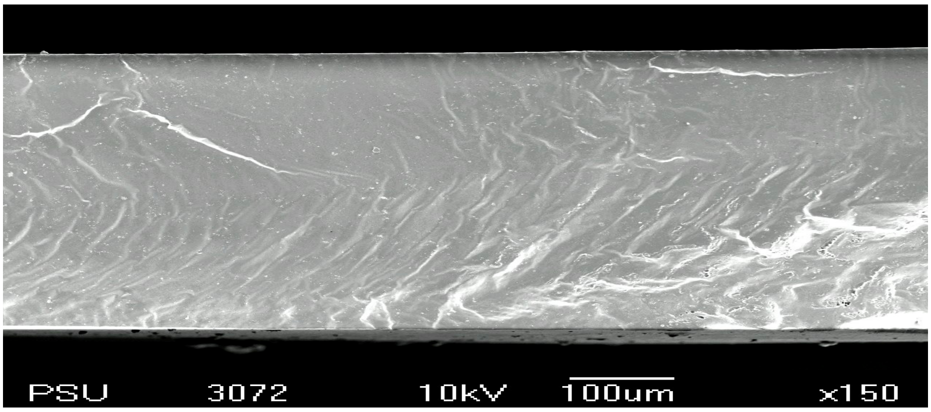
150×



c) Varying amount of TiO_2 Degussa P25 (Fixed; 1ml distilled water and 5ml latex)

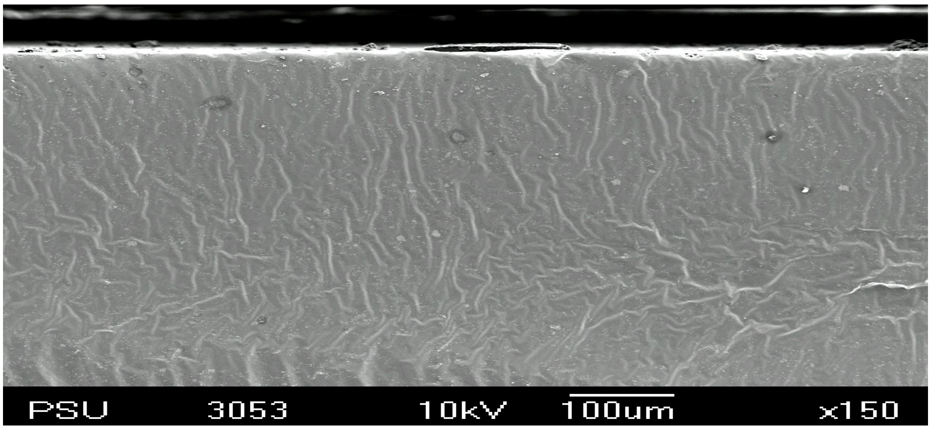
1c) 0.05 g

150×



2c) 0.1 g

150×



3c) 0.2 g

150×

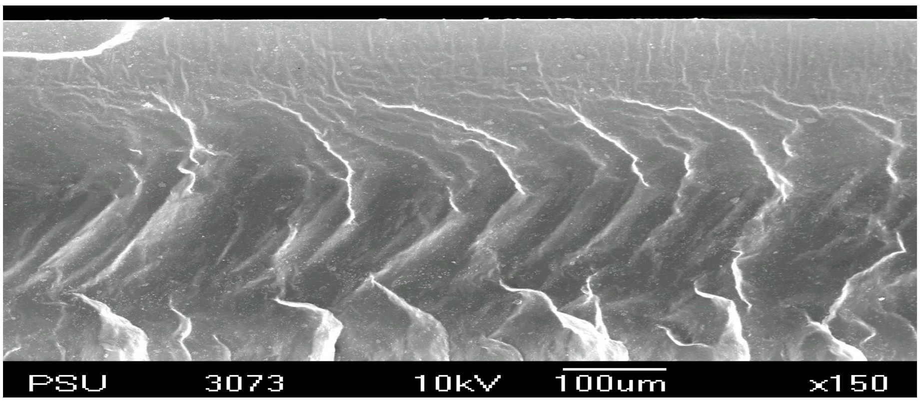


Figure 16 SEM cross section images of Immo-TiO_2 Degussa P25 films

Figure 15 shows the SEM micrographs of Immo-TiO_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_2 Degussa P25 (Figure 15c). In Figure 15a, the surface morphology and roughness of Immo-TiO_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_2 particles were lost from the surface of film causing the resulting film unstable. The surface morphology and roughness of Immo-TiO_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_2 Degussa P25, Figure 15c, the surface morphology and roughness of Immo-TiO_2 Degussa P25 film samples decreased with increasing amount of commercial TiO_2 Degussa P25 as shown in Figures 15(1c), (2c) and (3c), respectively.

The corresponding SEM cross sections of each Immo-TiO_2 Degussa P25 film samples are shown in Figure 16. 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 Degussa P25 films (Figure 16(2a), (3a), (4a), and (5a)). These separations were not observed in other samples indicating better mixing between TiO_2 particles and the rubber latex. The SEM images of Immo-TiO_2 anatase films generally show higher surface morphology and roughness than Immo-TiO_2 Degussa P25 films. The SEM images of surface and cross section of rubber substrate are shown in Figure 17 for comparison.

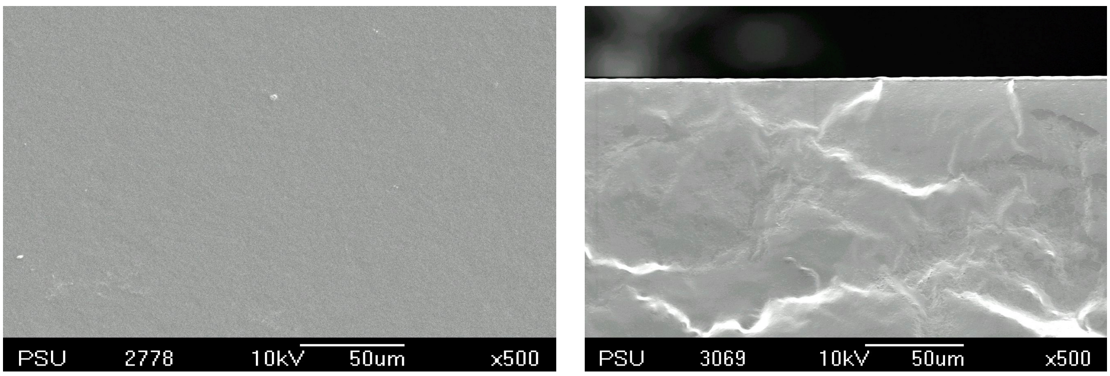


Figure 17 Left: the SEM image of rubber substrate surface ; right: the SEM of cross section of rubber substrate

3.1.2.2 X-ray powder diffraction (XRD)

The XRD pattern at 2θ = 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 2θ = 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.

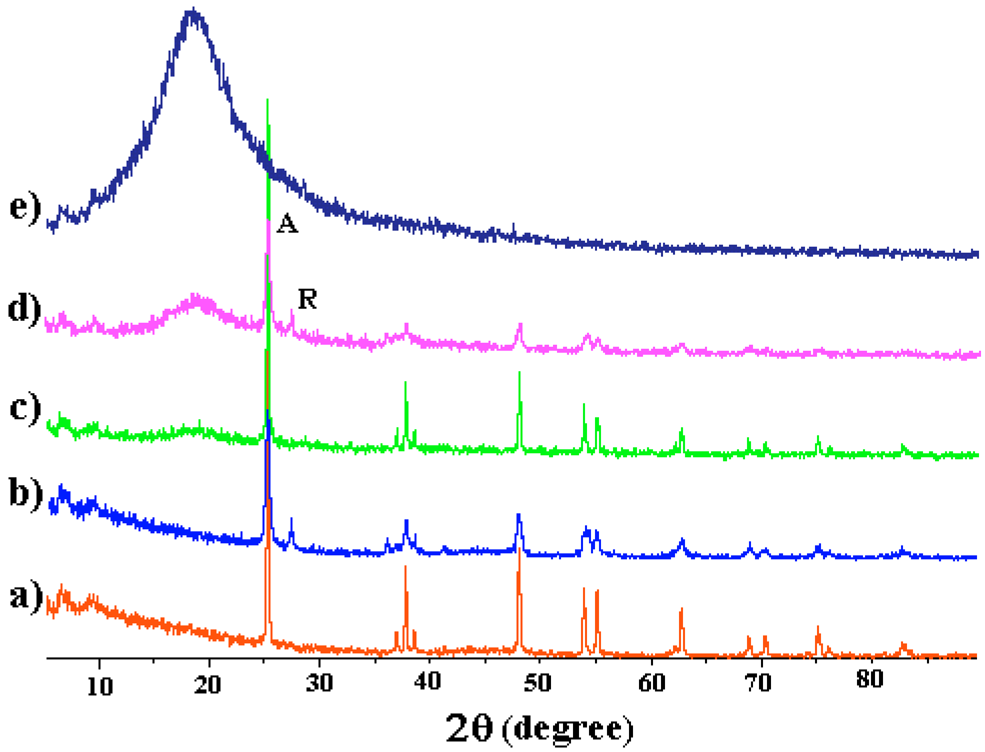


Figure 18 XRD patterns of both commercial TiO_2 powders; a) Anatase (Carlo Eaba), b) Degussa P25, c) Immo-TiO_2 anatase film, d) Immo-TiO_2 Degussa P25 film, and e) Rubber substrate

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.

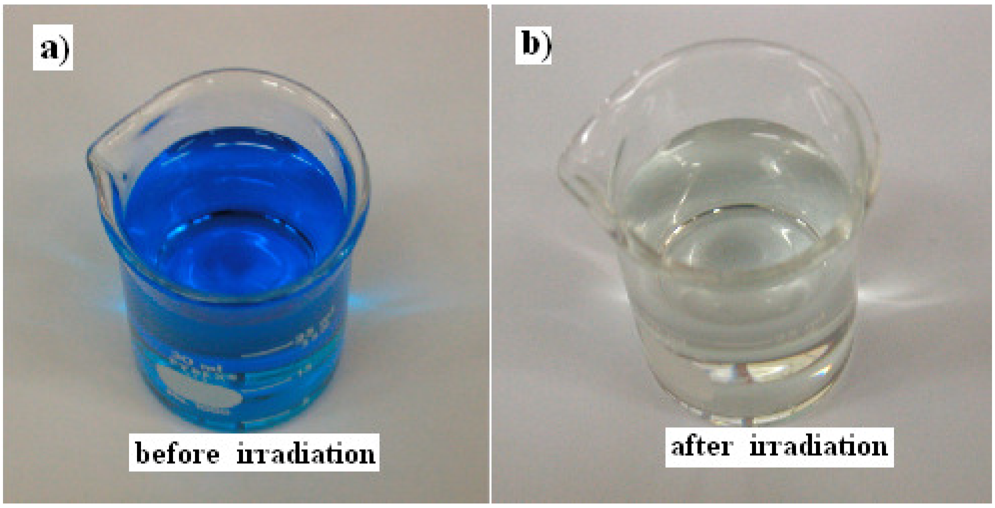


Figure 19 The photocatalytic degradation of methylene blue aqueous solution by Immo-TiO_2 film under UV irradiation

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 2.5×10^{-6} M to 3.0×10^{-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.

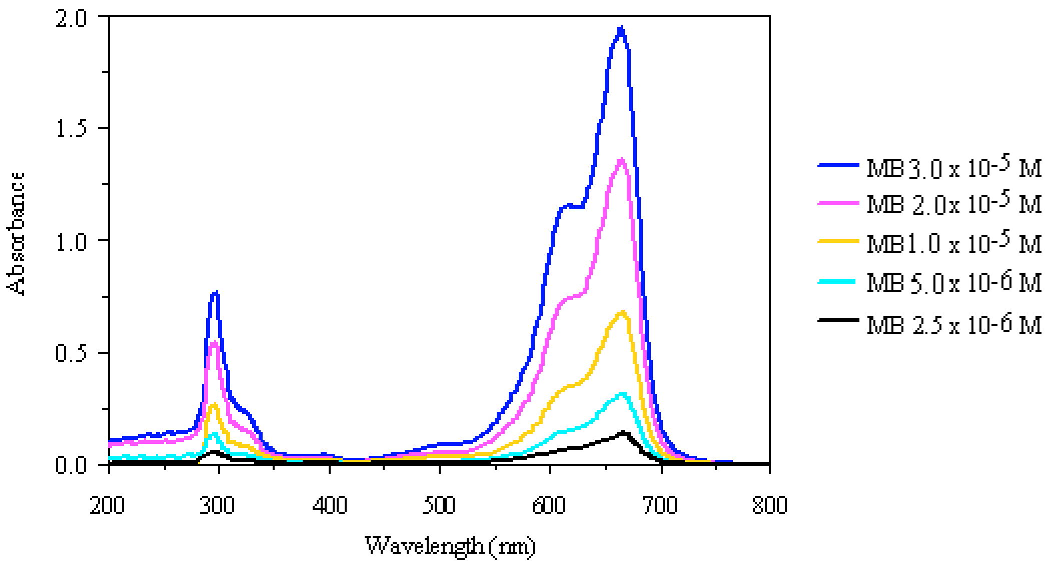


Figure 20 The absorption spectra of methylene blue solution in the range of 2.5×10^{-6} M to 3.0×10^{-5} M

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

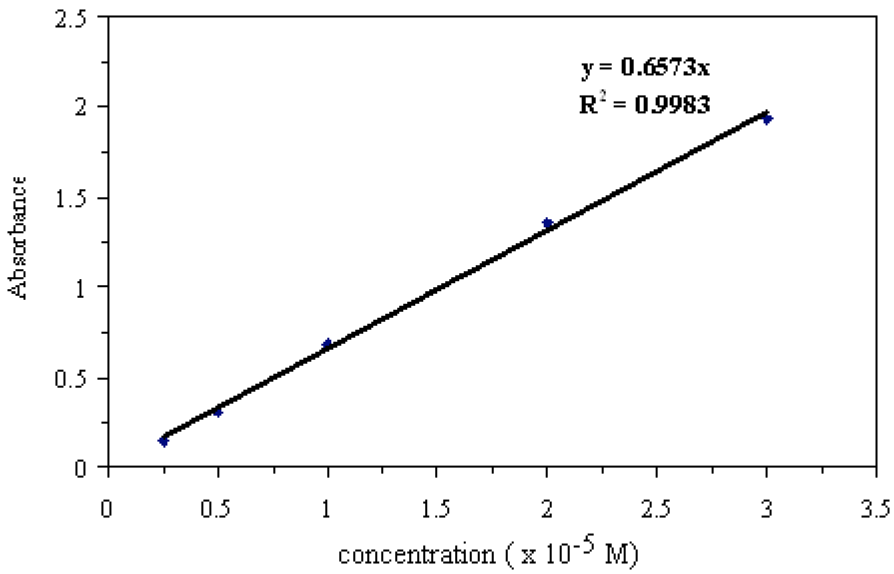


Figure 21 The standard calibration curve of methylene blue solution in the range of 2.5×10^{-6} M to 3.0×10^{-5} M

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 X 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).

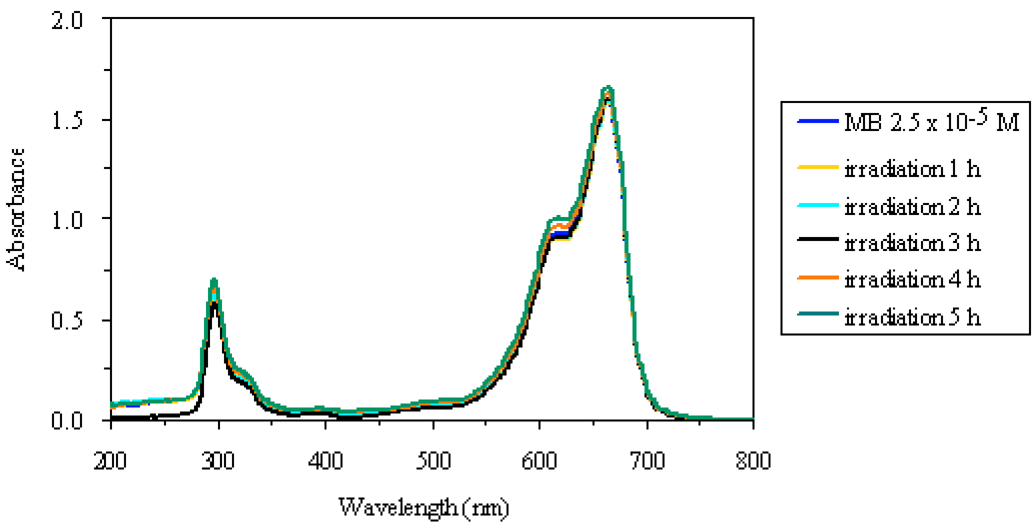


Figure 22 The absorption spectra of methylene blue solution alone under UV irradiation

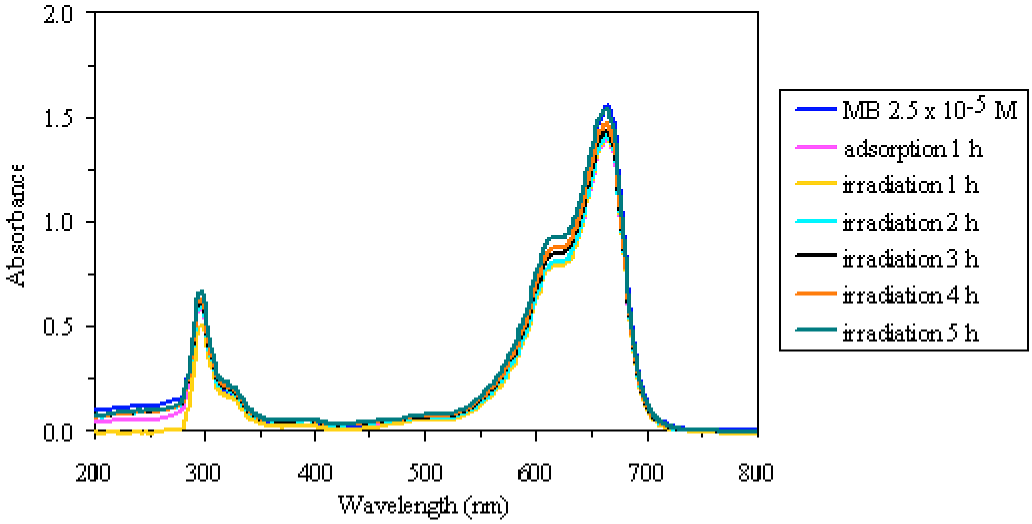
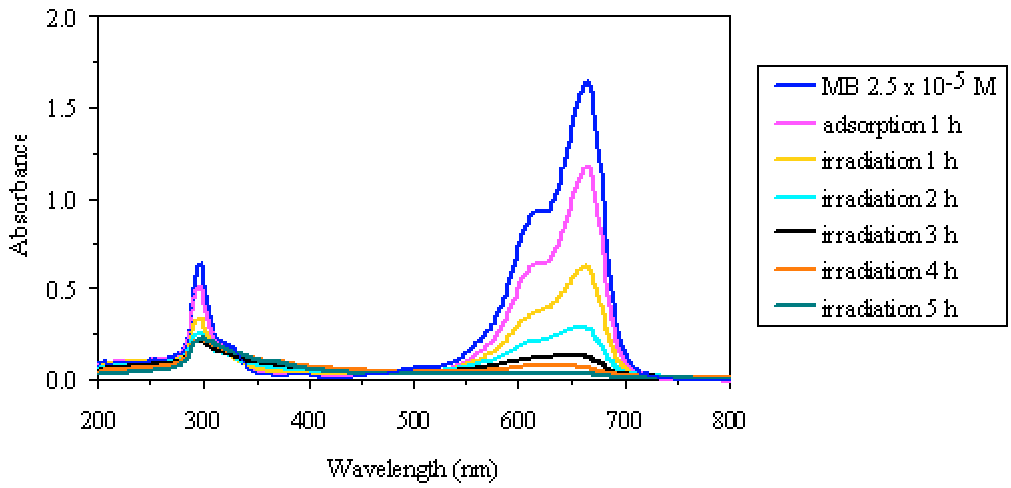


Figure 23 The absorption spectra of methylene blue solution with the rubber substrate under UV irradiation

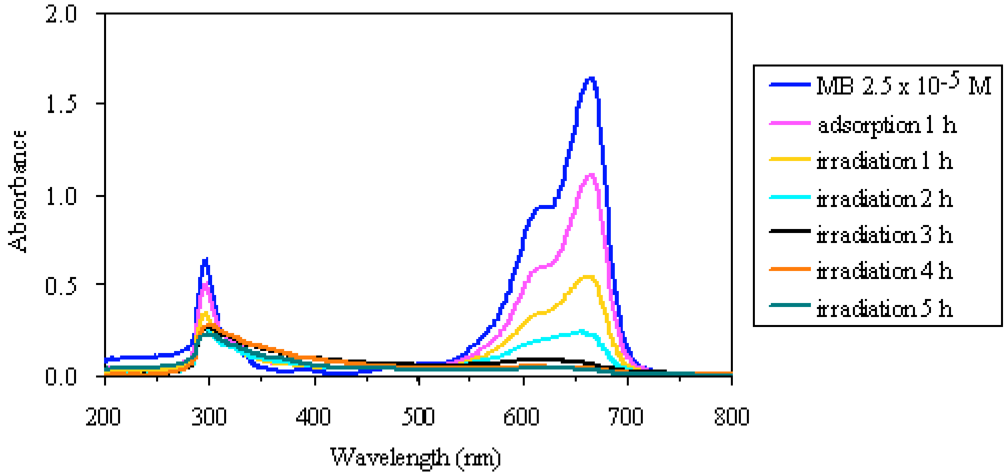
The results from the photocatalytic experiments of all Immo-TiO_2 anatase films and Immo-TiO_2 Degussa P25 films under UV irradiation as a function of times are shown in Figures 24 and 25, respectively. It can be seen that the absorption peak (λ = 665 nm) of MB solution will be slowly decreases with 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

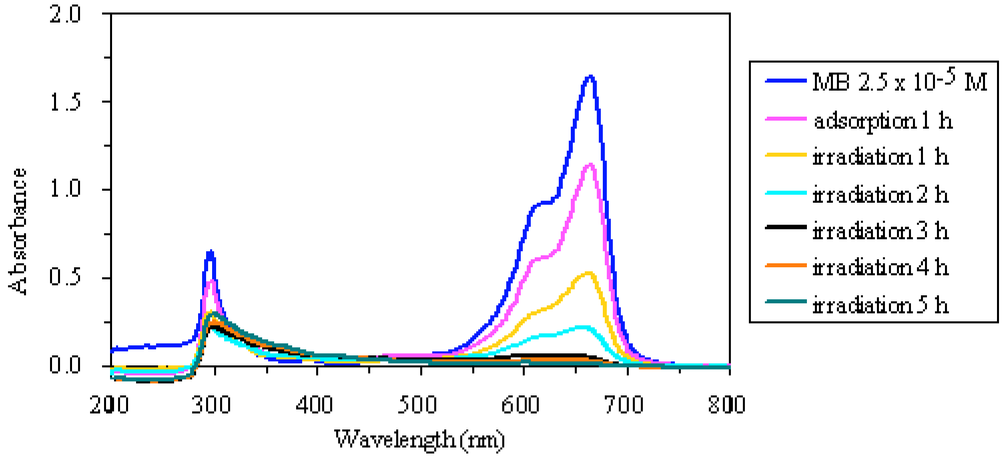
1a) 1ml



2a) 2 ml

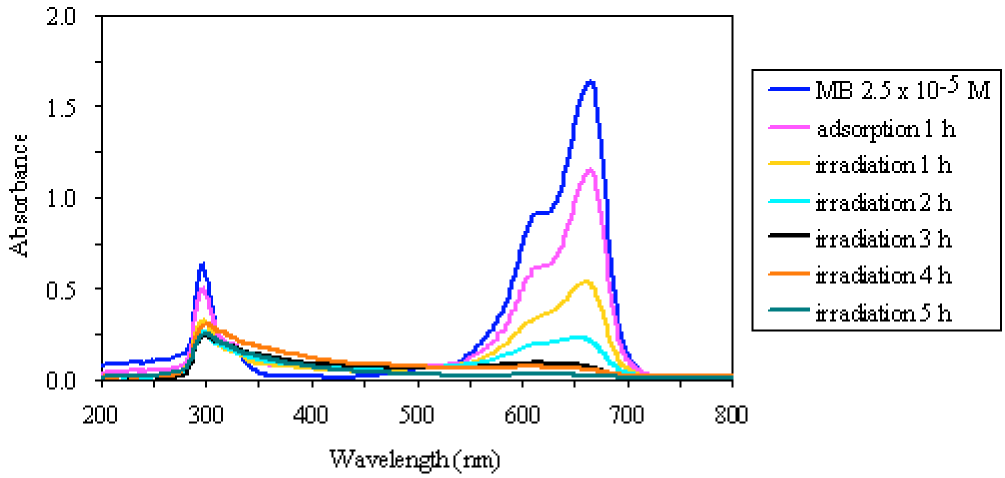


3a) 3 ml

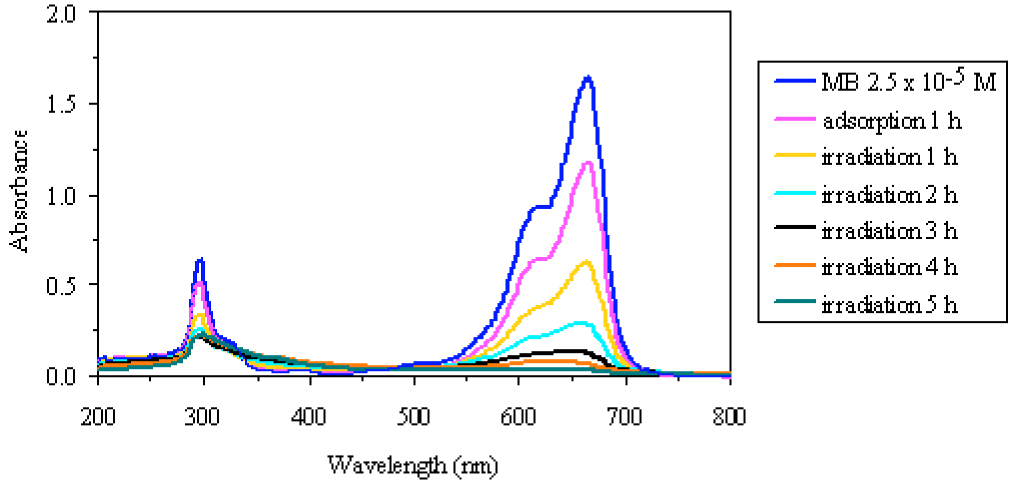


b) Films prepared by varying amount of latex

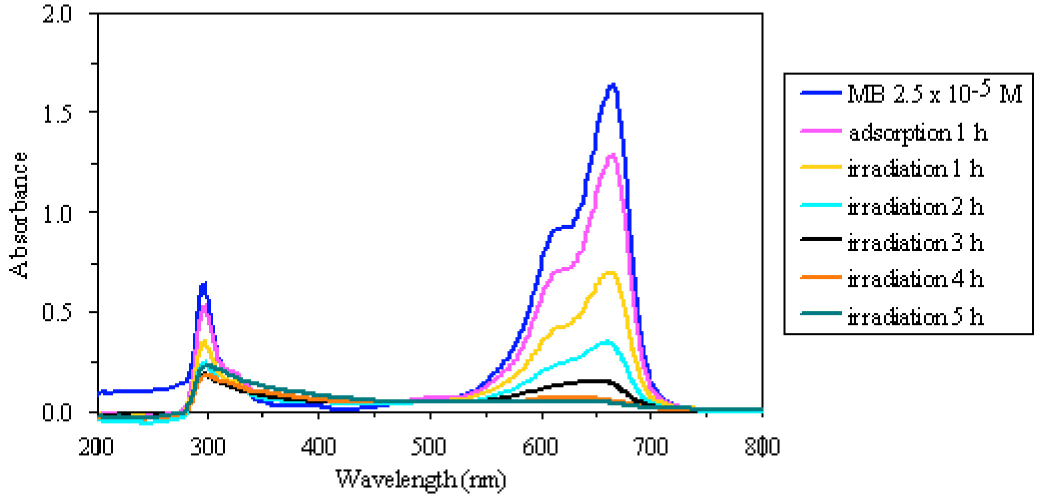
1b) 3 ml



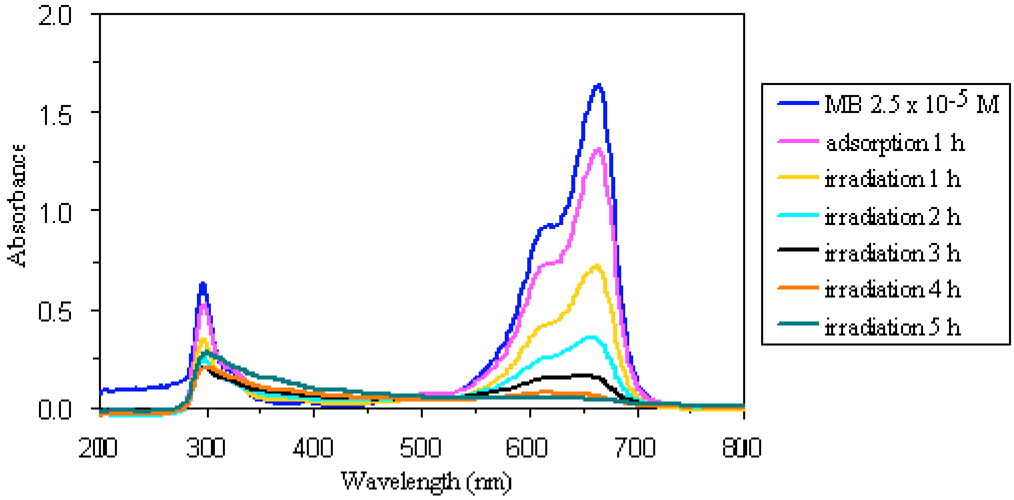
2b) 5 ml



3b) 7 ml

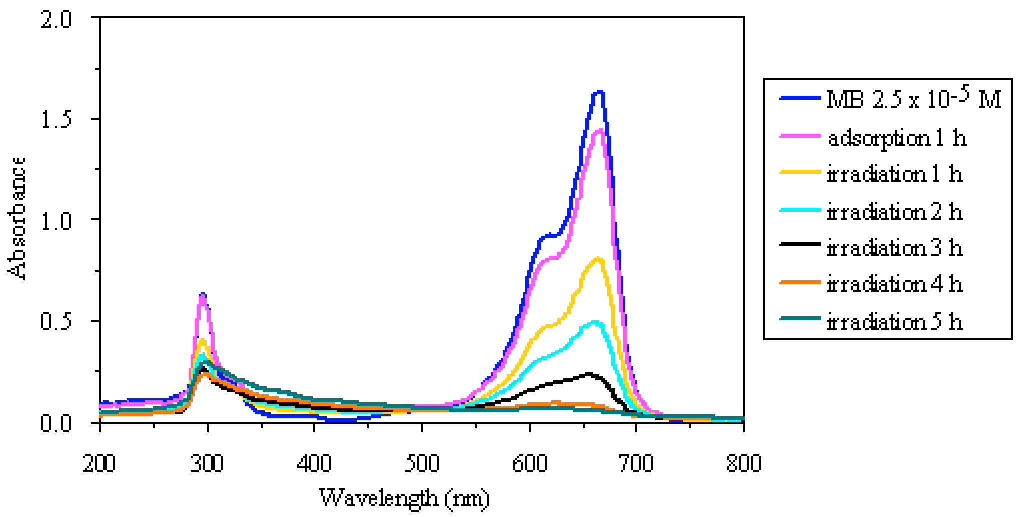


4b) 9 ml

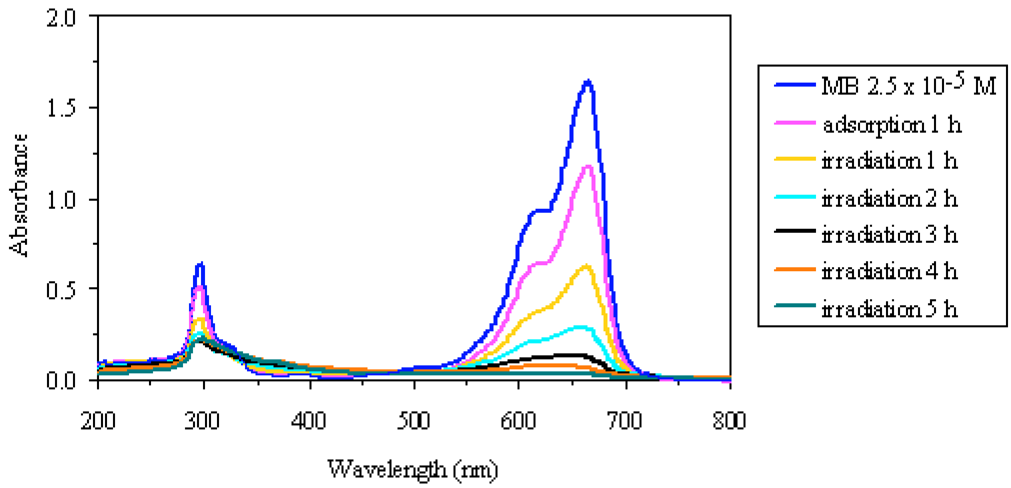


c) Films prepared by varying amount of TiO_2 anatase

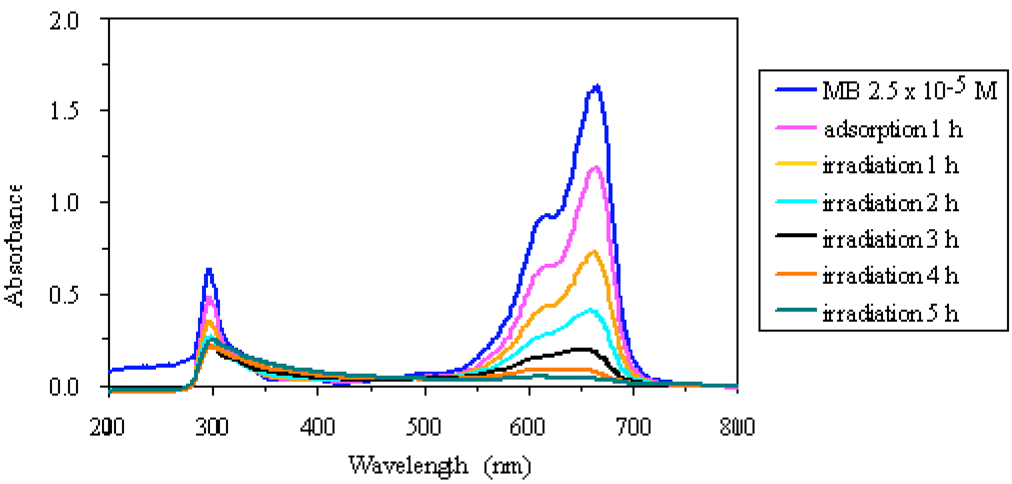
1c) 0.05 g



2c) 0.1 g



3c) 0.2 g



4c) 0.3 g

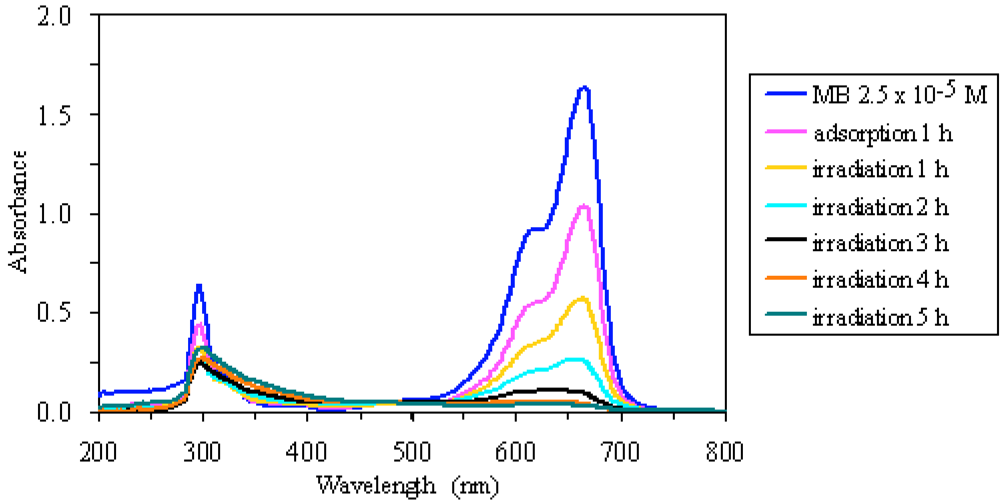
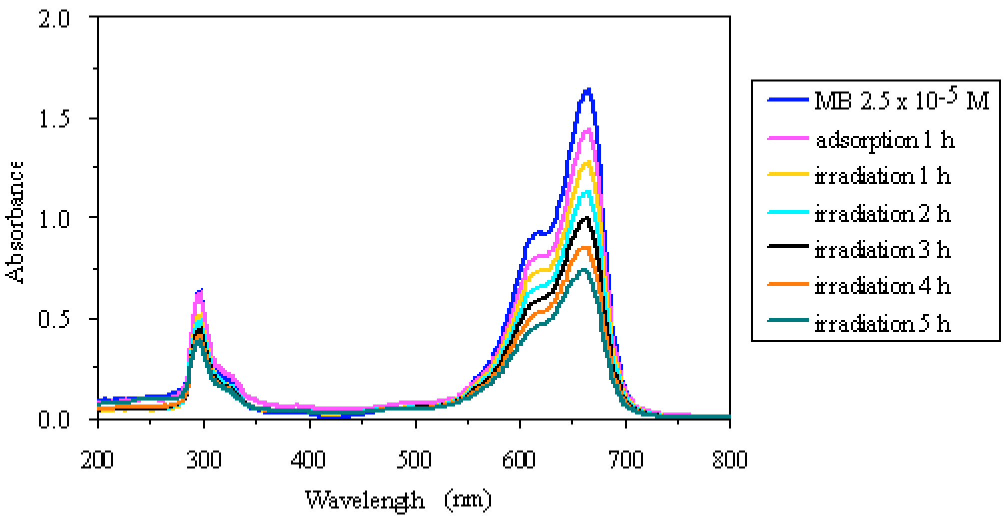


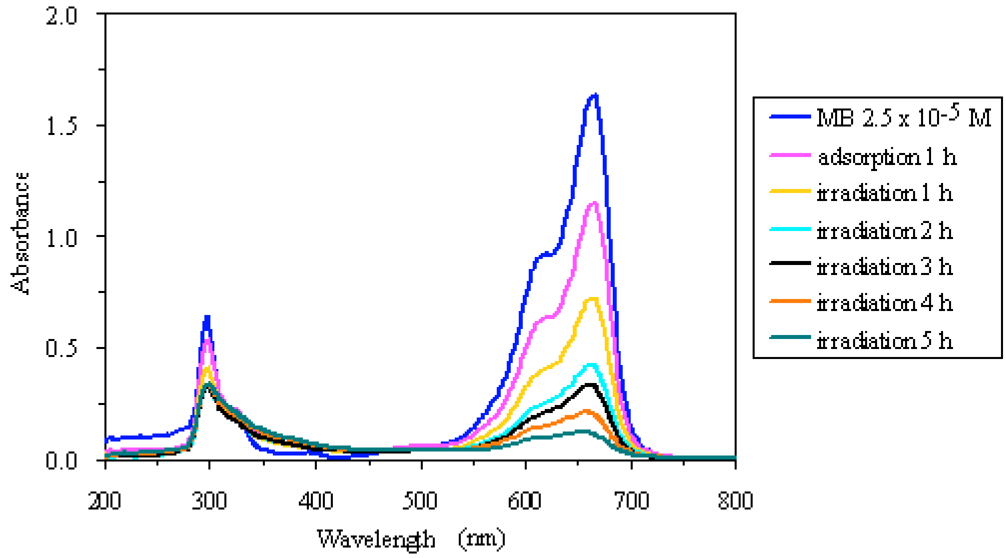
Figure 24 The UV-Vis spectral change of methylene blue with Immo-TiO_2 anatase film samples under UV irradiation as a function of times

a) Films prepared by varying amount of distilled water

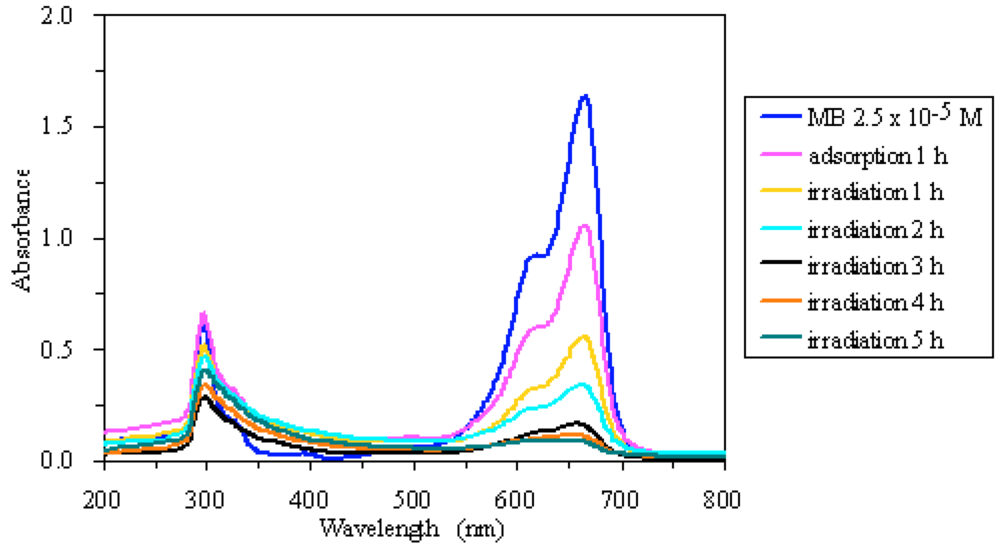
1a) 1 ml



2a) 3 ml

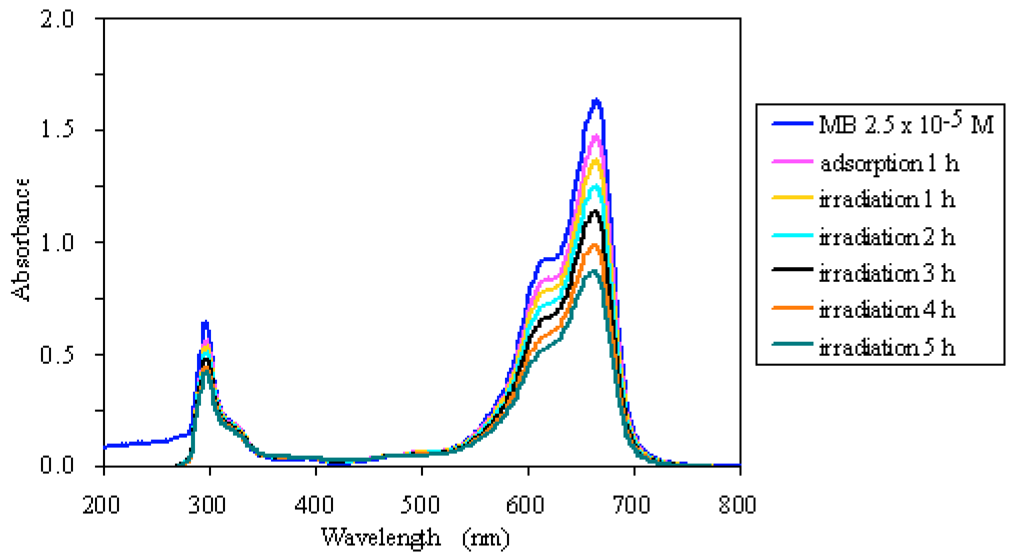


3a) 5 ml

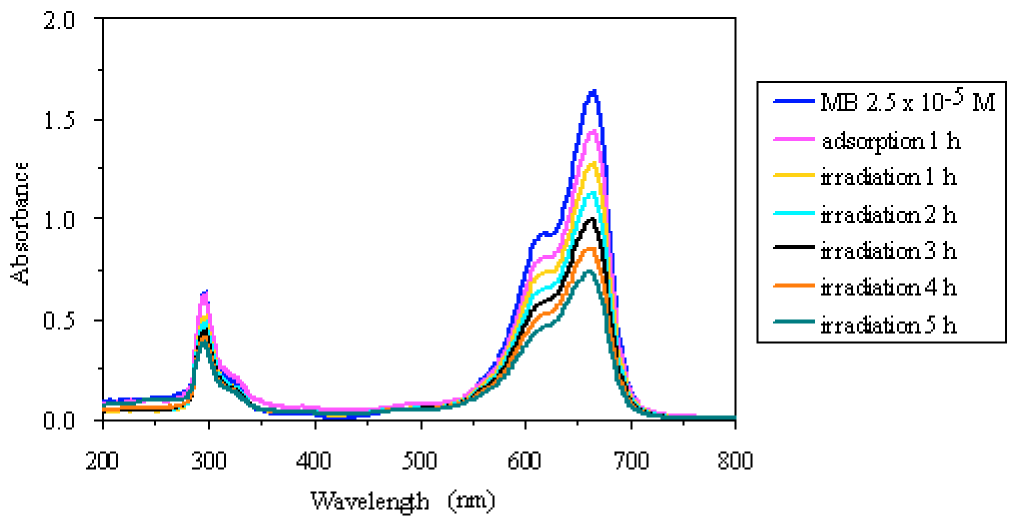


b) Films prepared by varying amount of latex

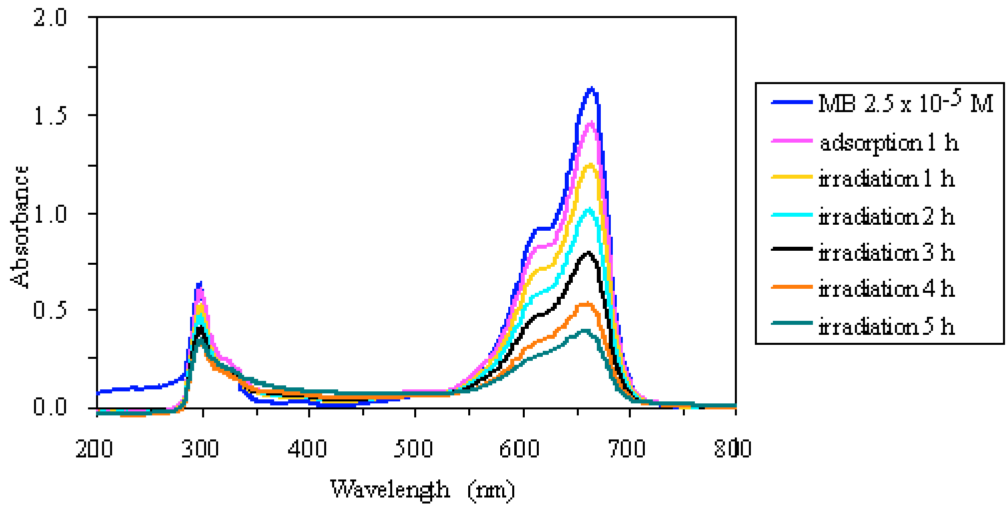
1b) 3 ml


2.0
1.5
1.0
0.5
0.0
Absorbance
200
300
400
500
600
700
800
Wavelength (nm)
MB 2.5 x 10-5 M
adsorption 1 h
irradiation 1 h
irradiation 2 h
irradiation 3 h
irradiation 4 h
irradiation 5 h

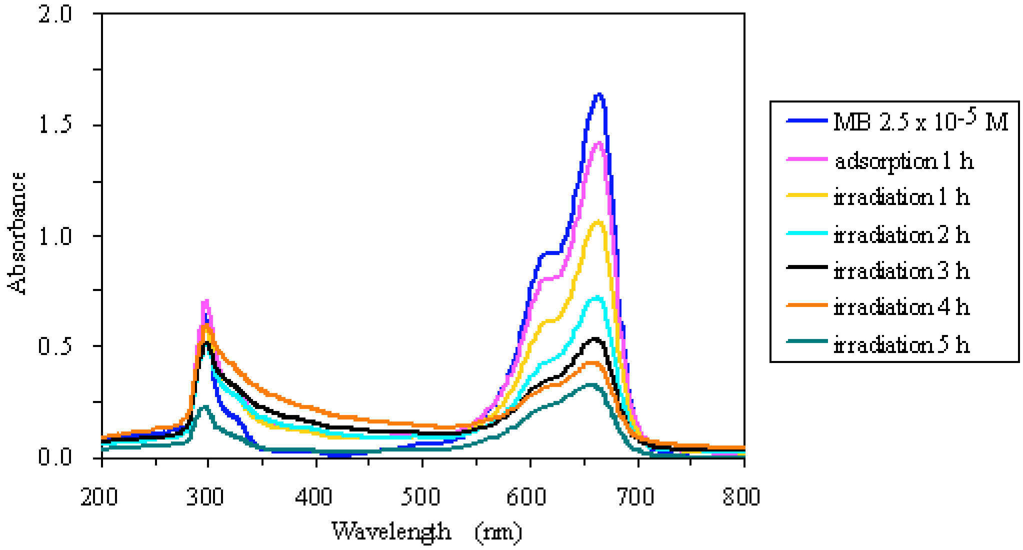
2b) 5 ml


2.0
1.5
1.0
0.5
0.0
Absorbance
200
300
400
500
600
700
800
Wavelength (nm)
MB 2.5 x 10-5 M
adsorption 1 h
irradiation 1 h
irradiation 2 h
irradiation 3 h
irradiation 4 h
irradiation 5 h

3b) 7 ml

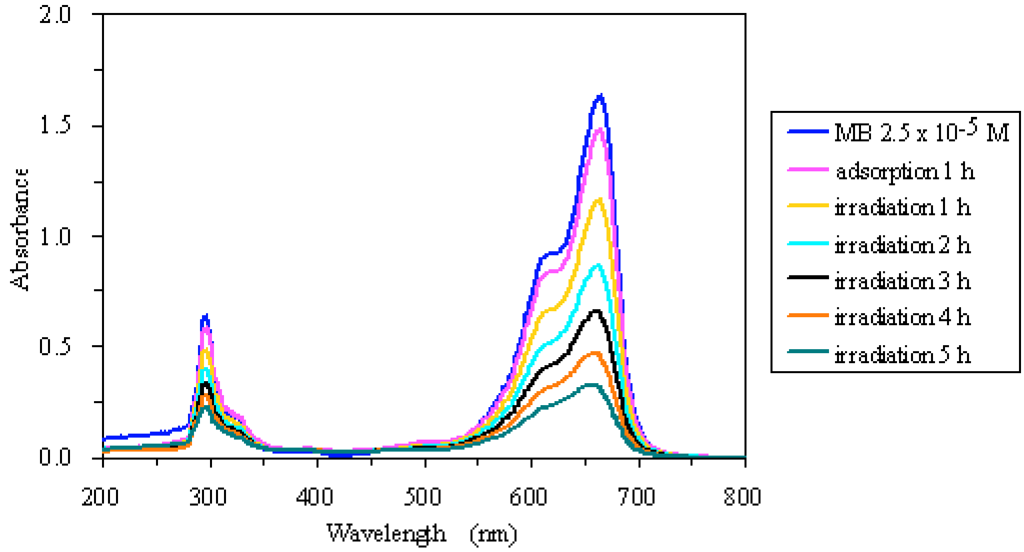

2.0
1.5
1.0
0.5
0.0
Absorbance
200
300
400
500
600
700
800
Wavelength (nm)
MB 2.5 x 10-5 M
adsorption 1 h
irradiation 1 h
irradiation 2 h
irradiation 3 h
irradiation 4 h
irradiation 5 h

4b) 9 ml

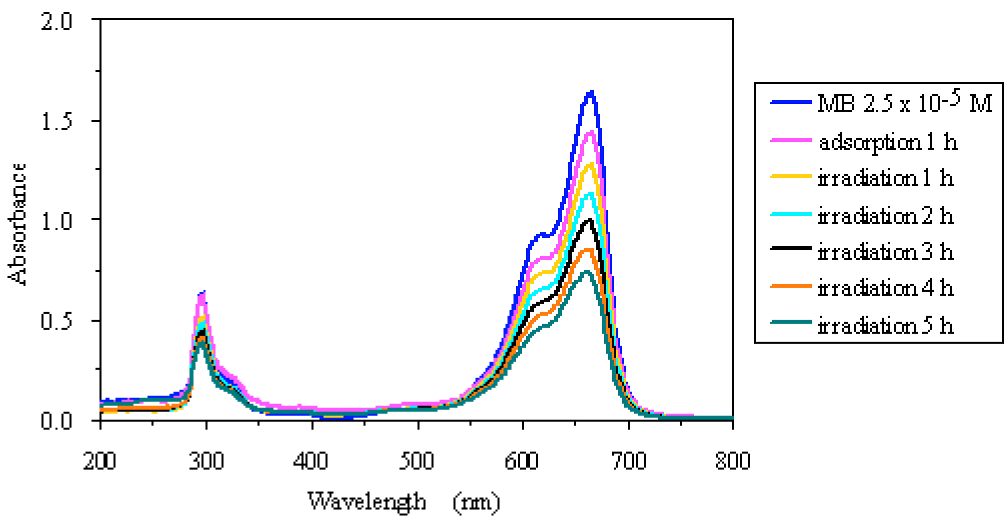


c) Films prepared by varying amount of TiO_2 Degussa P25

1c) 0.05 g



2c) 0.1 g



3c) 0.2 g

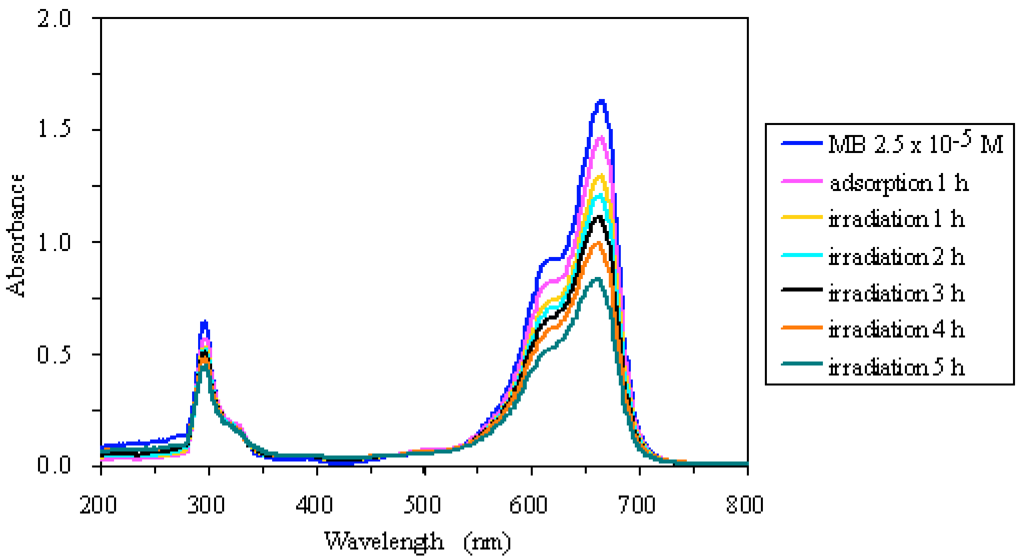


Figure 25 The UV-Vis spectral change of methylene blue with Immo-TiO_2 Degussa P25 film samples under UV irradiation as a function of times

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 (λ = 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.

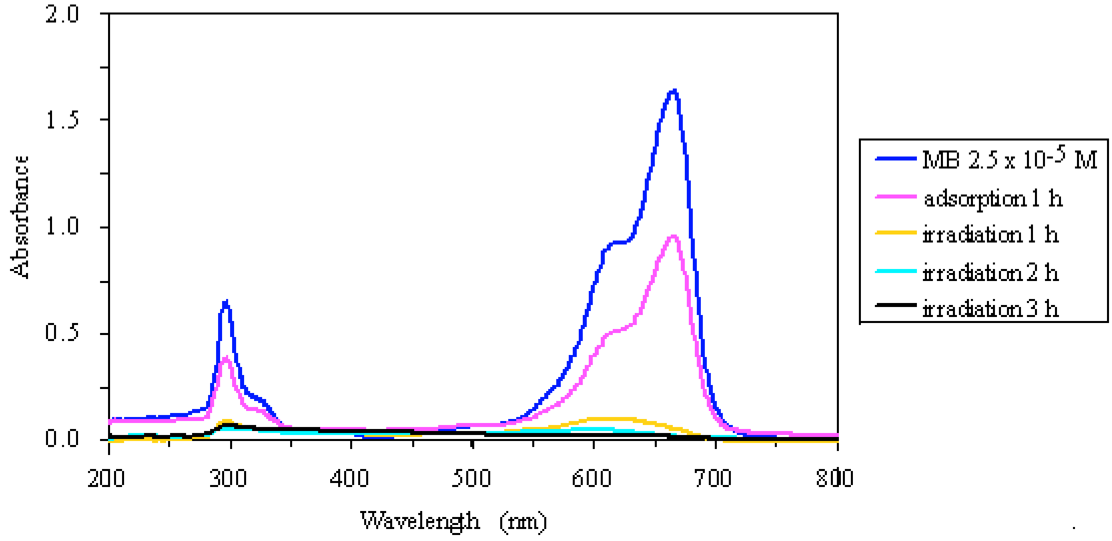


Figure 26 The UV-Vis spectral change of methylene blue by commercial TiO_2 anatase powder (Carlo Erba) under UV irradiation as a function of time

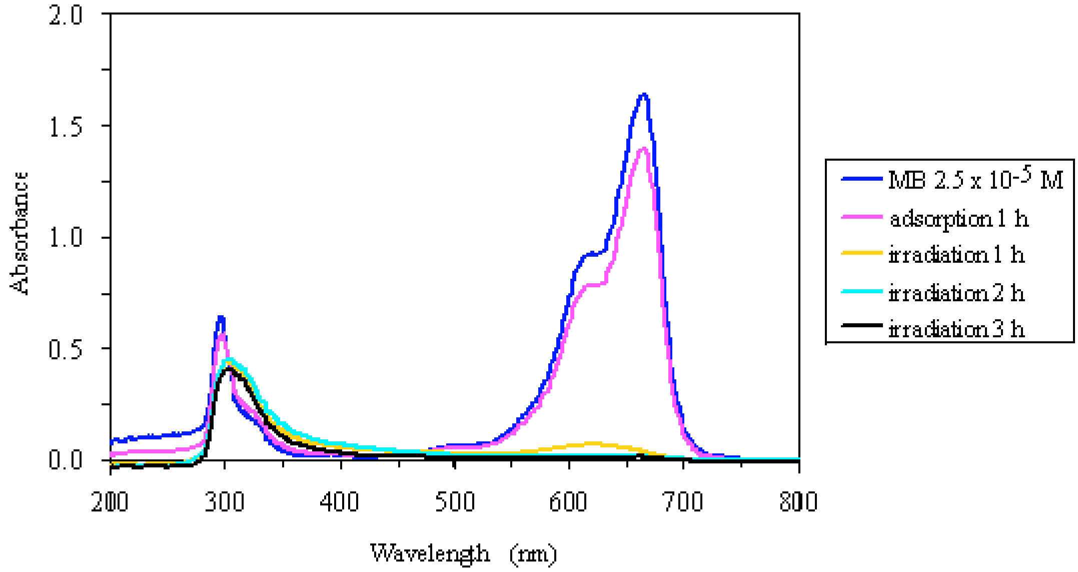


Figure 27 The UV-Vis spectral change of methylene blue by commercial TiO_2 Degussa P25 powder under UV irradiation as a function of times

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.

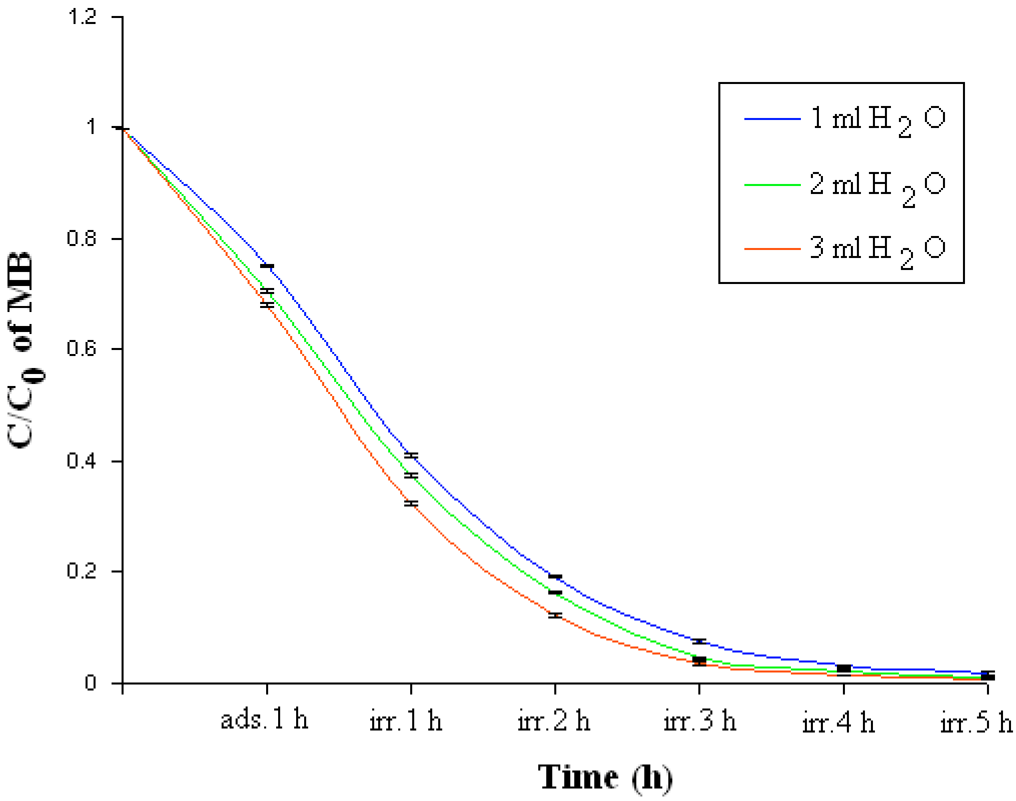


Figure 28 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film samples prepared by varying amount of distilled water as a function of irradiation times

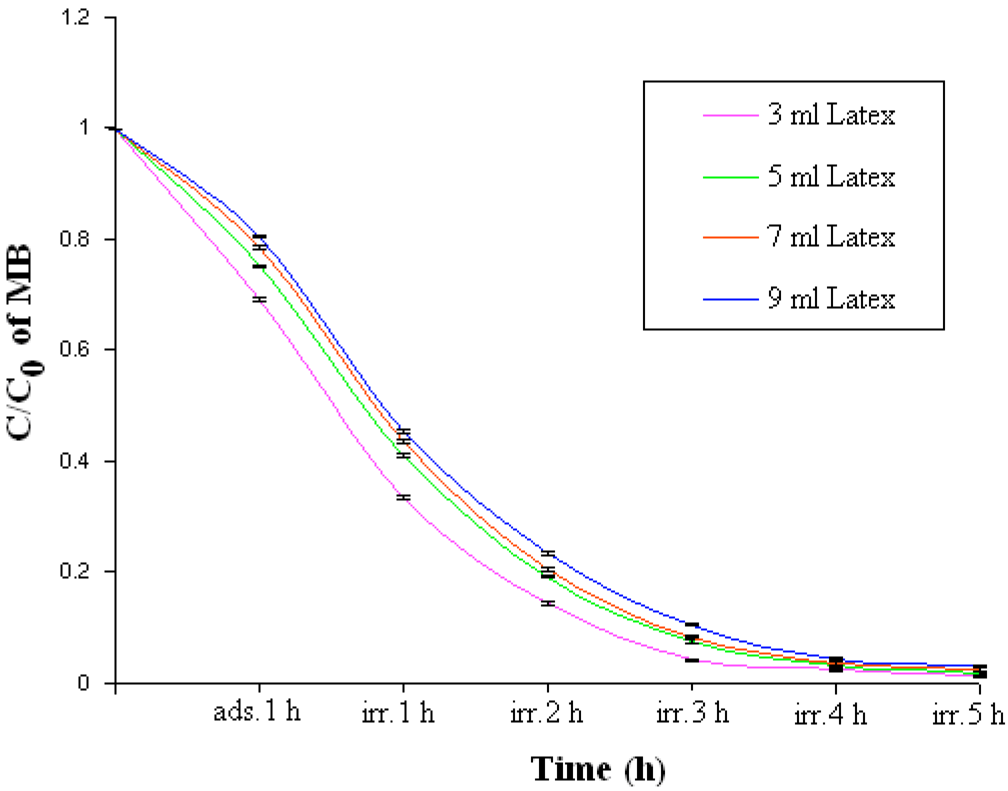


Figure 29 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film samples prepared by varying amount of latex as a function of irradiation times

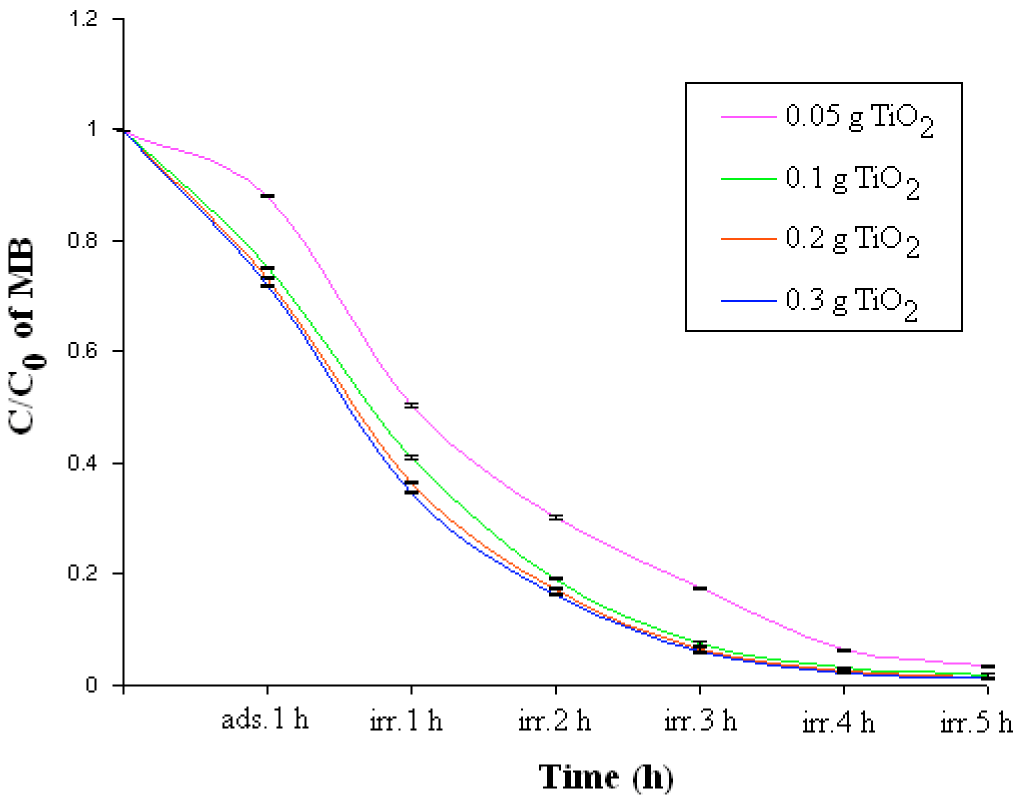


Figure 30 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film samples prepared by varying amount of commercial TiO_2 as a function of irradiation times

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.

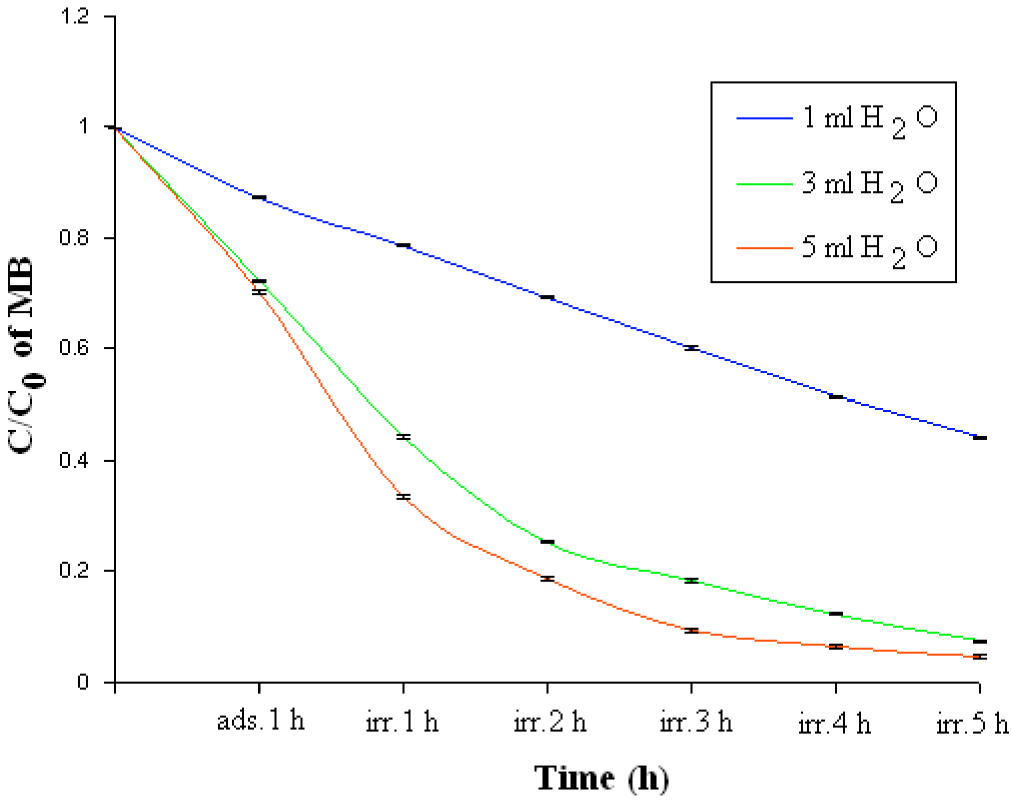


Figure 31 The relative remained C/C_0 of methylene blue by Immo-TiO_2 Degussa P25 film samples prepared by varying amount of distilled water as a function of irradiation times

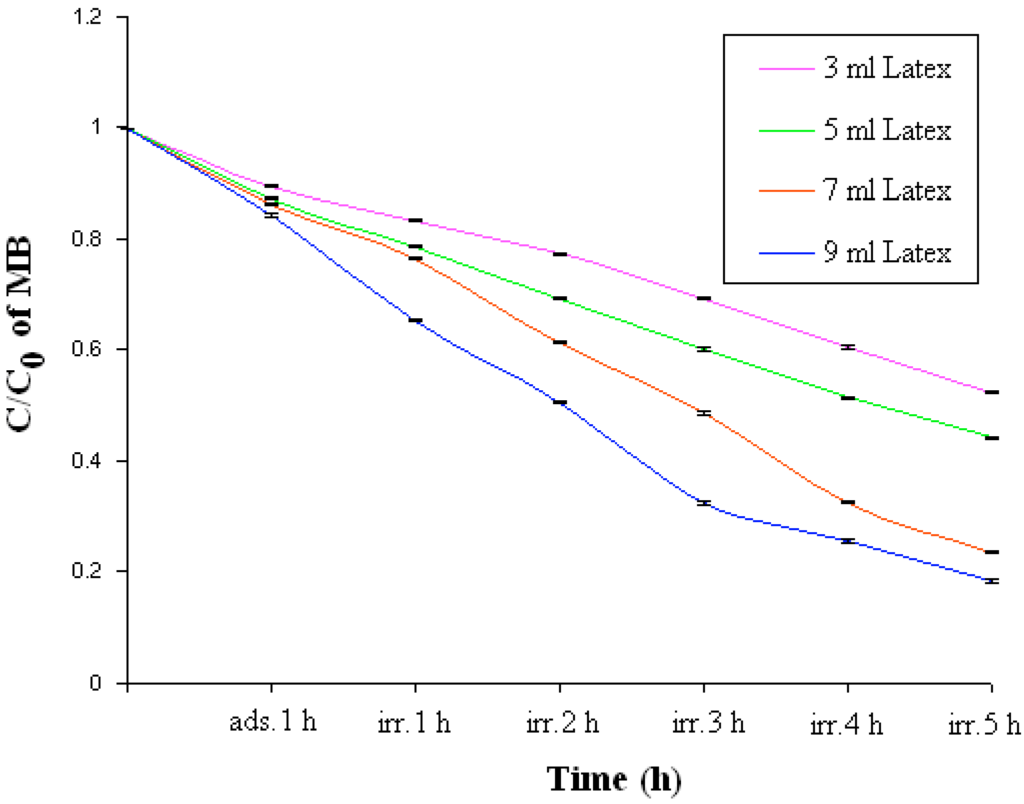


Figure 32 The relative remained C/C_0 of methylene blue by Immo-TiO_2 Degussa P25 film samples prepared by varying amount of latex as a function of irradiation times

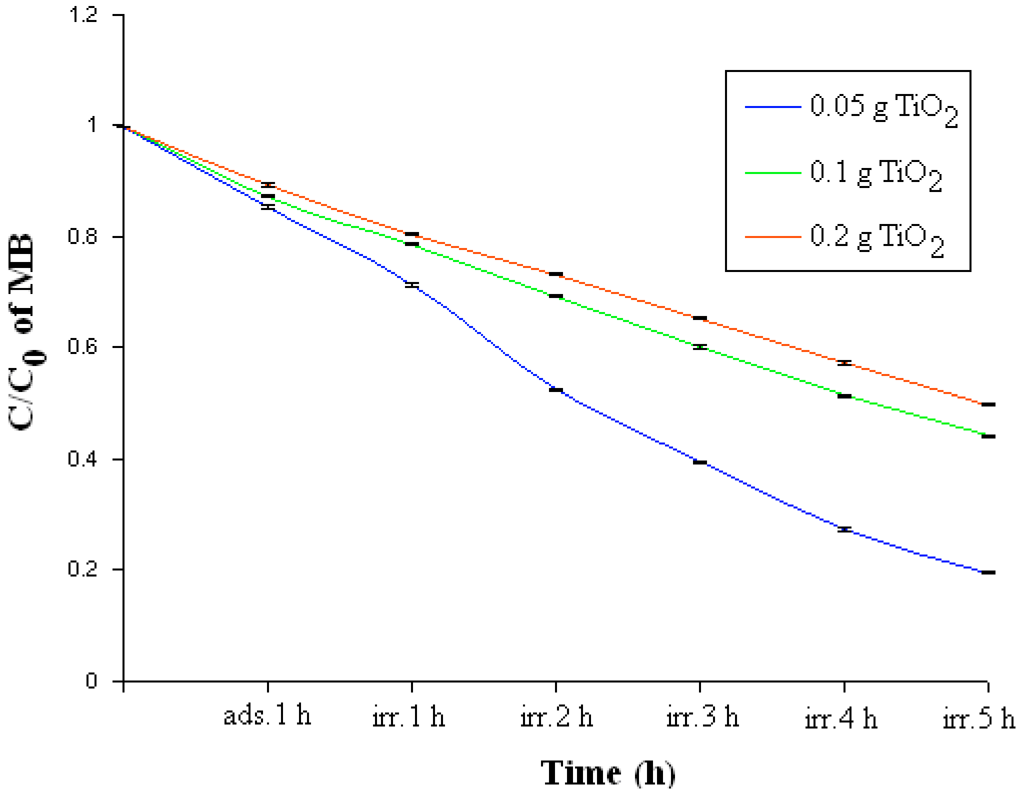


Figure 33 The relative remained C/C_0 of methylene blue by Immo-TiO_2 Degussa P25 film samples prepared by varying amount of commercial TiO_2 as a function of irradiation times

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.

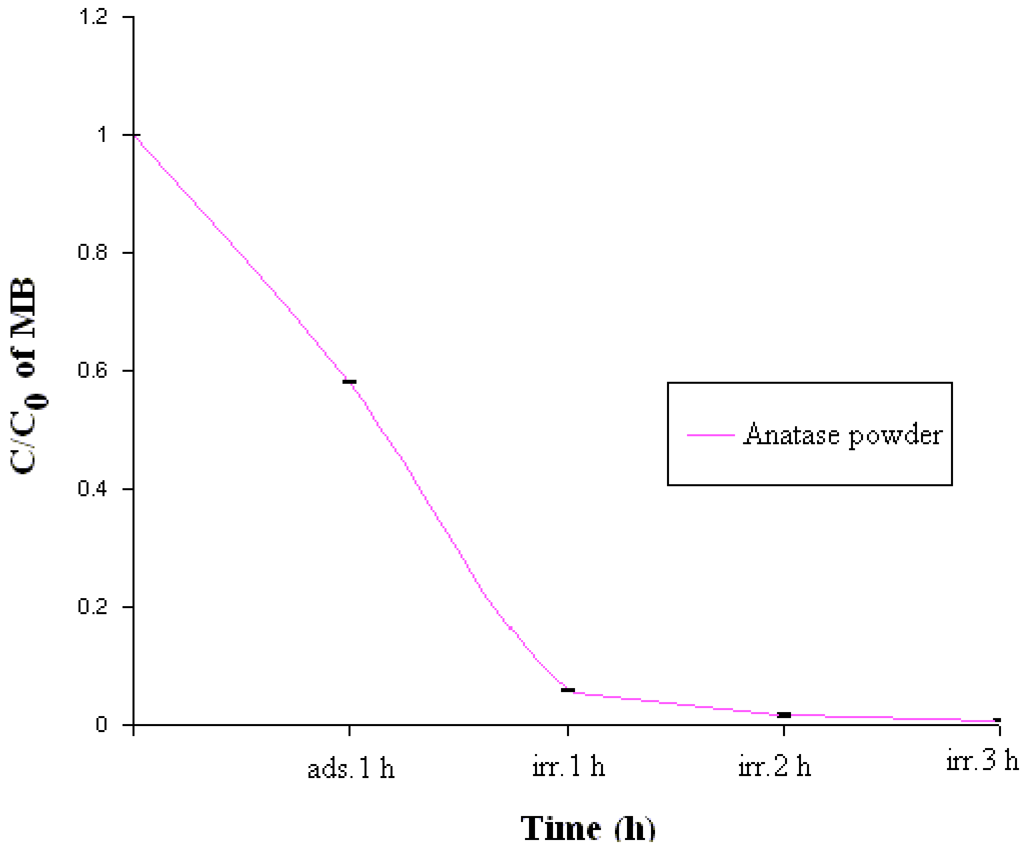


Figure 34 The relative remained C/C_0 of methylene blue by commercial TiO_2 anatase powder (Carlo Erba) as a function of irradiation times

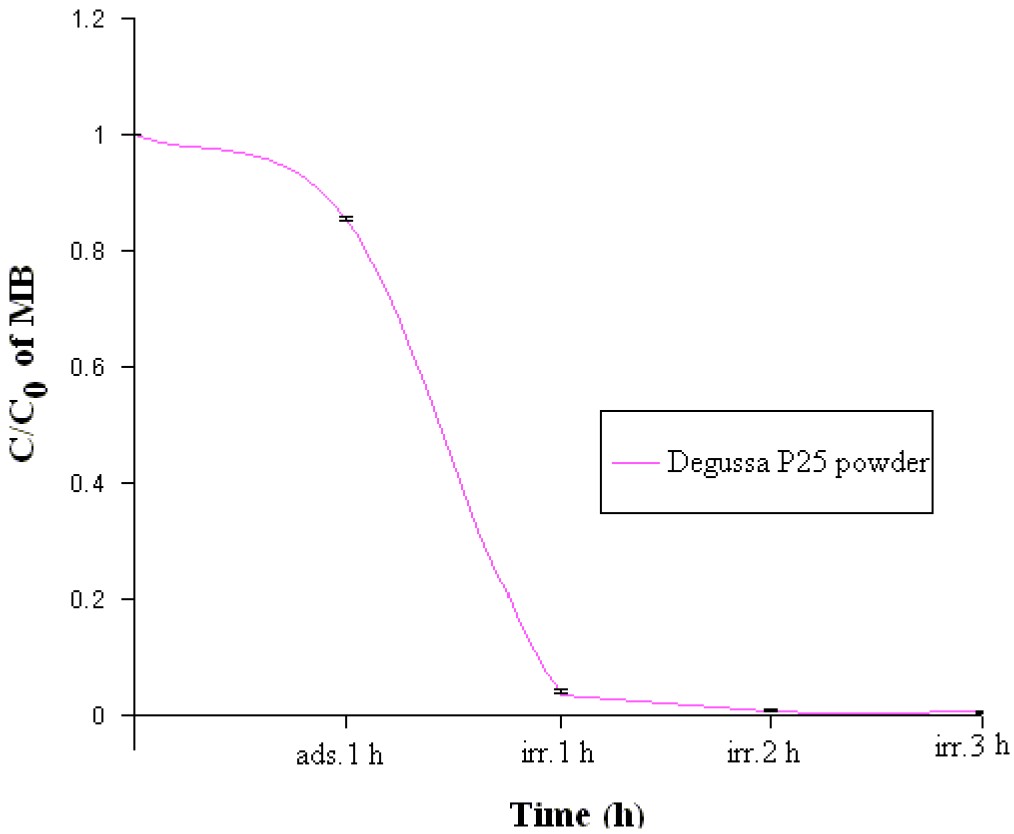


Figure 35 The relative remained C/C_0 of methylene blue by commercial TiO_2 Degussa P25 powder as a function of irradiation times

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)

Immo-TiO_2 anatase thin films	% Degradation of MB (average)*				
	1 h	2 h	3 h	4 h	5 h
Anatase powder	93.36±0.17	98.16±0.20	99.33±0.26	-	-
Degussa P25 powder	96.10±0.22	99.37±0.25	99.67±0.12	-	-
a) films prepared by varying amount of distilled water					
1 ml	58.90±0.37	80.80±0.16	92.43±0.29	96.93±0.17	98.20±0.29
2 ml	62.43±0.45	83.63±0.20	95.37±0.20	97.67±0.34	98.90±0.08
3 ml	68.63±0.45	87.67±0.29	96.47±0.20	98.63±0.10	99.30±0.08
4 ml **	-	-	-	-	-
5 ml **	-	-	-	-	-
b) films prepared by varying amount of latex					
3 ml	66.60±0.33	85.60±0.24	95.81±0.21	97.53±0.12	98.57±0.25
5 ml	58.90±0.37	80.80±0.16	92.43±0.29	96.93±0.17	98.20±0.29
7 ml	56.53±0.20	79.43±0.37	91.40±0.22	96.57±0.33	97.63±0.12
9 ml	55.57±0.25	76.53±0.29	89.47±0.25	95.53±0.20	96.87±0.26
c) films prepared by varying amount of TiO_2					
0.05 g	49.43±0.34	69.67±0.34	82.43±0.12	93.67±0.12	96.47±0.25
0.1 g	58.90±0.37	80.80±0.16	92.43±0.29	96.93±0.17	98.23±0.26
0.2 g	63.50±0.17	82.63±0.20	93.63±0.26	97.47±0.29	98.63±0.25
0.3 g	65.37±0.17	83.63±0.25	94.00±0.24	97.87±0.12	98.67±0.20

* 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-TiO_2 Degussa P25 film samples as a function of irradiation times (including adsorption)

Immo-TiO_2 Degussa P25 thin films	% Degradation of MB (average)*				
	1 h	2 h	3 h	4 h	5 h
Anatase powder	93.36±0.17	98.16±0.20	99.33±0.26	-	-
Degussa P25 powder	96.10±0.22	99.37±0.25	99.67±0.12	-	-
a) films prepared by varying amount of distilled water					
1 ml	21.37±0.17	30.70±0.21	39.83±0.38	48.60±0.24	55.73±0.20
3 ml	55.57±0.31	74.73±0.20	81.67±0.26	87.67±0.12	92.53±0.17
5 ml	66.47±0.25	81.43±0.25	90.67±0.17	93.54±0.34	95.47±0.30
6 ml **	-	-	-	-	-
7 ml **	-	-	-	-	-
b) films prepared by varying amount of latex					
3 ml	16.70±0.22	22.70±0.22	30.67±0.20	39.53±0.26	47.60±0.24
5 ml	21.37±0.17	30.70±0.21	39.83±0.38	48.60±0.24	55.73±0.20
7 ml	23.53±0.25	38.57±0.25	51.47±0.31	67.47±0.21	76.37±0.17
9 ml	34.60±0.22	49.43±0.26	67.53±0.38	74.53±0.34	81.63±0.25
c) films prepared by varying amount of TiO_2					
0.05 g	28.70±0.23	47.53±0.25	60.43±0.25	72.53±0.33	80.50±0.16
0.1 g	21.37±0.17	30.70±0.21	39.83±0.38	48.60±0.24	55.73±0.20
0.2 g	19.57±0.17	26.70±0.24	34.73±0.20	42.63±0.26	50.23±0.17

* 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_2 anatase film samples prepared by varying amount of distilled water, amount of latex, amount of commercial

TiO_2 anatase are summarized in Table 3 and compared with the commercial 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 TiO_2 in powder form. The optimal conditions for preparation of Immo-TiO_2 anatase film were: 3 ml of distilled water, 5 ml of latex, and 0.1 g of commercial TiO_2 anatase. This recipe was then used to prepare the film for the rest of the following experiments.

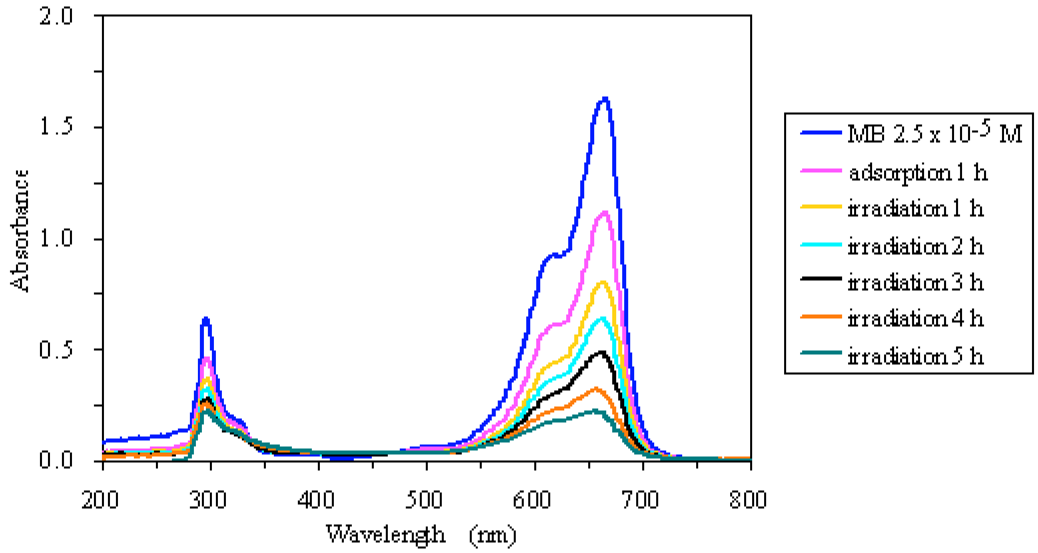
The photocatalytic activities of Immo-TiO_2 Degussa P25 film samples prepared by varying amount of distilled water, amount of latex, amount of commercial TiO_2 Degussa P25 are summarized in Table 4 and compared with the commercial TiO_2 samples in powder form; anatase (Carlo Erba) and Degussa P25. In 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 TiO_2 in powder form. The optimal conditions for preparation of Immo-TiO_2 Degussa P25 film were: 5 ml of distilled water, 5 ml of latex, and 0.1 g of commercial 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-TiO_2 films

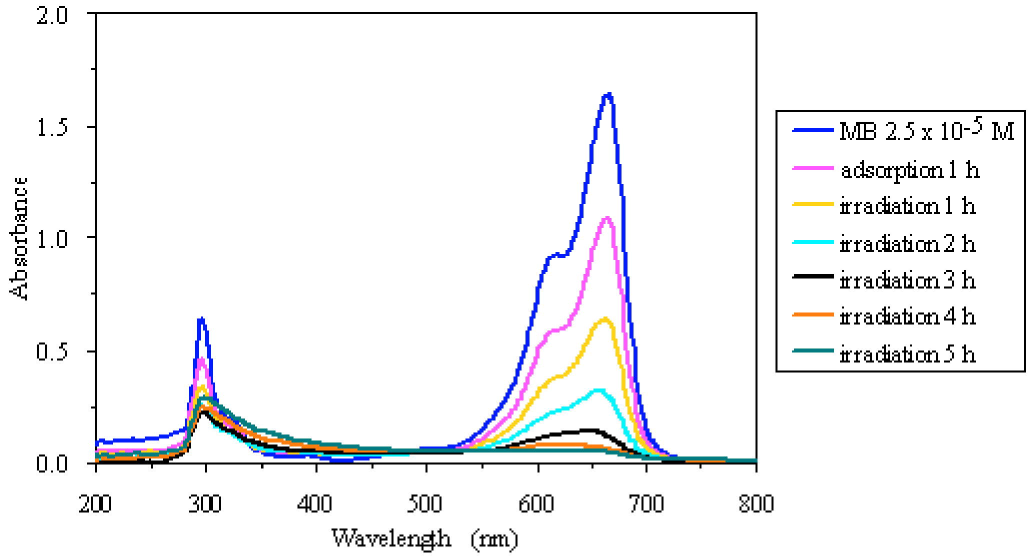
In this work, the effect of UV light intensity on the photocatalytic degradation of Immo-TiO_2 anatase film and Immo-TiO_2 Degussa P25 film were investigated by increasing light sources: 1 tube, 3 tubes, and 5 tubes. The absorption spectra of methylene blue solution by Immo-TiO_2 anatase film and Immo-TiO_2 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 (λ = 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 tube



b) 3 tubes



c) 5 tubes

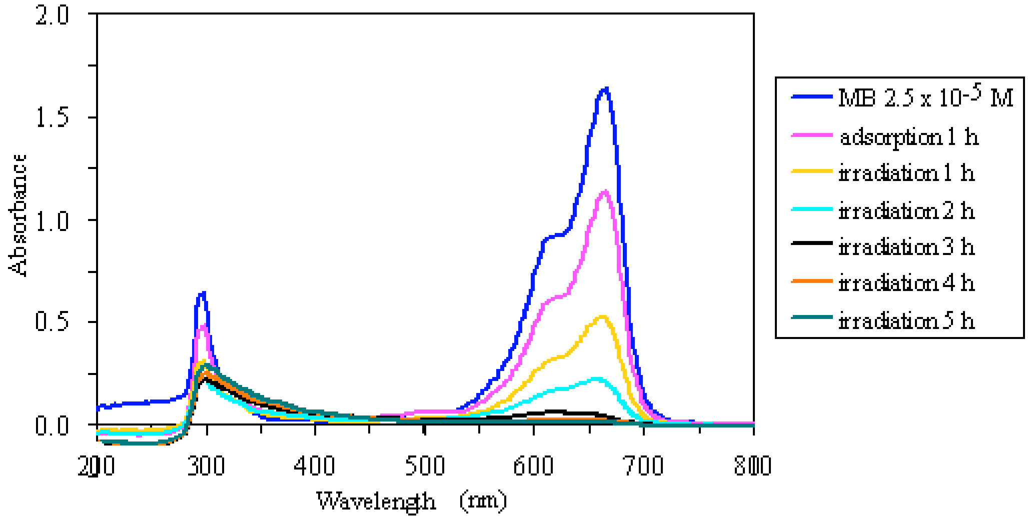
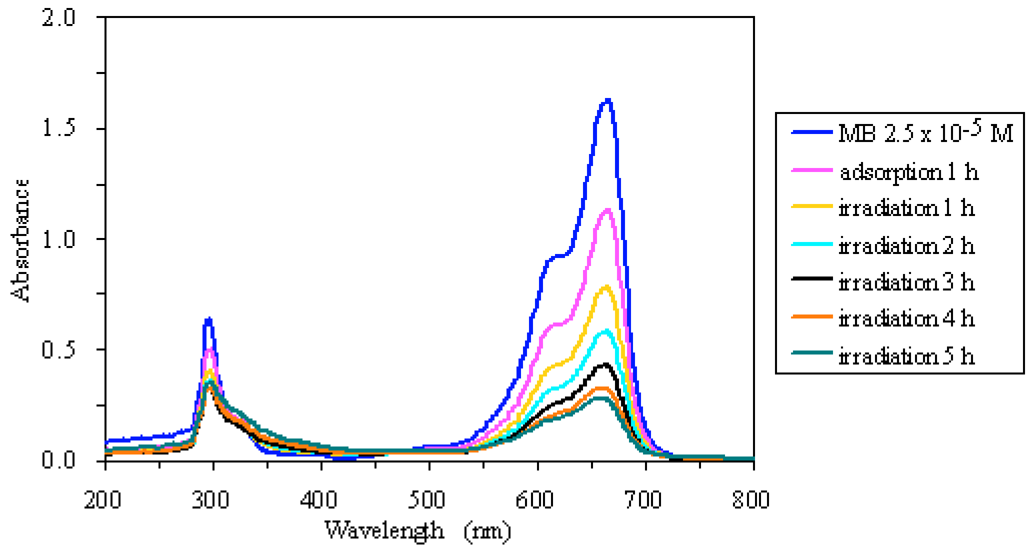


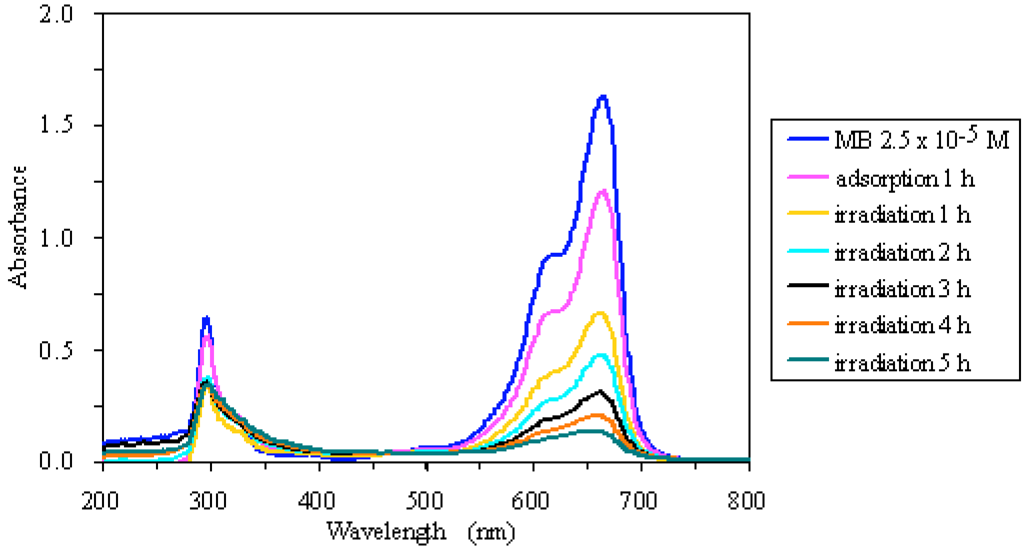
Figure 36 The UV-Vis spectral change of methylene blue by Immo-TiO_2 anatase film under various UV light intensity

Immo-TiO_2 Degussa P25 film

a) 1 tube



b) 3 tubes



c) 5 tubes

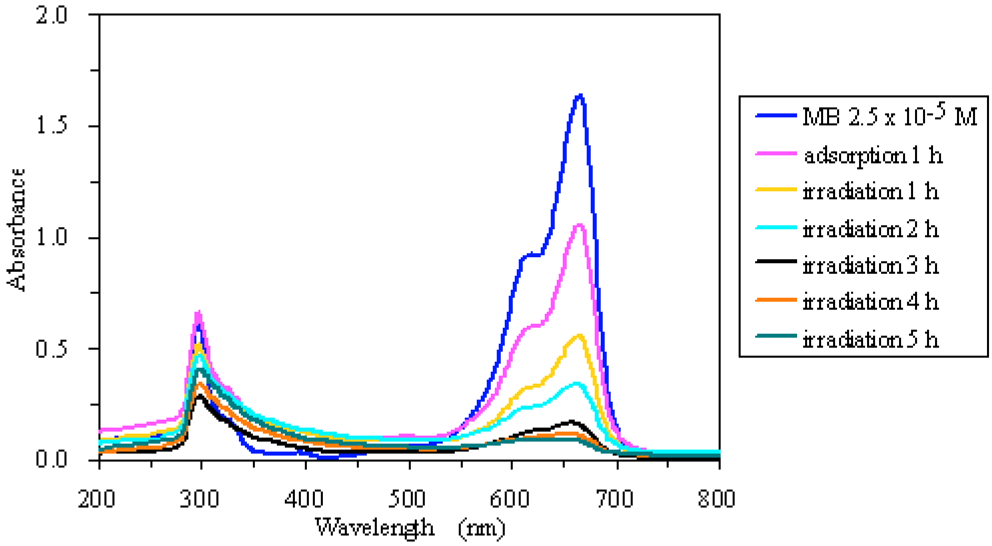


Figure 37 The UV-Vis spectral change of methylene blue by Immo-TiO_2 Degussa P25 film under various amount of UV light intensity

The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film and Immo-TiO_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_2 film samples.

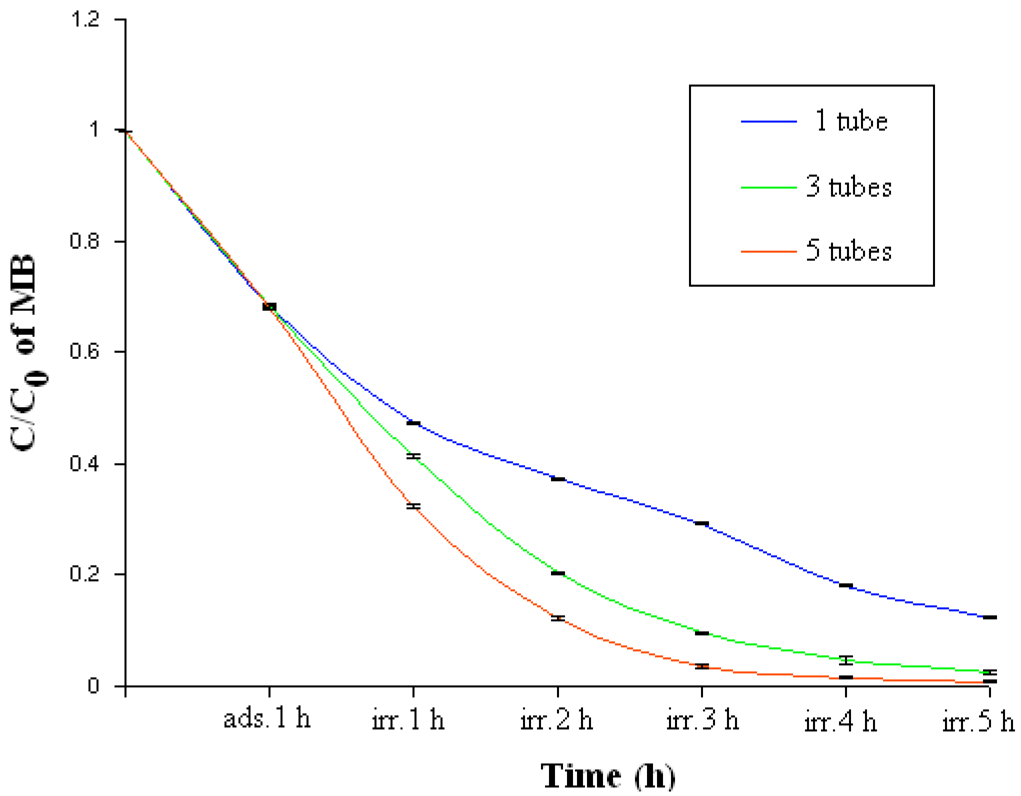


Figure 38 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film under various UV light intensity as a function of irradiation times

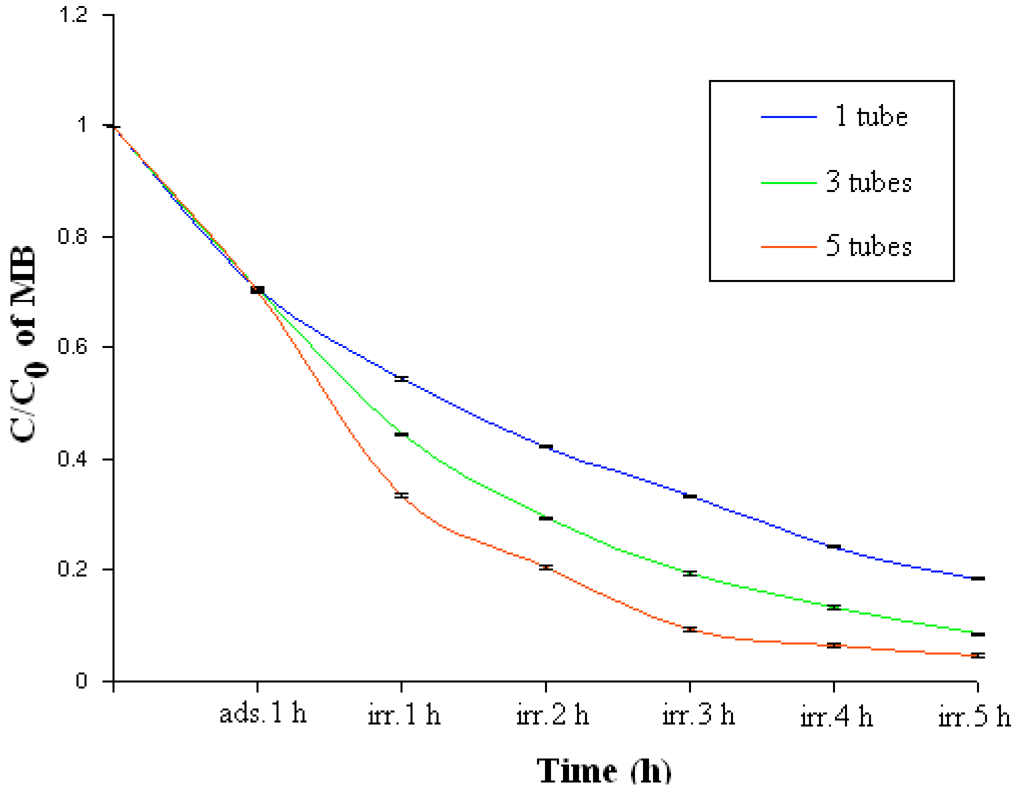


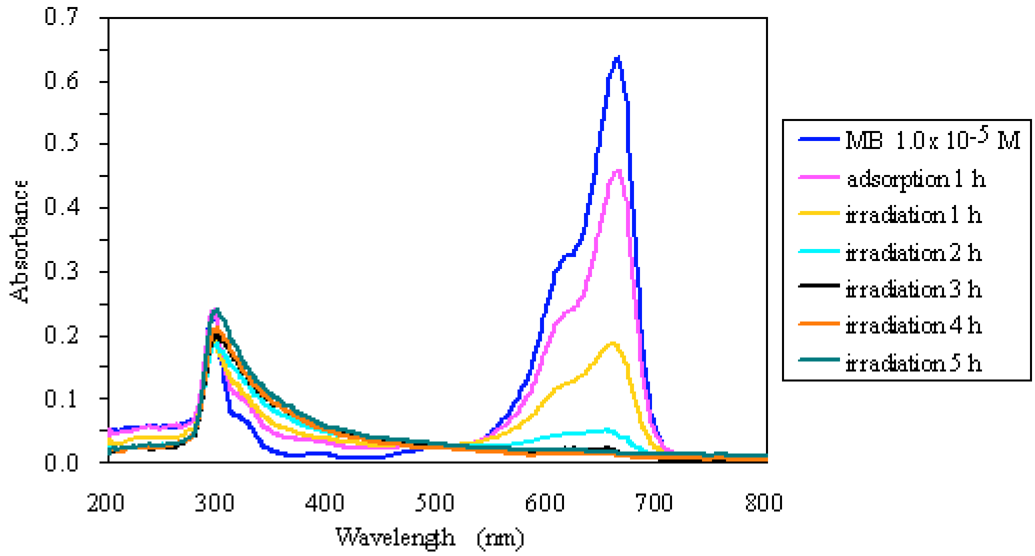
Figure 39 The relative remained C/C_0 of methylene blue by Immo-TiO_2 Degussa P25 film under various UV light intensity as a function of irradiation time

3.2.4 The effect of initial concentration of MB on the photocatalytic degradation of Immo-TiO_2 films

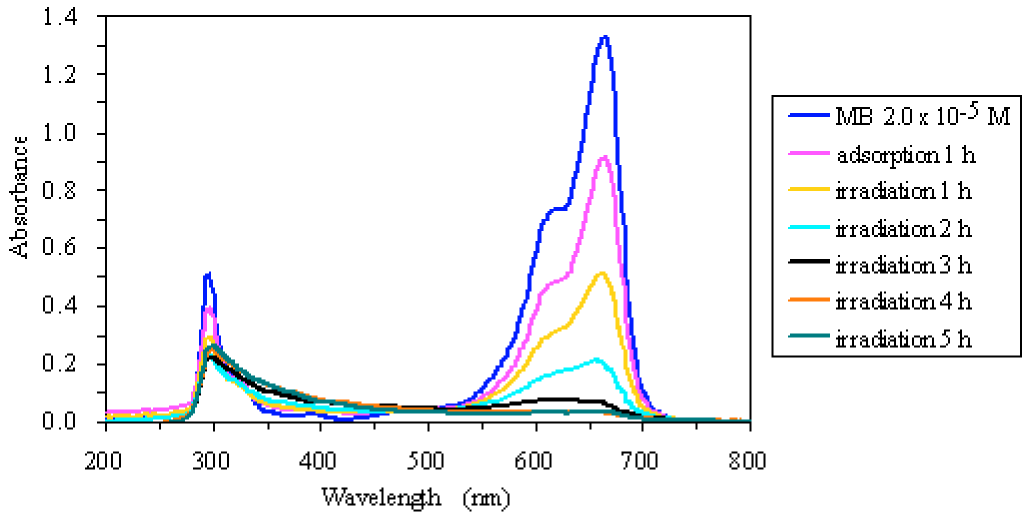
The effect of initial concentration of MB on the photocatalytic degradation of Immo-TiO_2 anatase film and Immo-TiO_2 Degussa P25 film were investigated under the concentration of MB solution at 1.0 x 10^{-5}M, 2.0 x 10^{-5} M and 3.0 x 10^{-5} M. The absorption spectra of methylene blue solution by 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 (λ = 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 x 10^{-5}M



b) 2.0 x 10^{-5}M



c) 3.0 x 10^{-5}M

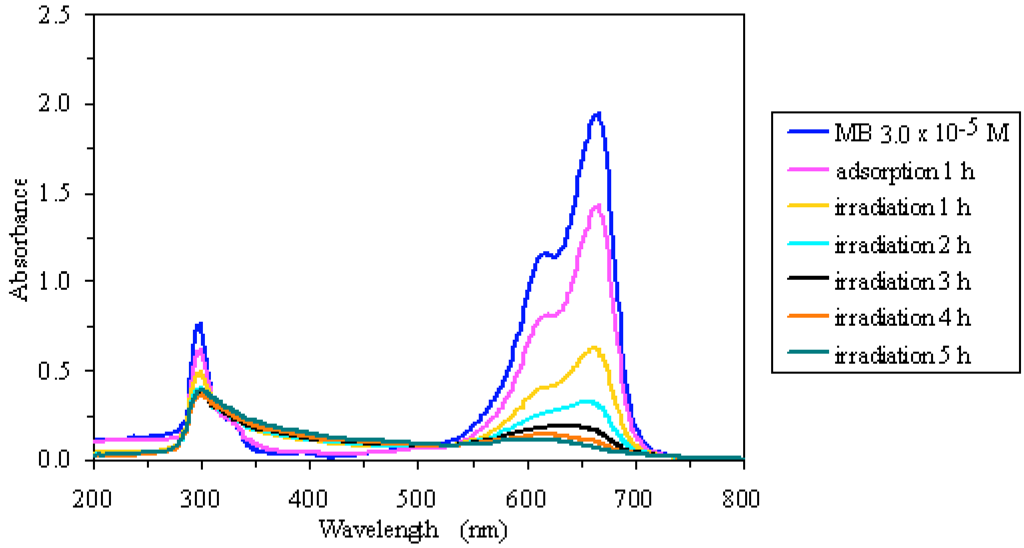
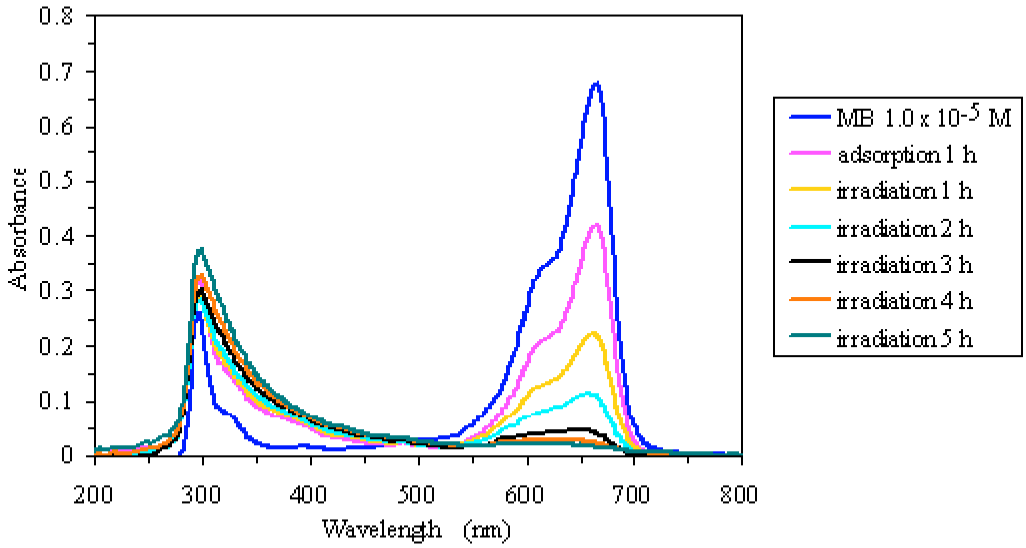


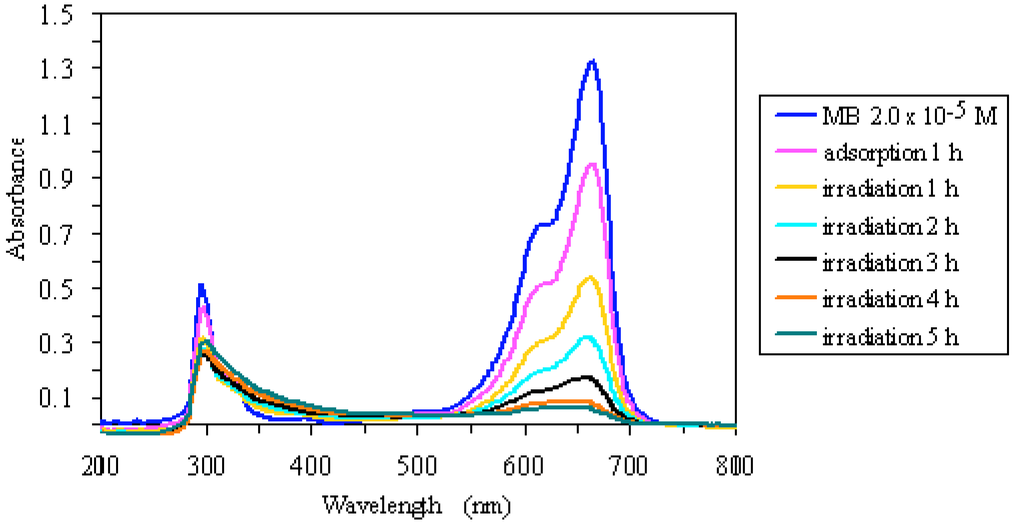
Figure 40 The UV-Vis spectral change of methylene blue by Immo-TiO_2 anatase film under various initial concentration of MB as a function of irradiation times

Immo-TiO_2 Degussa P25 film

a) 1.0×10^{-5} M



b) 2.0 x 10^{-5} M



c) 3.0 x 10^{-5} M

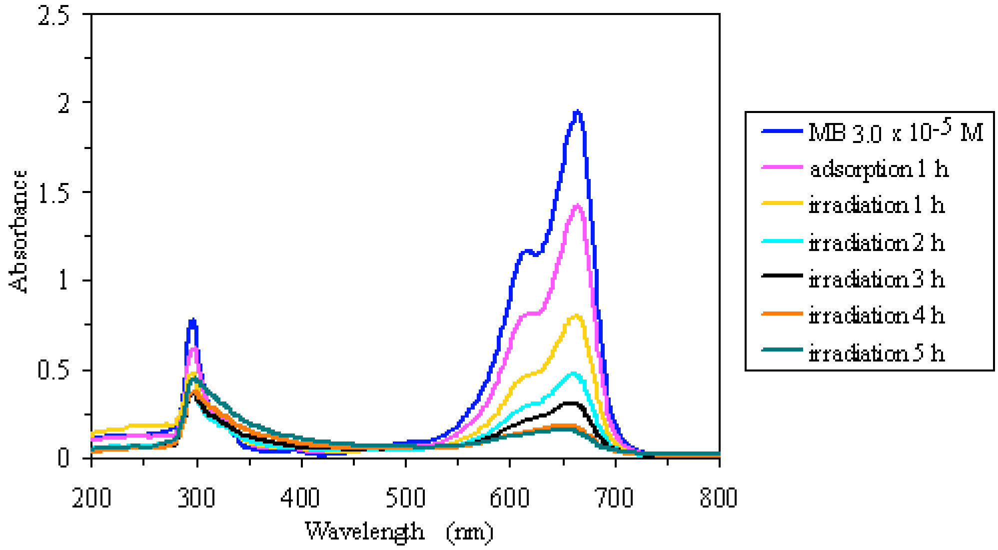


Figure 41 The UV-Vis spectral change of methylene blue by Immo-TiO_2 Degussa P25 film under various initial concentration of MB as a function of irradiation times

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.

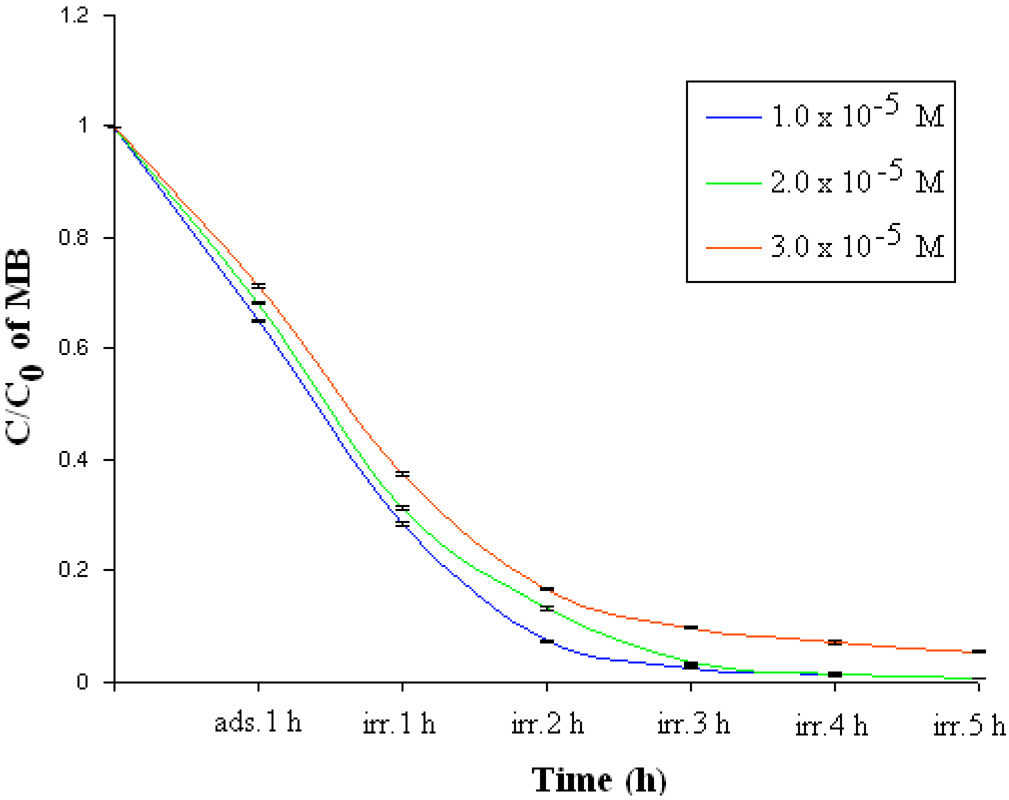


Figure 42 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film under various initial concentration of MB as a function of irradiation times

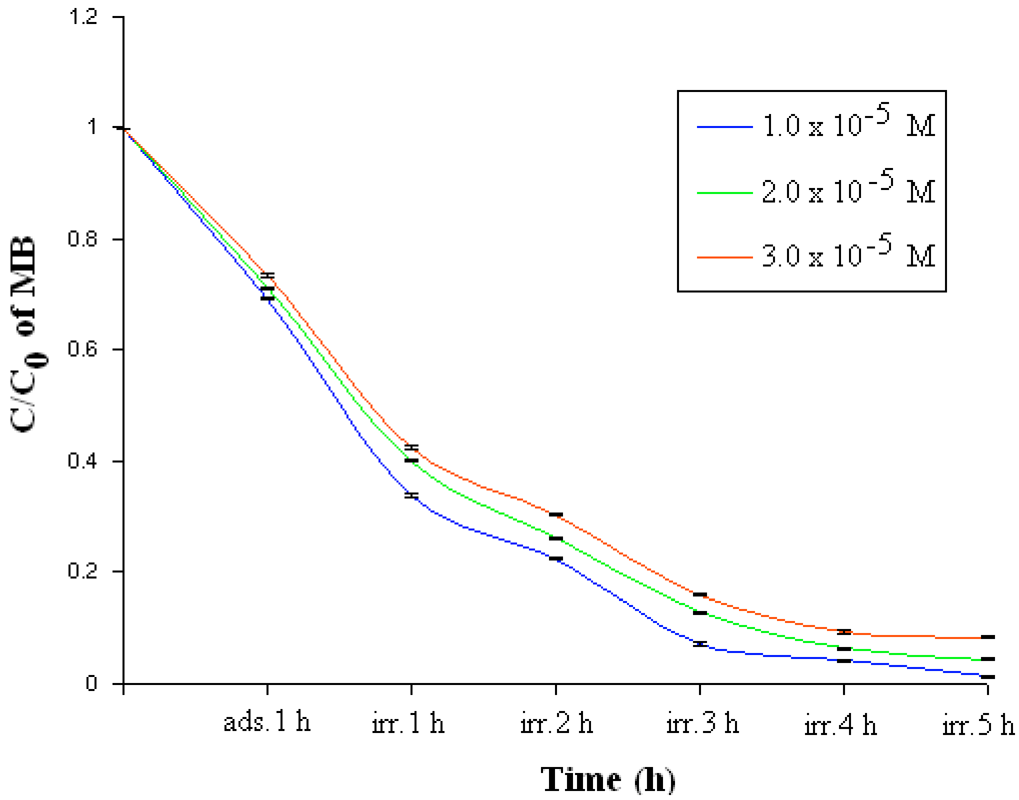


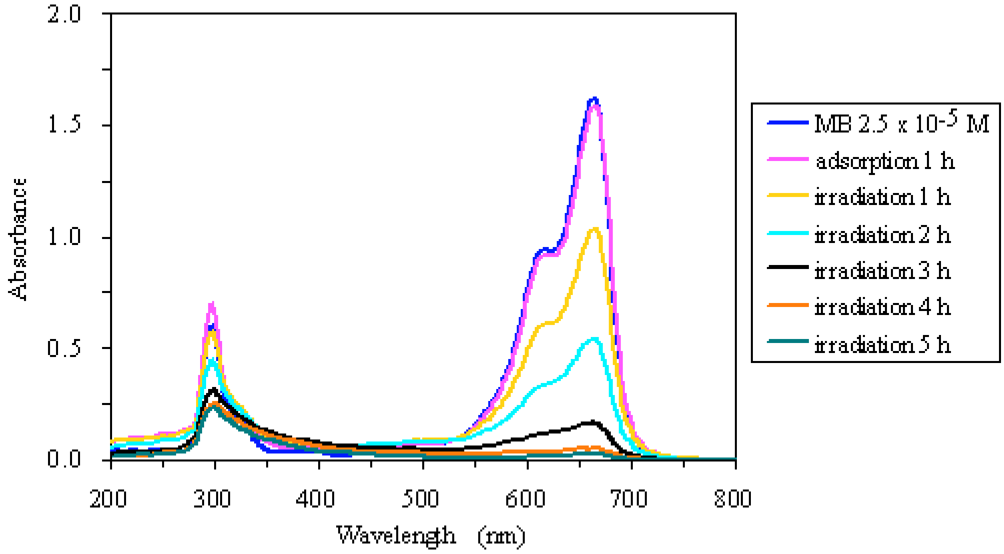
Figure 43 The relative remained C/C_0 of methylene blue by Immo-TiO_2 Degussa P25 film under various initial concentration of MB as a function of irradiation times

3.2.5 The effect of pH on the photocatalytic degradation of Immo-TiO_2 films

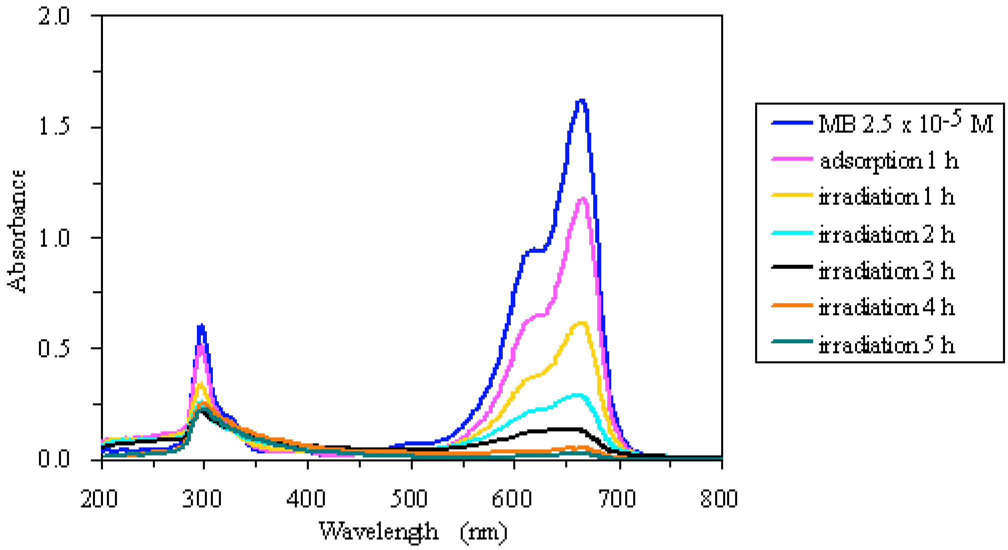
The effect of pH on the photocatalytic degradation of Immo-TiO_2 anatase film and Immo-TiO_2 Degussa P25 film were investigated under the pH of MB dye solution in the range of 3 to 9. The natural pH of MB aqueous solution in this work was 6.86. The pH of MB dye solution was adjusted by adding dilute aqueous solution of HCl and NaOH. The absorption spectra of methylene blue solutions by Immo-TiO_2 anatase film and Immo-TiO_2 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-TiO_2 film samples.

Immo-TiO_2 anatase film

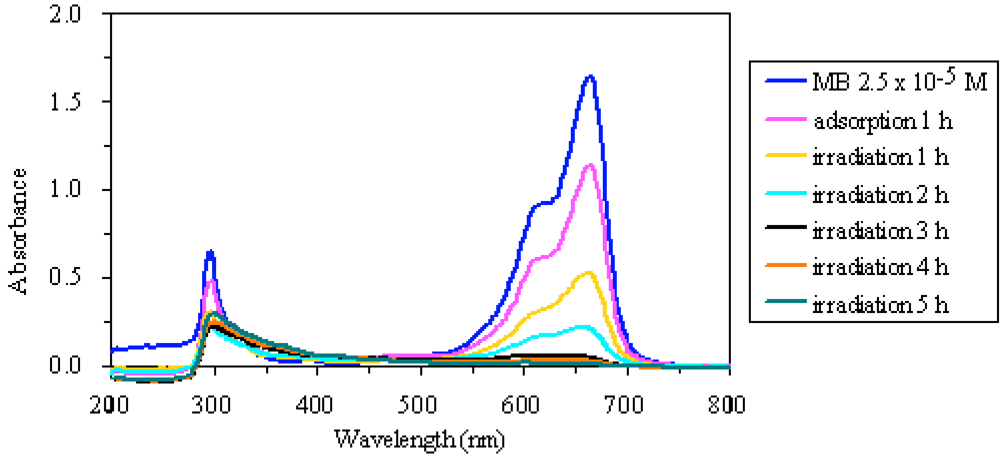
a) at pH = 3



b) at pH = 5



c) at pH = 6.86



d) at pH = 8

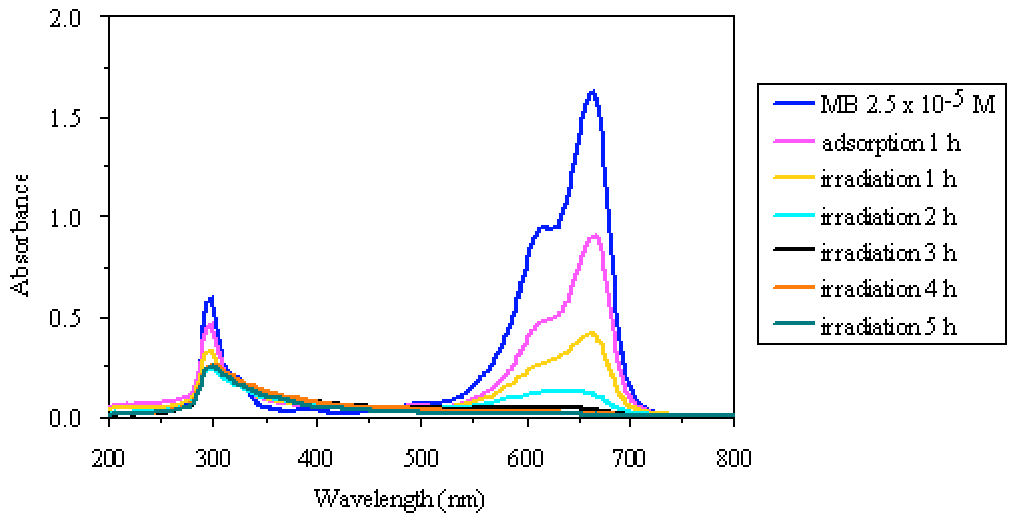
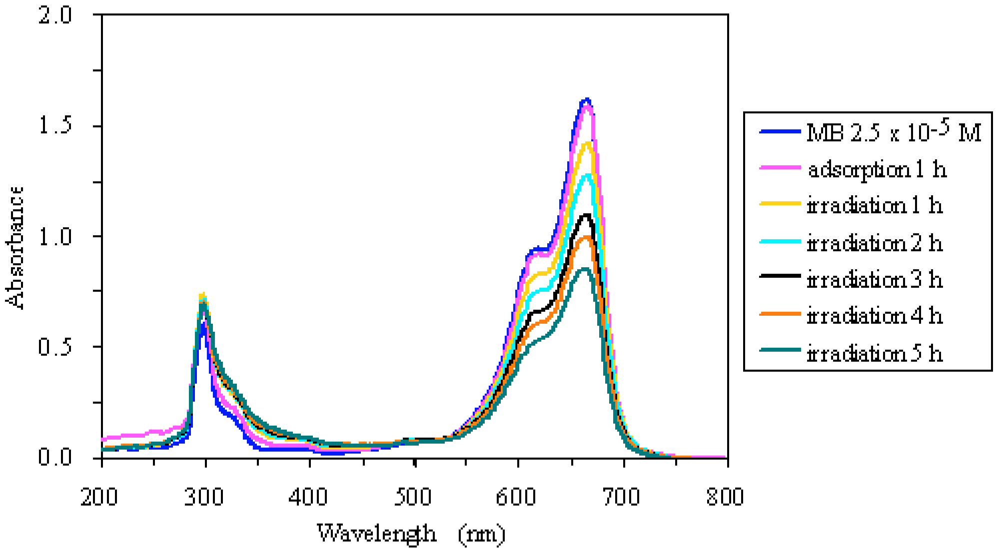


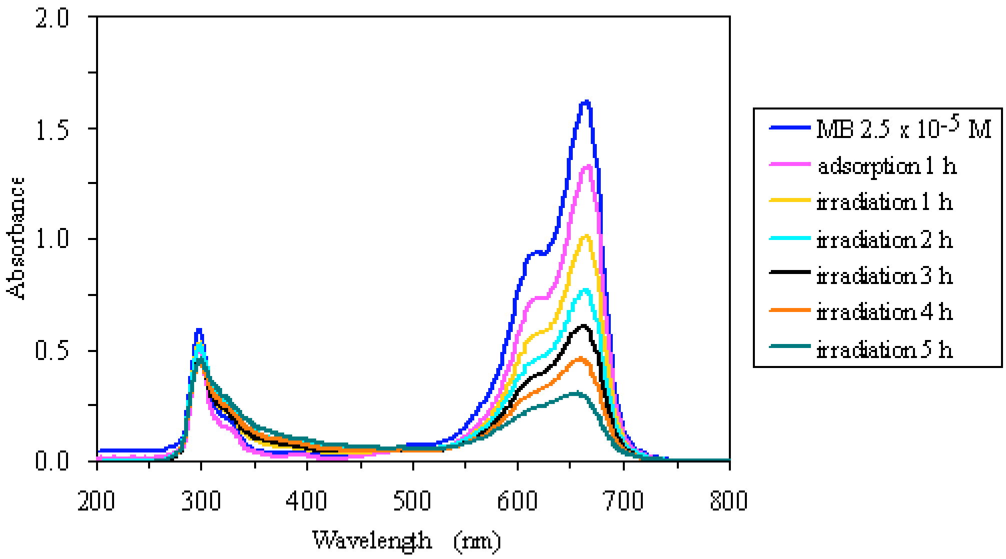
Figure 44 The UV-Vis spectral change of methylene blue by Immo-TiO_2 anatase film under various pH of MB aqueous solution as a function of irradiation times

Immo-TiO_2 Degussa P25 film

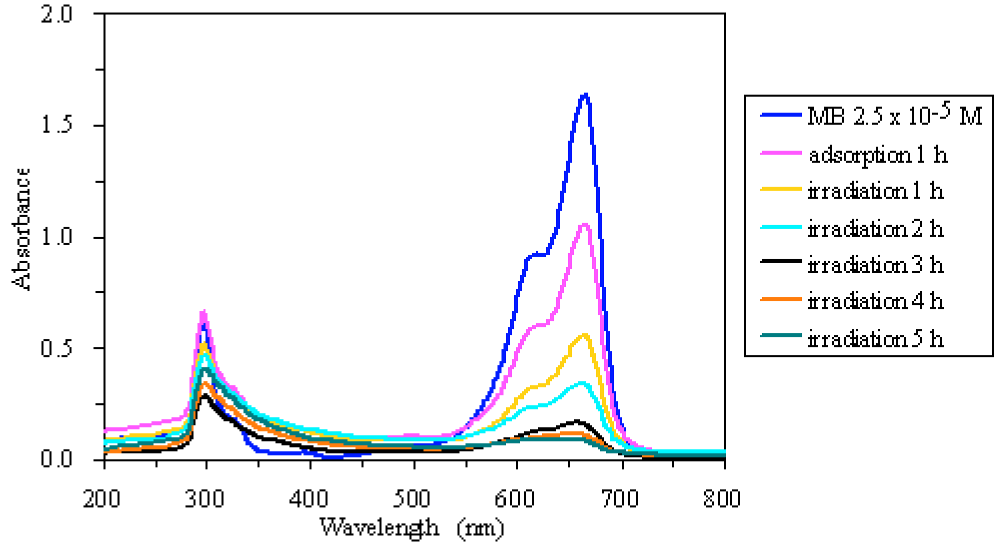
a) at pH = 3



b) at pH = 5



c) at pH = 6.86



d) at pH = 8

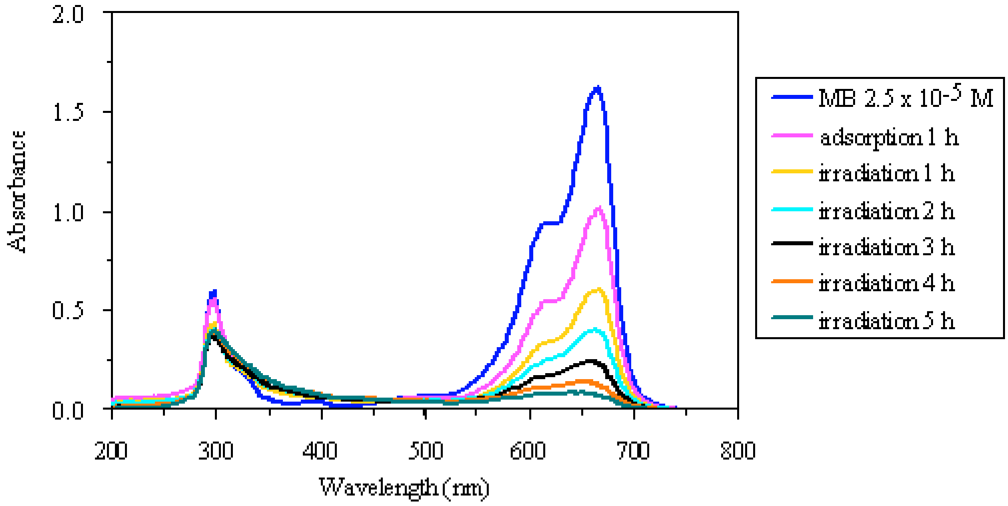


Figure 45 The UV-Vis spectral change of methylene blue by Immo-TiO_2 Degussa P25 film under various pH of MB aqueous solution as a function of irradiation times

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.

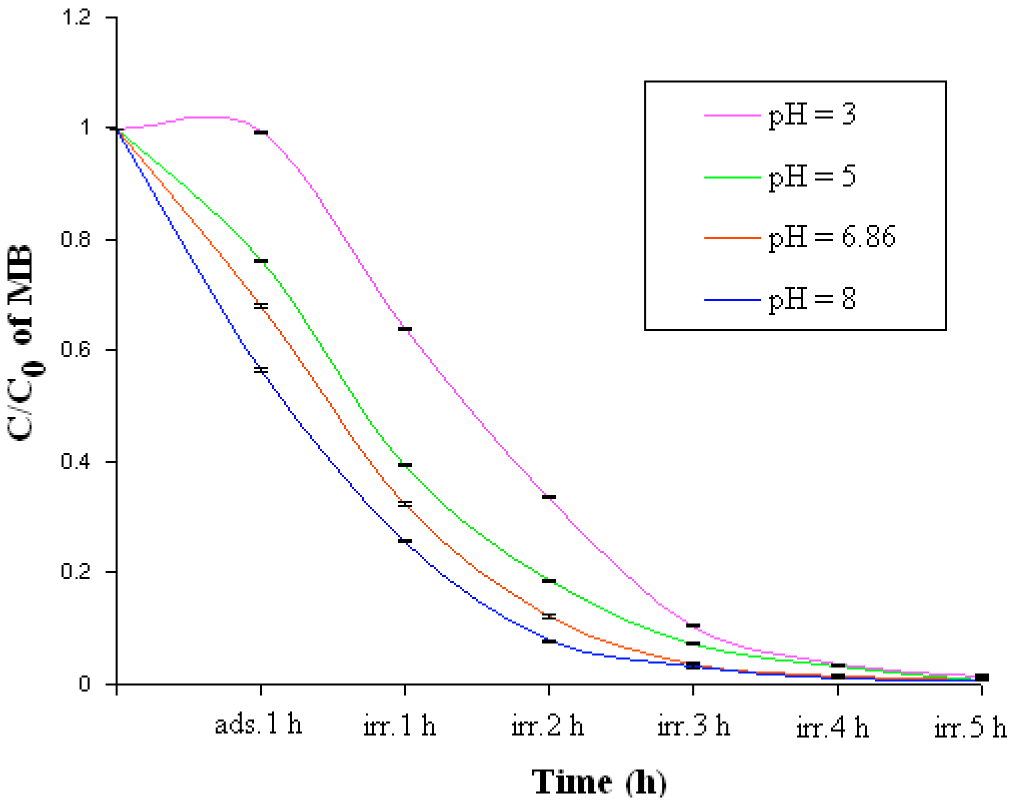


Figure 46 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film under various pH of MB solution as a function of irradiation times

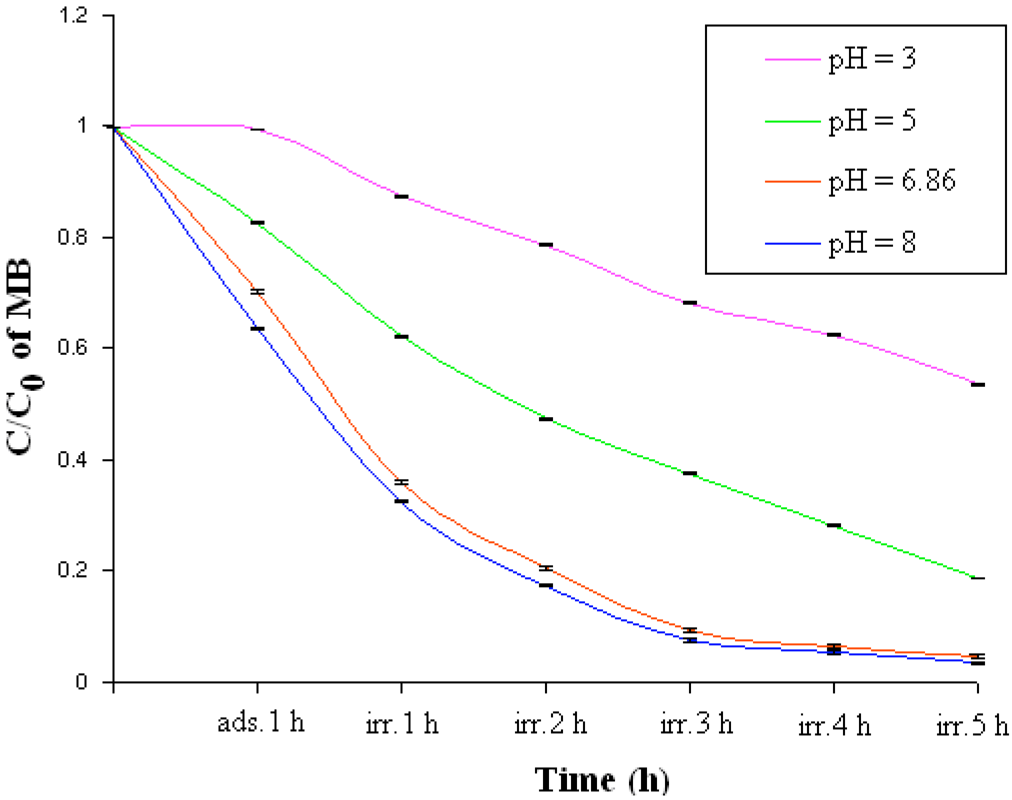


Figure 47 The relative remained C/C_0 of methylene blue by Immo-TiO_2 Degussa P25 film under various pH of MB solution as a function of irradiation times

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)

Immo-TiO_2 anatase thin film	% Degradation of MB (average)*				
	1 h	2 h	3 h	4 h	5 h
a) UV light intensity (amount of blacklight)					
1 tube	52.57±0.17	62.17±0.20	70.63±0.33	81.83±0.25	87.67±0.26
3 tubes	58.63±0.29	79.57±0.20	90.40±0.24	94.60±0.25	97.53±0.28
5 tubes	67.63±0.45	87.67±0.29	96.47±0.20	98.63±0.09	99.30±0.08
b) concentration of MB					
1.0×10^{-5} M	71.53±0.29	92.57±0.17	97.43±0.20	98.50±0.16	99.27±0.12
2.0×10^{-5} M	68.63±0.20	86.70±0.29	96.50±0.16	98.63±0.12	99.20±0.08
3.0×10^{-5} M	62.67±0.20	83.40±0.16	90.30±0.08	92.88±0.17	94.53±0.20
c) pH of MB solution					
at = 3	35.90±0.22	66.33±0.20	89.47±0.20	96.57±0.26	98.47±0.25
at = 5	60.60±0.29	81.37±0.09	92.66±0.26	96.60±0.27	99.10±0.16
at = 6.86**	67.63±0.45	87.67±0.29	96.47±0.20	98.63±0.09	99.30±0.08
at = 8	74.37±0.17	92.07±0.12	97.27±0.20	98.83±0.17	99.27±0.12

* 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)

Immo-TiO_2 Degussa P25 thin film	% Degradation of MB (average)*				
	1 h	2 h	3 h	4 h	5 h
a) UV light intensity (amount of blacklight)					
1 tube	45.67±0.29	57.73±0.20	66.63±0.20	75.37±0.25	81.30±0.16
3 tubes	55.43±0.20	70.60±0.24	80.50±0.24	86.73±0.19	91.50±0.16
5 tubes	64.06±0.34	81.43±0.25	90.67±0.17	93.53±0.34	95.47±0.31
b) concentration of MB					
1.0×10^{-5} M	66.13±0.20	77.50±0.22	92.70±0.29	95.73±0.12	98.67±0.17
2.0×10^{-5} M	59.67±0.45	73.73±0.20	87.13±0.12	93.60±0.24	95.53±0.29
3.0×10^{-5} M	57.50±0.22	69.57±0.29	83.97±0.20	90.57±0.29	91.69±0.16
c) pH of MB solution					
at = 3	12.60±0.29	21.31±0.16	31.77±0.17	37.50±0.22	46.47±0.20
at = 5	37.77±0.20	52.47±0.20	62.43±0.20	71.80±0.22	81.27±0.12
at = 6.86**	64.06±0.34	81.43±0.25	90.67±0.17	93.53±0.34	95.47±0.31
at = 8	67.47±0.17	82.60±0.16	92.43±0.26	94.67±0.20	96.50±0.22

* 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.

a) before use b) after use

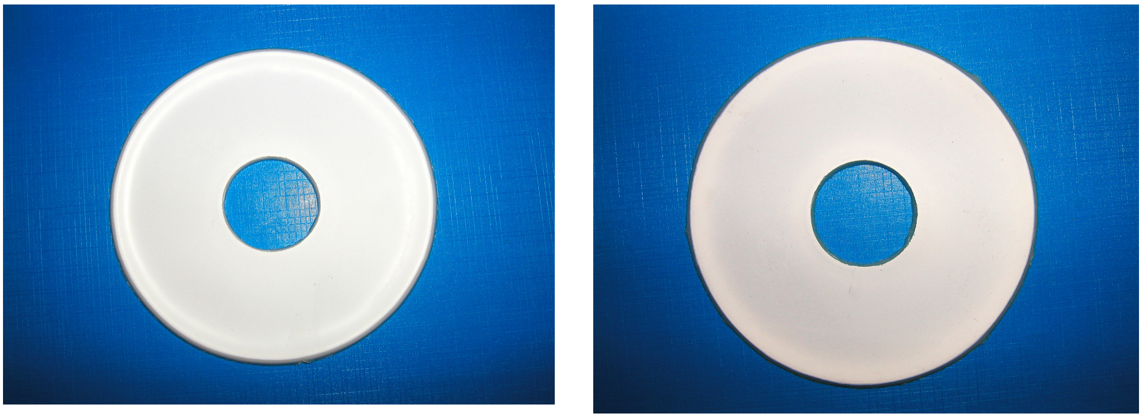


Figure 48 The photographs of Immo-TiO_2 anatase film; a) before and b) after use on the photocatalytic degradation of MB solution

a) before use b) after use

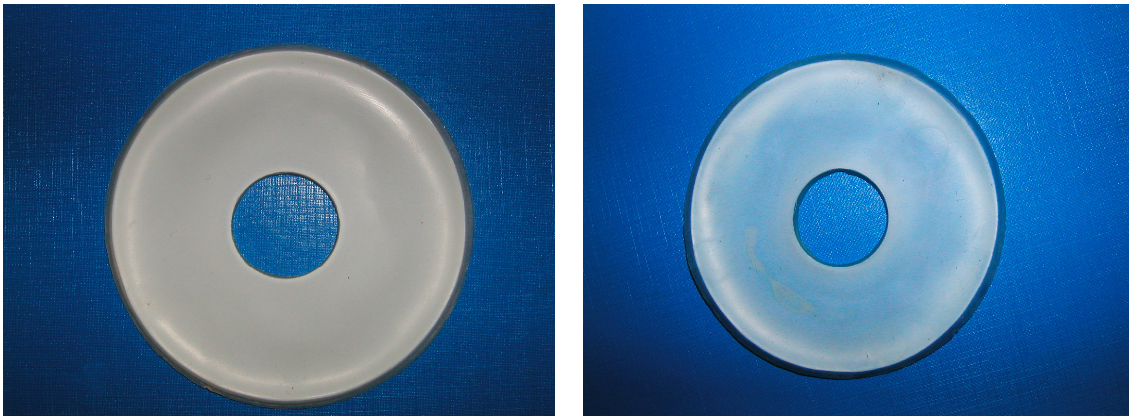
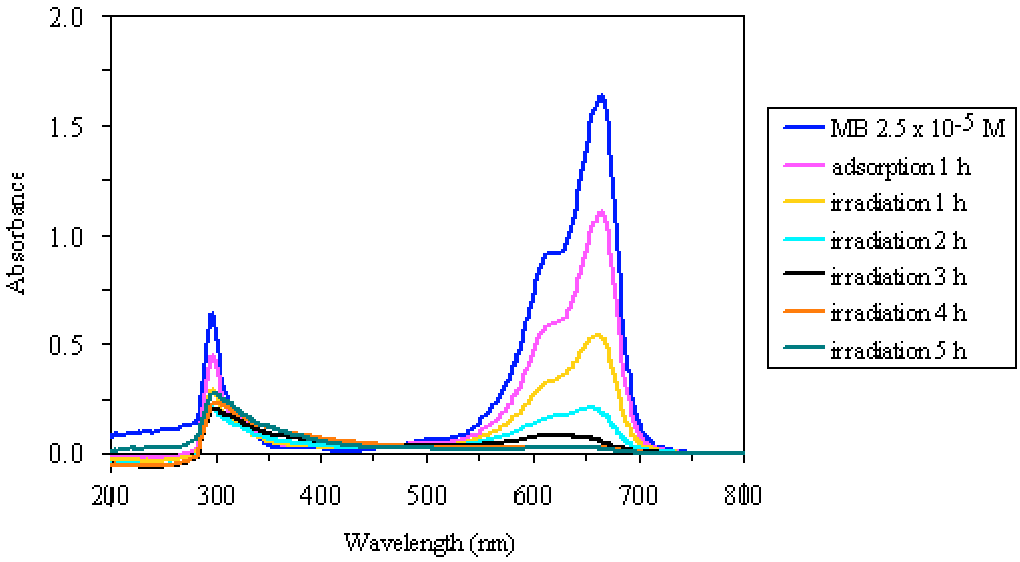


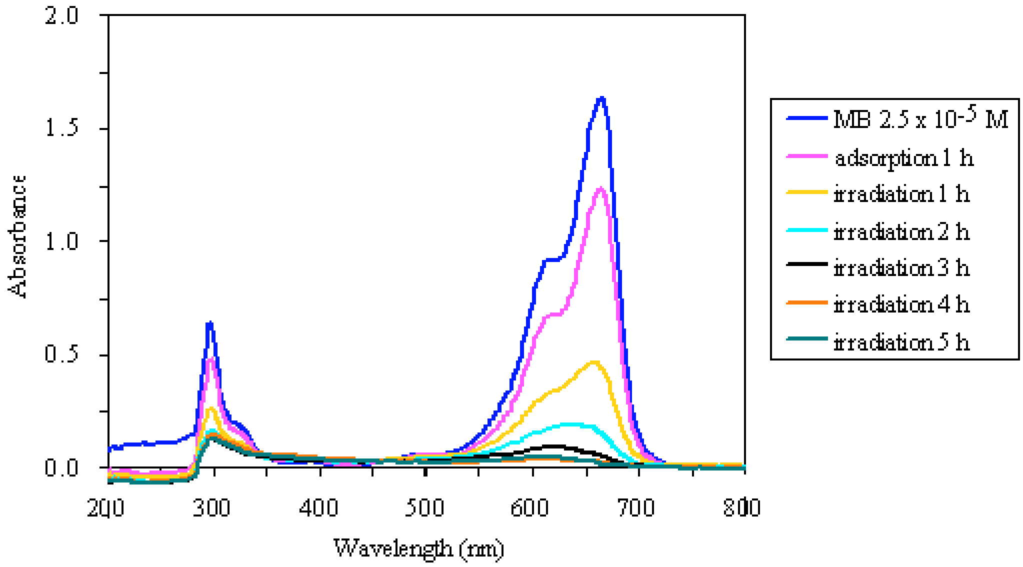
Figure 49 The photographs of Immo-TiO_2 Degussa P25 film; a) before and b) after use on the photocatalytic degradation of MB solution

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 (λ = 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 anatase film.

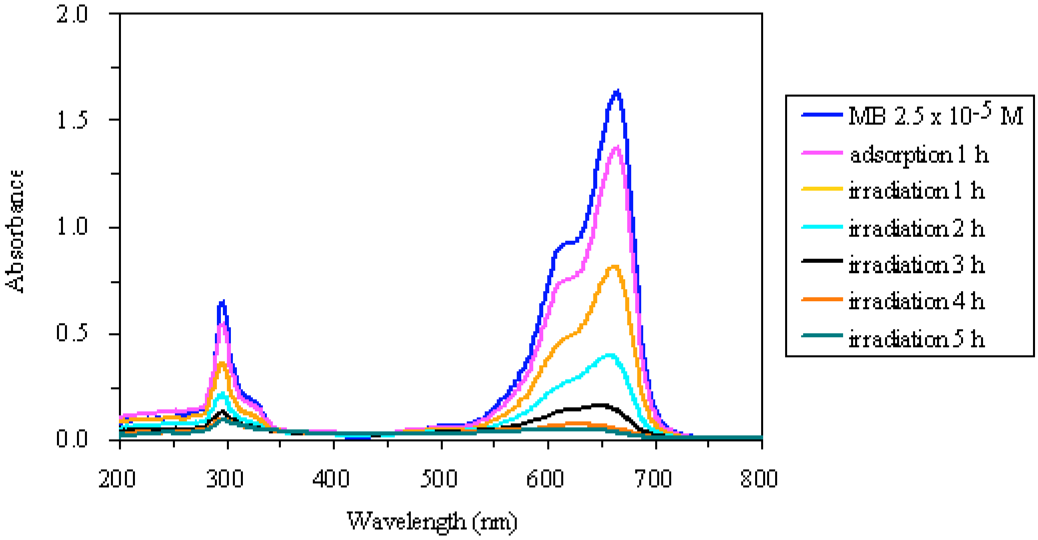
a) First use



b) Second use



c) Third use



d) Fourth use

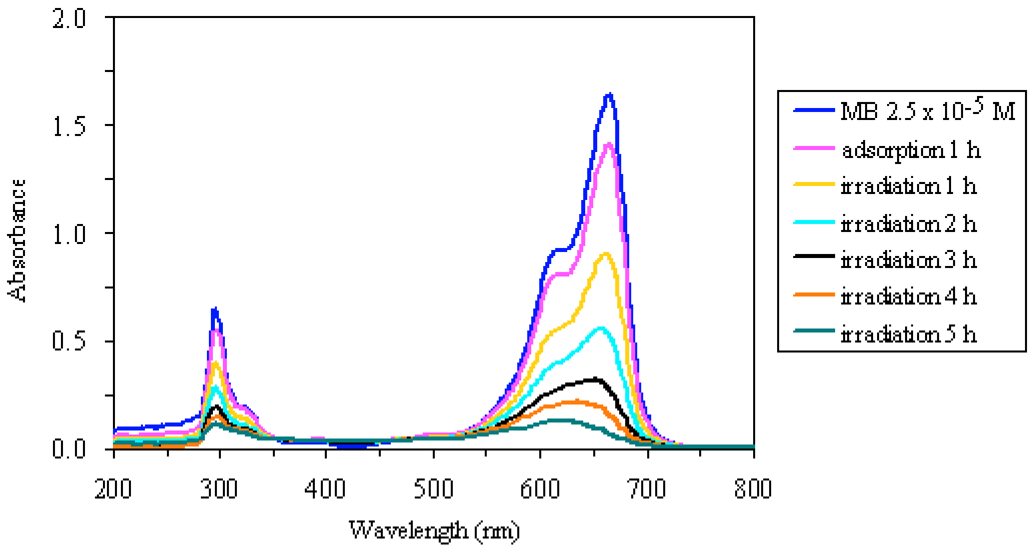


Figure 50 The UV-Vis spectral change of methylene blue by Immo-TiO_2 anatase film in the repeated uses four times

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.

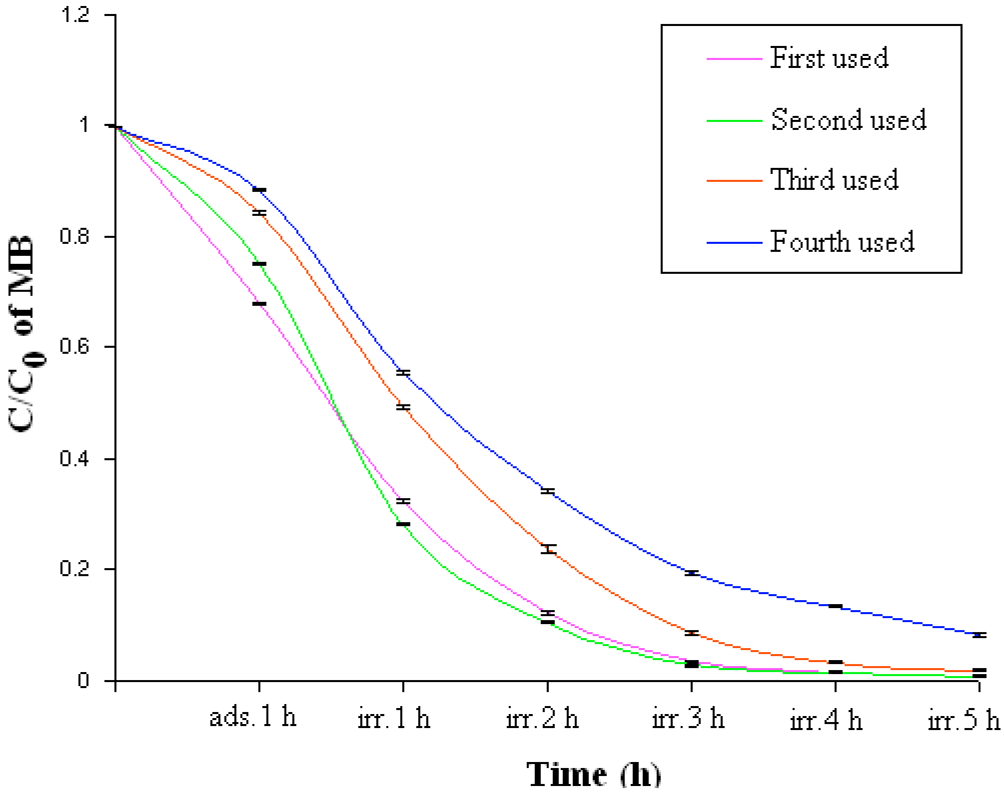


Figure 51 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film in the repeated uses four times

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 cloud be cleaned easily by submerging film in water and illuminating with UV light (5 tubes) for10 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 b) after second use

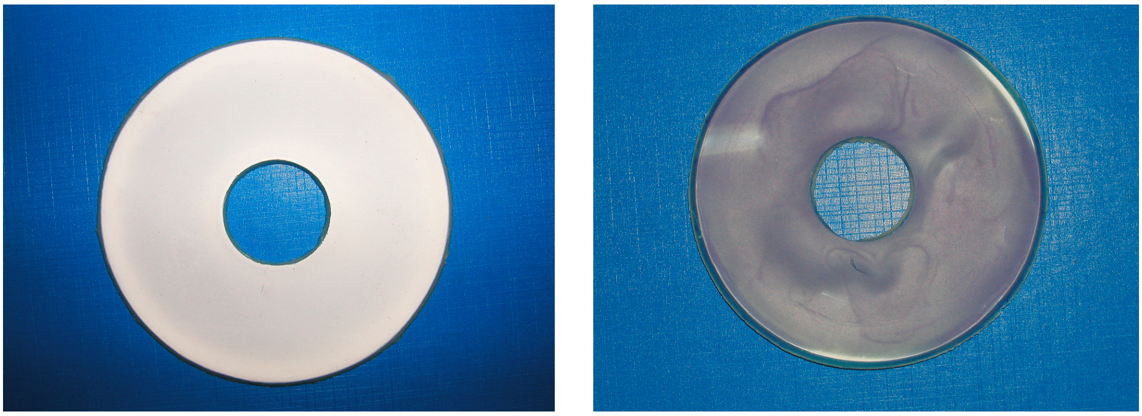


Figure 52 The photographs of Immo-TiO_2 anatase film a) before second use b) after second use on the photocatalytic degradation of MB

a) before UV illuminating b) after UV illuminating

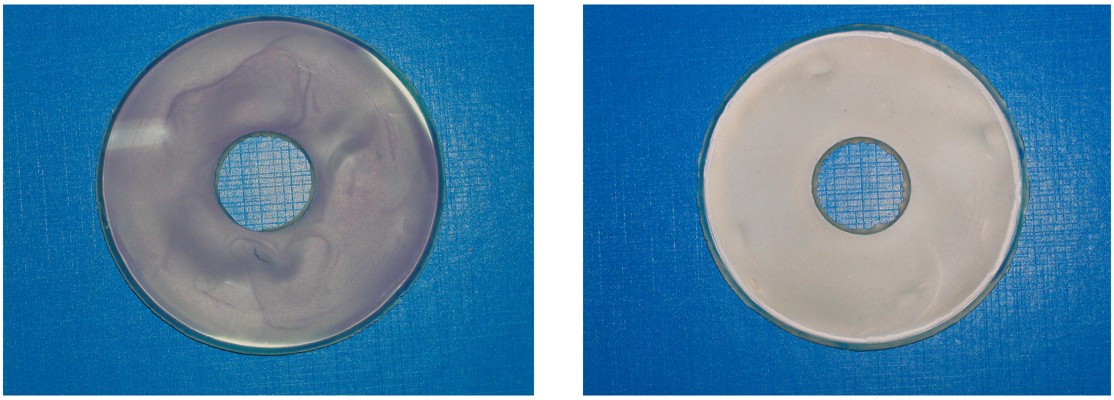
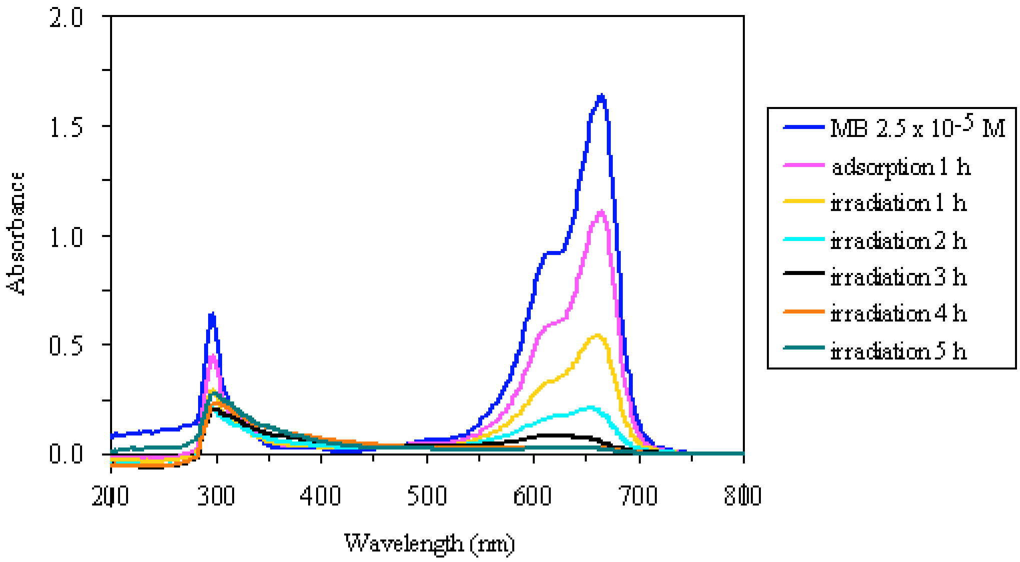


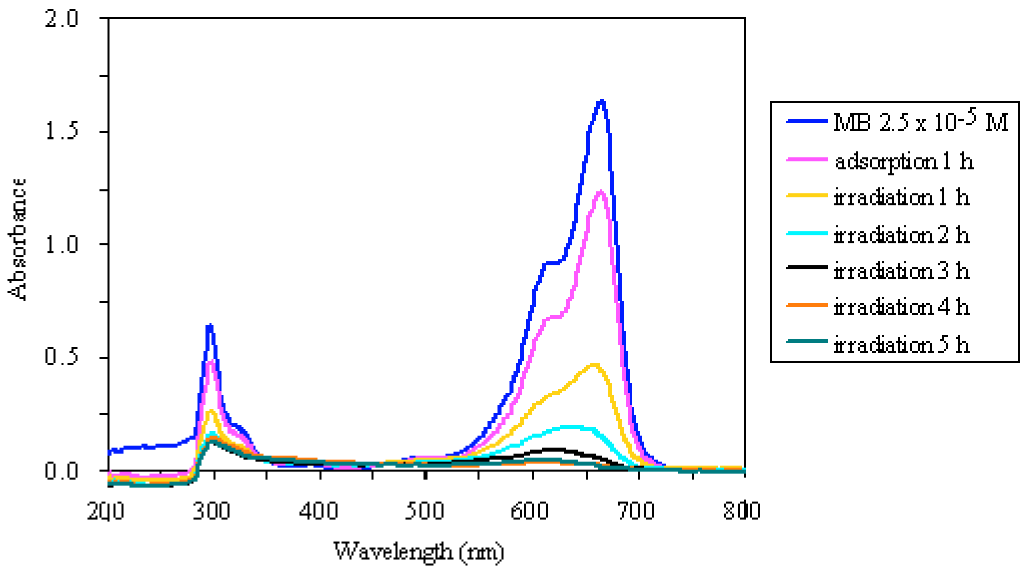
Figure 53 The photographs of Immo-TiO_2 anatase film a) before cleaning b) after cleaning

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 (λ = 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.

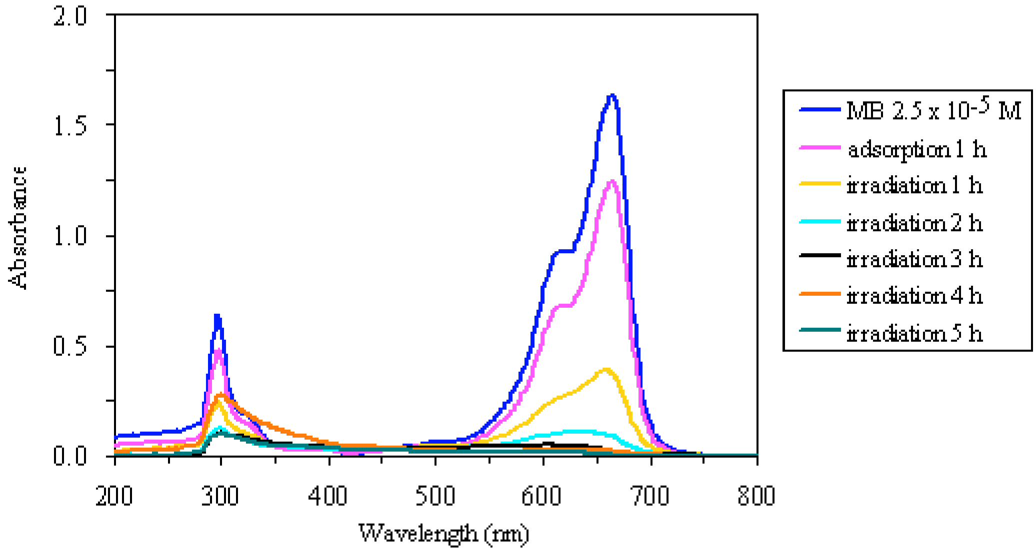
a) First use



b) Second use



c) Third use (cleaning before use)



d) Fourth use (cleaning before use)

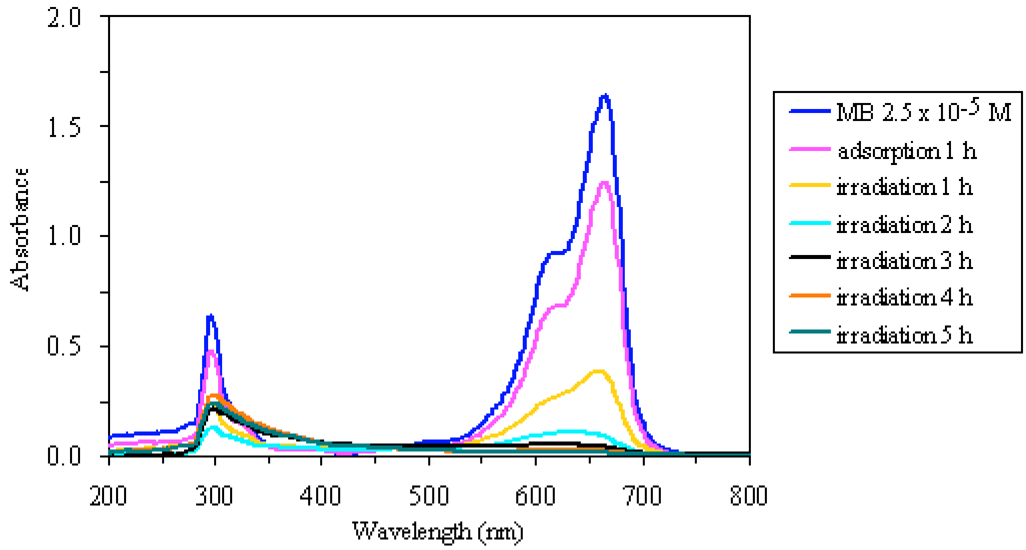


Figure 54 The UV-Vis spectral change of methylene blue by Immo-TiO_2 anatase film in the repeated uses four times (with self-cleaning after use)

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.

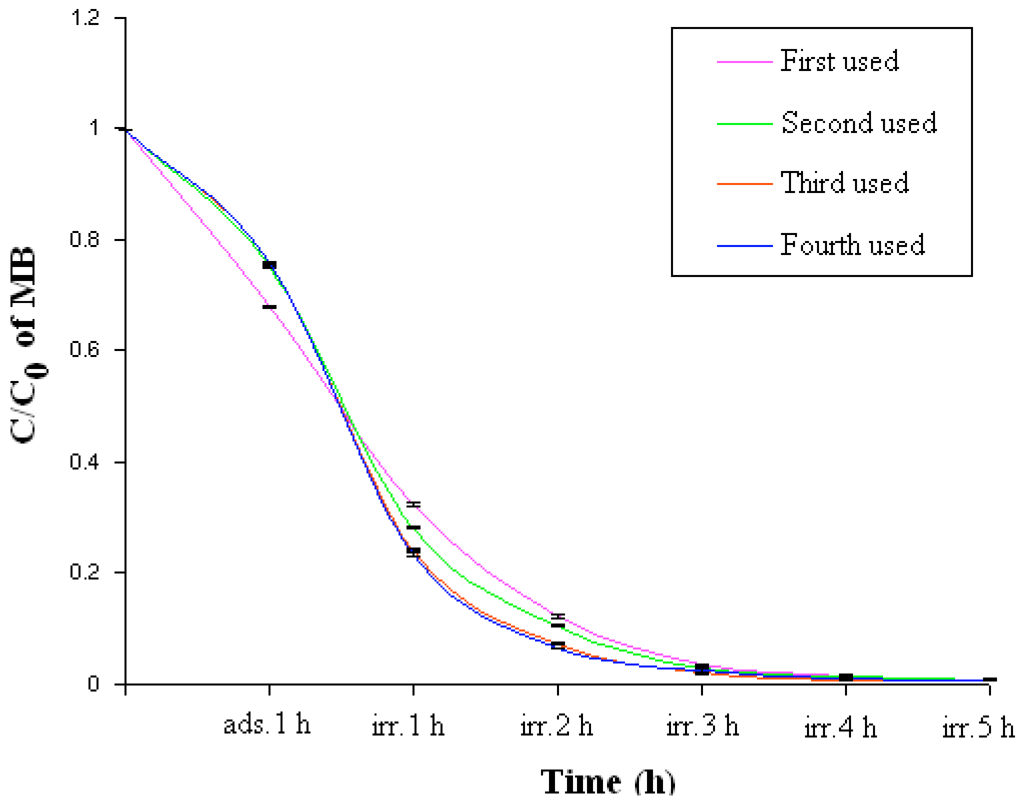


Figure 55 The relative remained C/C_0 of methylene blue by Immo-TiO_2 anatase film in the repeated uses (with "self-cleaning" after use)

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)

Immo-TiO_2 anatase thin film	% Degradation of MB (average)*				
	1 h	2 h	3 h	4 h	5 h
a) continuous use					
First use	67.63±0.45	87.67±0.27	96.47±0.20	98.63±0.09	99.30±0.08
Second use	71.73±0.20	98.50±0.16	97.17±0.17	98.50±0.12	99.50±0.17
Third use	50.57±0.25	77.50±0.22	91.47±0.20	96.63±0.20	98.10±0.16
Fourth use	44.47±0.20	65.73±0.25	80.47±0.33	86.53±0.20	91.67±0.25
b) cleaning before use					
First use	67.63±0.45	87.67±0.27	96.47±0.20	98.63±0.09	99.30±0.08
Second use	71.73±0.20	98.50±0.16	97.17±0.17	98.50±0.12	99.50±0.17
Third used**	75.73±0.12	92.83±0.12	97.67±0.17	99.13±0.12	99.27±0.12
Fourth used***	76.67±0.17	94.10±0.16	98.23±0.20	99.13±0.12	99.43±0.13

* n=3, average ± SD

** cleaning before use (after second use)

*** cleaning before use (after third use)