Chapter 3

Results

3.1 Syntheses and characterizations of titanium dioxides

3.1.1 Syntheses of undoped TiO_2 and trivalent (Al, B)-doped TiO_2

In the present study, the undoped TiO_2 and trivalent (Al, B)-doped TiO_2 were prepared by sol-gel method. In the case of trivalent (Al, B)-doped TiO_2, these samples were further studied for several parameters such as the amount of trivalent ion doping, type of acids (CH_3COOH, HCl, HNO_3, H_2SO_4, H_3PO_4), amount of distilled water (50, 100, 150, 200 mL), and calcined temperature (400, 500, 600, 700, 800°C).

In sol-gel synthesis of titanium dioxide, the reaction consisted of hydrolysis and condensation reactions of titanium tetrachloride aqueous solution. Titanium tetrachloride was first diluted in cold-distilled water to reduce the high heat of exothermic reaction. The hydrolysis and condensation reaction started immediately upon heating the titanium tetrachloride solution at 95°C as indicated by the rapid increase in turbidity and the formation of flocs which precipitated at the bottom of the reaction vessel. In this work, different additives such as CH_3COOH, HCl, HNO_3, H_2SO_4, H_3PO_4 were used as hydrolysis catalyst which added to the solution in order to affect the hydrolysis reaction of titanium tetrachloride in water.

3.1.2 Characterizations of titanium dioxides

3.1.2.1 X-ray powder diffraction patterns (XRD)

The crystalline structure of the phases and their crystallite size of each phase present in these samples were obtained by x-ray powder diffraction, using a diffractometer with CuK_α radiation. The identification of a species from its powder diffraction pattern is based upon the position of the lines (in terms of 2θ) and their relative intensities (Skoog and Leary, 1992). 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 peak 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 analysed.

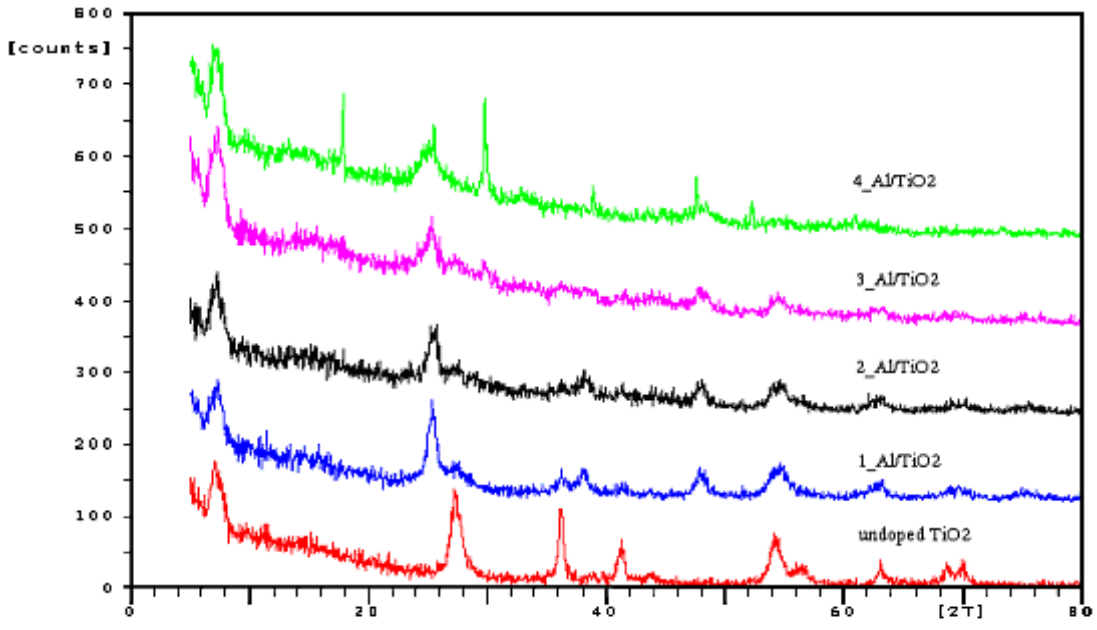
The crystallite size of each phase present can also be determined from the broadening of corresponding x-ray spectral peaks by the Scherrer formula ;

$$L = \kappa\lambda / (\beta\cos\theta) \qquad \text{..... (12)}$$

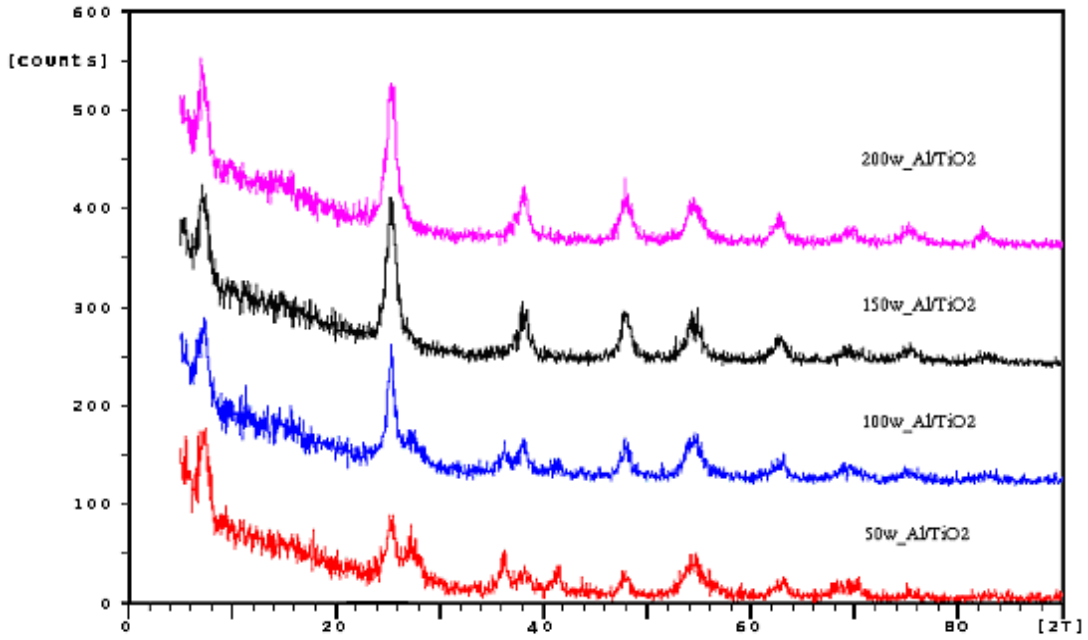
where L is the crystallite size, λ is the wavelength of the x-ray radiation (CuK_α = 0.15418), κ is a constant and usually taken as 0.89, and β is the line width at half-maximum height. This is a generally accepted method to estimate the mean crystallite size of nanoparticle (J. Liqiang, et al., 2004).

The powder XRD patterns of all Al-doped TiO_2 samples and B-doped TiO_2 samples are shown in Figure 18 and Figure 19, respectively.

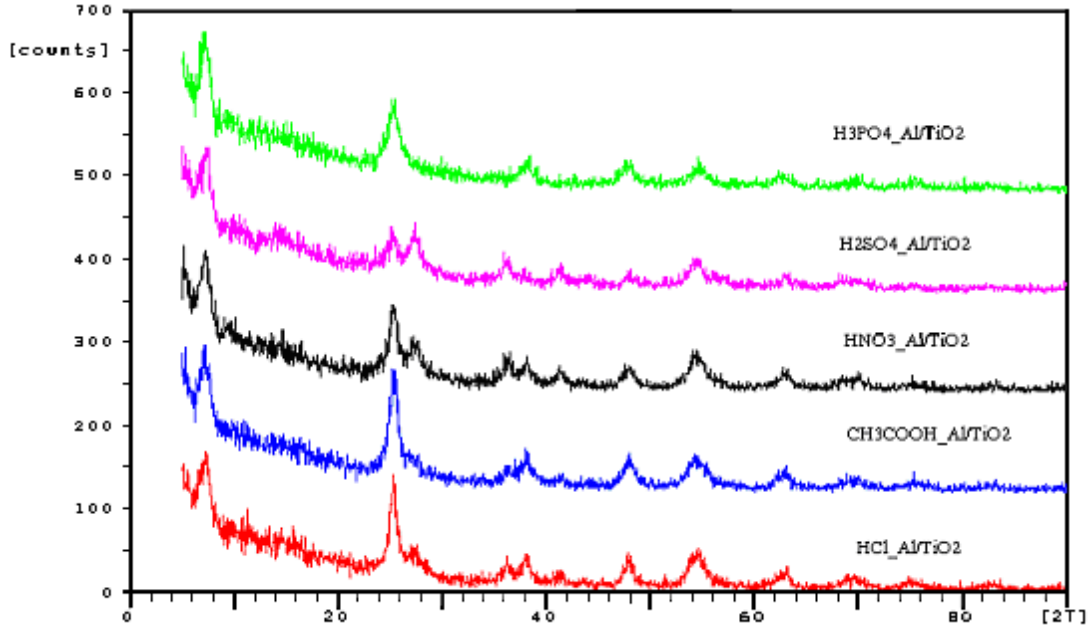
a) amount_Al doped TiO_2



b) water_ Al doped TiO_2



c) acid_ Al doped TiO_2



d) calcined_ Al doped TiO_2

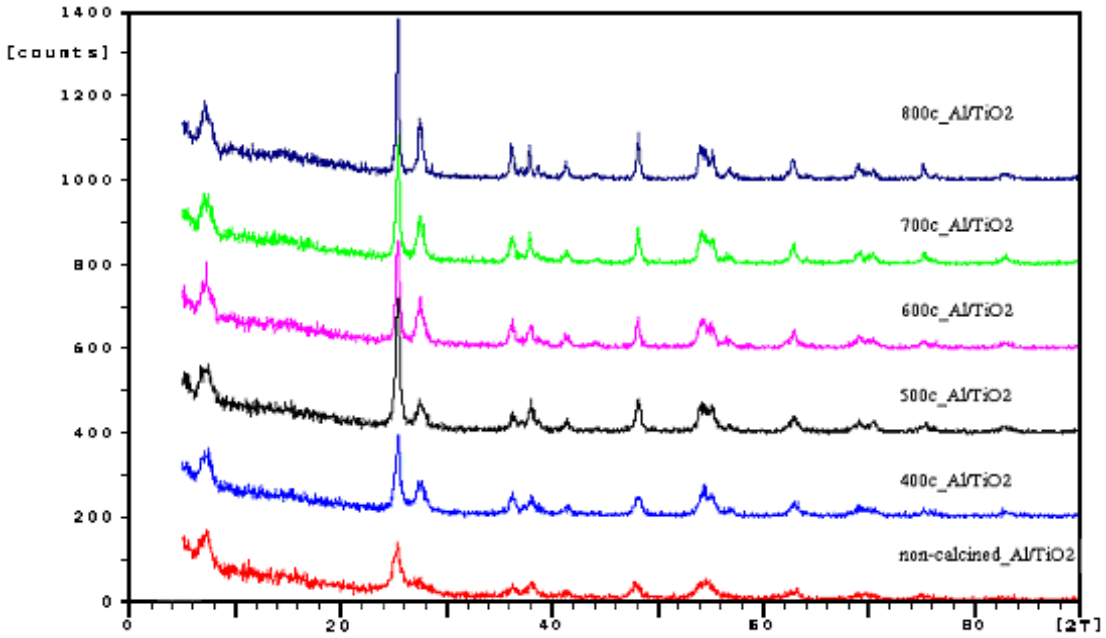
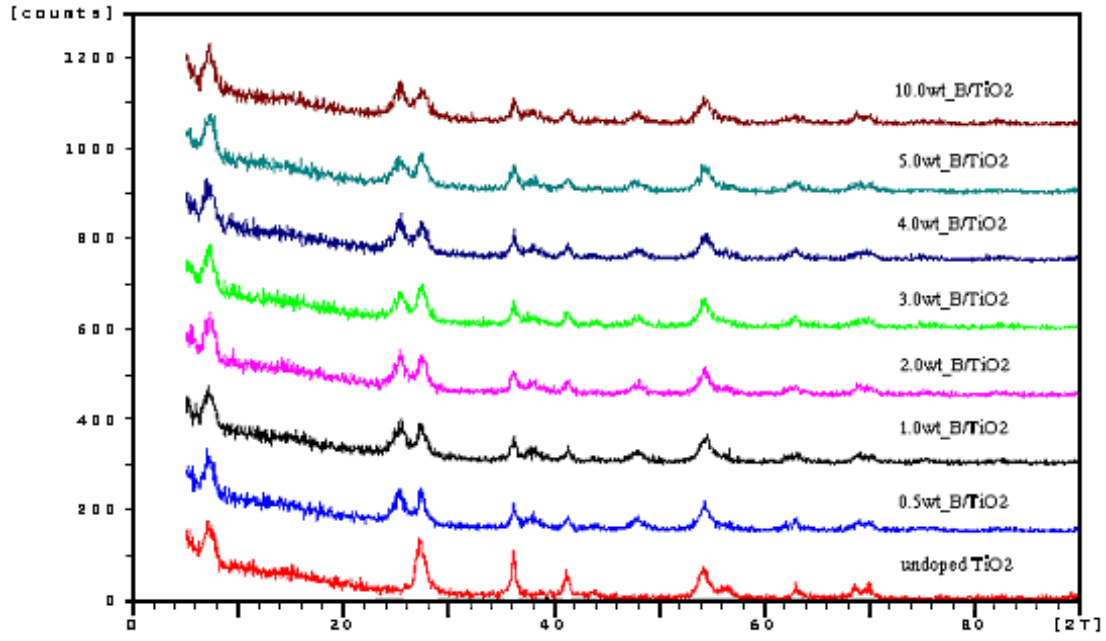
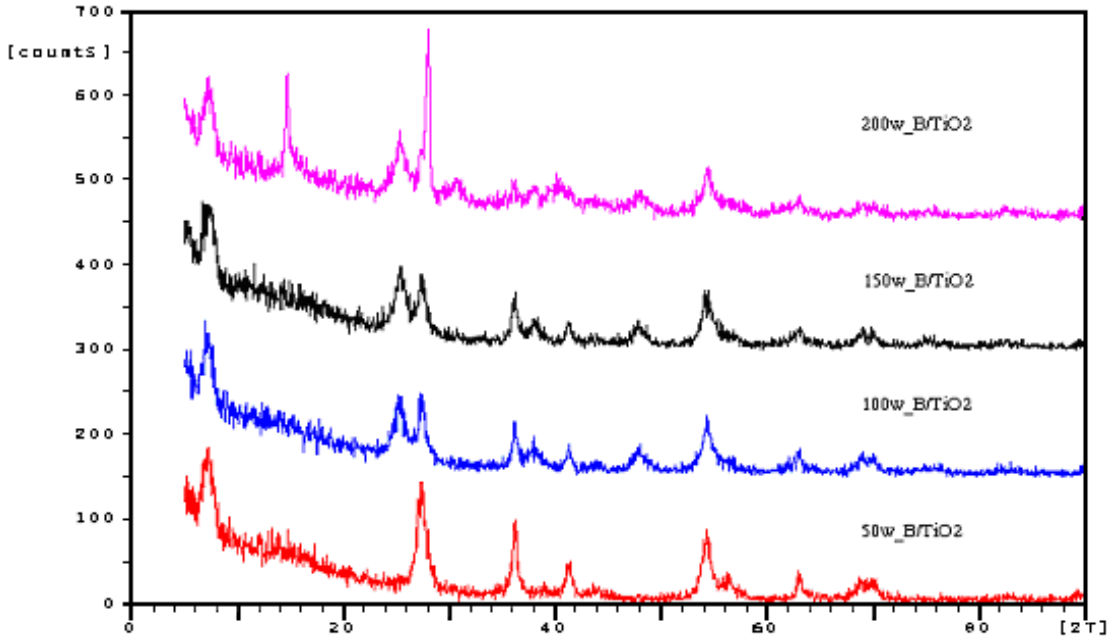


Figure 18 XRD patterns of Al-doped TiO_2 samples with various parameters varied : a) amount_ Al doped TiO_2, b) water_ Al doped TiO_2, c) acid_ Al doped TiO_2, and d) calcined_ Al doped TiO_2 samples.

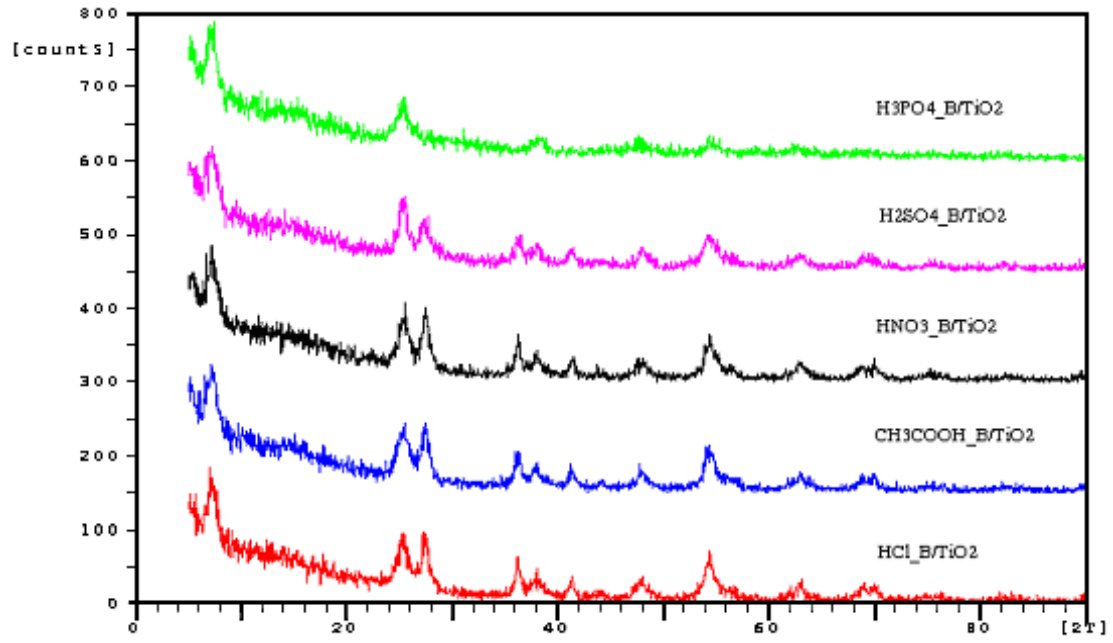
a) amount_ B doped TiO_2



b) water_ B doped TiO_2



c) acid_ B doped TiO_2



d) calcined_ B doped TiO_2

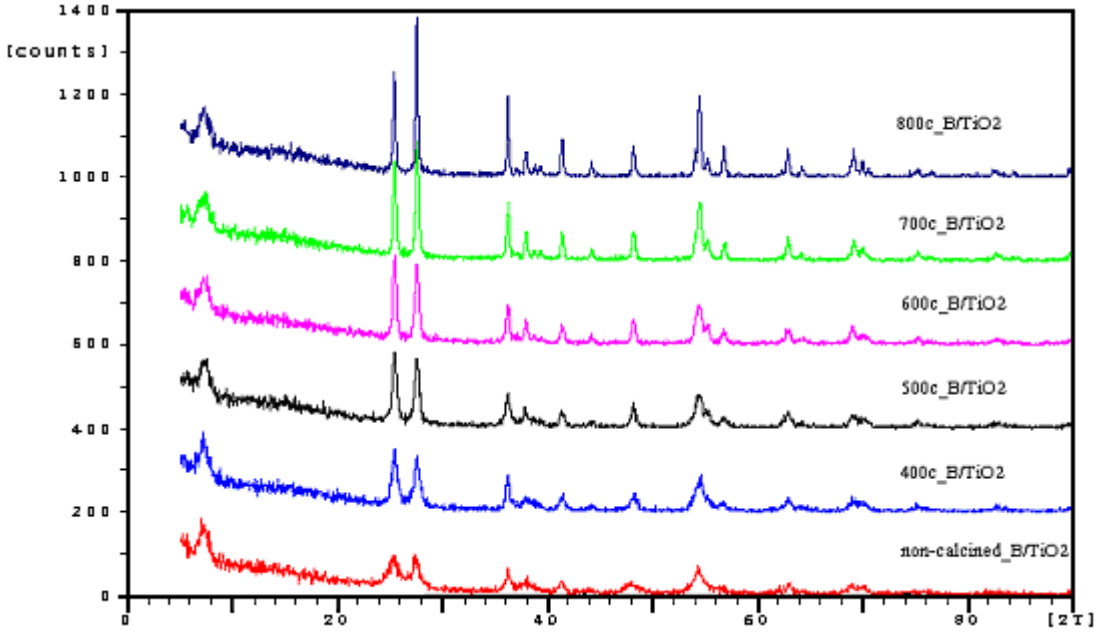


Figure 19 XRD patterns of B-doped TiO_2 samples with various parameters varied : a) amount_ B doped TiO_2, b) water_ B doped TiO_2, c) acid_ B doped TiO_2, and d) calcined_ B doped TiO_2 samples.

The data of the crystalline phase present in each sample in all synthesized Al-doped TiO_2 samples and B-doped TiO_2 samples are shown in Table 6 and Table 7, respectively. The crystallite sizes of the sample were estimated by the Sherrer formula and these data are shown in Table 8 and Table 9 for Al-doped TiO_2 and B-doped TiO_2 samples, respectively. The crystallite sizes are found to be in nanometer region for all trivalent (Al, B)-doped TiO_2 samples.

Table 6 The crystalline phase of Al-doped TiO_2 samples

Al doped TiO_2 samples	Crystalline phase
undoped TiO_2	rutile
a)amount_Al/TiO_2	
1_Al/TiO_2	anatase
2_Al/TiO_2	anatase + rutile
3_Al/TiO_2	anatase + aluminium oxonium sulfate hydrate
4_Al/TiO_2	anatase + aluminium oxonium sulfate hydrate
b)water_Al/TiO_2	
50w_Al/TiO_2	anatase + rutile
100w_Al/TiO_2	anatase
150w_Al/TiO_2	anatase
200w_Al/TiO_2	anatase
c)acid_Al/TiO_2	
CH_3COOH_Al/TiO_2	anatase
HCl_Al/TiO_2	anatase
HNO_3_Al/TiO_2	anatase + rutile
H_2SO_4_Al/TiO_2	anatase + rutile
H_3PO_4_Al/TiO_2	anatase
d)calcined_Al/TiO_2	
400c_Al/TiO_2	anatase + rutile
500c_Al/TiO_2	anatase + rutile
600c_Al/TiO_2	anatase + rutile
700c_Al/TiO_2	anatase + rutile
800c_Al/TiO_2	anatase + rutile

Note : The formula of aluminium oxonium sulfate hydrate is $(H_2O)Al_3(SO_4)_2(OH)_6$.

Table 7 The crystalline phase of B-doped TiO_2 samples

B doped TiO_2 samples	Crystalline phase
undoped TiO_2	rutile
a)amount_B/TiO_2	
0.50wt_B/TiO_2	anatase + rutile
1.0wt_B/TiO_2	anatase + rutile
2.0wt_B/TiO_2	anatase + rutile
3.0wt_B/TiO_2	anatase + rutile
4.0wt_B/TiO_2	anatase + rutile
5.0wt_B/TiO_2	anatase + rutile
10.0wt_B/TiO_2	anatase + rutile
b)water_B/TiO_2	
50w_B/TiO_2	rutile
100w_B/TiO_2	anatase + rutile
150w_B/TiO_2	anatase + rutile
200w_B/TiO_2	anatase + B_2O_3
c)acid_B/TiO_2	
CH_3COOH_B/TiO_2	anatase + rutile
HCl_B/TiO_2	anatase + rutile
HNO_3_B/TiO_2	anatase + rutile
H_2SO_4_B/TiO_2	anatase + rutile
H_3PO_4_B/TiO_2	anatase + rutile
d)calcined_B/TiO_2	
400c_B/TiO_2	anatase + rutile
500c_B/TiO_2	anatase + rutile
600c_B/TiO_2	anatase + rutile
700c_B/TiO_2	anatase + rutile
800c_B/TiO_2	anatase + rutile

Table 8 The crystallite size of Al-doped TiO_2 samples

Al doped TiO_2 samples	Crystallite size (nm)	
	Anatase	Rutile
undoped TiO_2	-	6.16
a)amount_Al/TiO_2		
1_Al/TiO_2	7.04	-
2_Al/TiO_2	7.33	8.15
3_Al/TiO_2	6.51	-
4_Al/TiO_2	4.09	-
b)water_Al/TiO_2		
50w_Al/TiO_2	5.85	6.42
100w_Al/TiO_2	7.04	-
150w_Al/TiO_2	5.85	-
200w_Al/TiO_2	6.27	-
c)acid_Al/TiO_2		
CH_3COOH_Al/TiO_2	5.85	-
HCl_Al/TiO_2	7.04	-
HNO_3_Al/TiO_2	6.76	5.78
H_2SO_4_Al/TiO_2	5.85	6.39
H_3PO_4_Al/TiO_2	5.17	-
d)calcined_Al/TiO_2		
400c_Al/TiO_2	12.60	8.94
500c_Al/TiO_2	11.00	8.94
600c_Al/TiO_2	12.60	11.27
700c_Al/TiO_2	17.54	14.90
800c_Al/TiO_2	22.35	14.90

Table 9 The crystallite size of B-doped TiO_2 samples

B doped TiO_2 samples	Crystallite size (nm)	
	Anatase	Rutile
undoped TiO_2	-	6.16
a)amount_B/TiO_2		
0.50wt_B/TiO_2	6.39	9.76
1.0wt_B/TiO_2	8.10	9.24
2.0wt_B/TiO_2	5.50	5.61
3.0wt_B/TiO_2	7.04	6.42
4.0wt_B/TiO_2	5.66	5.97
5.0wt_B/TiO_2	4.95	9.18
10.0wt_B/TiO_2	6.66	6.24
b)water_B/TiO_2		
50w_B/TiO_2	-	5.95
100w_B/TiO_2	6.39	9.76
150w_B/TiO_2	6.27	7.49
200w_B/TiO_2	6.66	11.18
c)acid_B/TiO_2		
CH_3COOH_B/TiO_2	5.90	6.24
HCl_B/TiO_2	6.39	9.76
HNO_3_B/TiO_2	7.66	9.18
H_2SO_4_B/TiO_2	6.66	5.57
H_3PO_4_B/TiO_2	4.03	-
d)calcined_B/TiO_2		
400c_B/TiO_2	11.00	11.18
500c_B/TiO_2	12.83	12.05
600c_B/TiO_2	12.83	15.57
700c_B/TiO_2	22.00	12.05
800c_B/TiO_2	17.11	22.35

The content of anatase and rutile crystallines in the synthesized titanium dioxide samples were calculated from the equation (13) and (14), respectively.

$$\frac{I_{unknown}}{I_{unknown+anatase}} = \frac{x}{x + A\%} \qquad .....(13)$$

where $I_{unknown}$ = intensity of anatase peak in sample ($2\theta = 25.50$)

$I_{unknown+anatase}$ = intensity of anatase peak in standard sample ($2\theta = 25.50$)

x = percentage of anatase in sample

A = percentage of anatase in standard sample

$$\frac{I_{unknown}}{I_{unknown+rutile}} = \frac{y}{y + R\%} \qquad .....(14)$$

where $I_{unknown}$ = intensity of rutile peak in sample ($2\theta = 27.50$)

$I_{unknown+rutile}$ = intensity of rutile peak in standard sample ($2\theta = 27.50$)

y = percentage of rutile in sample

R = percentage of rutile in standard sample

The content of anatase and rutile in the trivalent (Al, B)-doped TiO_2 are shown in Table 10 and Table 11.

Table 10 The content of anatase and rutile crystalline in Al-doped TiO_2 samples

Al doped TiO_2 samples	Content of crystalline (%)	
	Anatase	Rutile
undoped TiO_2	-	30.00
a)amount_Al/TiO_2		
1_Al/TiO_2	13.98	-
2_Al/TiO_2	21.50	10.26
3_Al/TiO_2	19.06	-
4_Al/TiO_2	23.84	-
b)water_Al/TiO_2		
50w_Al/TiO_2	9.09	11.47
100w_Al/TiO_2	13.98	-
150w_Al/TiO_2	23.38	-
200w_Al/TiO_2	20.88	-
c)acid_Al/TiO_2		
CH_3COOH_Al/TiO_2	15.46	-
HCl_Al/TiO_2	13.98	-
HNO_3_Al/TiO_2	12.77	9.21
H_2SO_4_Al/TiO_2	7.34	13.55
H_3PO_4_Al/TiO_2	8.57	-
d)calcined_Al/TiO_2		
non-calcined_ Al/TiO_2	13.98	-
400c_Al/TiO_2	21.17	10.72
500c_Al/TiO_2	56.47	6.86
600c_Al/TiO_2	26.61	16.84
700c_Al/TiO_2	45.75	15.82
800c_Al/TiO_2	49.91	19.28

Table 11 The content of anatase and rutile crystalline in B-doped TiO_2 samples

B doped TiO_2 samples	Content of crystalline (%)	
	Anatase	Rutile
undoped TiO_2	-	30.00
a)amount_B/TiO_2		
0.50wt_B/TiO_2	6.16	10.87
1.0wt_B/TiO_2	7.02	10.00
2.0wt_B/TiO_2	6.69	9.59
3.0wt_B/TiO_2	5.03	11.33
4.0wt_B/TiO_2	7.36	8.64
5.0wt_B/TiO_2	4.77	9.20
10.0wt_B/TiO_2	6.37	8.46
b)water_B/TiO_2		
50w_B/TiO_2	-	48.33
100w_B/TiO_2	6.16	10.87
150w_B/TiO_2	6.27	6.84
200w_B/TiO_2	10.00	-
c)acid_B/TiO_2		
CH_3COOH_B/TiO_2	5.96	10.21
HCl_B/TiO_2	6.16	10.87
HNO_3_B/TiO_2	7.25	10.87
H_2SO_4_B/TiO_2	6.80	7.14
H_3PO_4_B/TiO_2	6.92	-
d)calcined_B/TiO_2		
non-calcined_ B/TiO_2	6.16	10.87
400c_B/TiO_2	12.40	17.53
500c_B/TiO_2	18.87	38.18
600c_B/TiO_2	16.94	31.45
700c_B/TiO_2	21.98	24.83
800c_B/TiO_2	23.81	63.33

3.1.2.2 Surface area and pore size

The surface area is an average measurement of the external surface of a large number of particles and expressed in term of the area per unit mass (m^2/g). There are two main analysis techniques for measuring surface area; gas adsorption and gas permeability. In this work gas adsorption surface area analysis was used.

The gas adsorption approach starts with a clean surface achieved through vacuum or inert gas break-out. The clean powder surface is exposed to varying partial pressure of known adsorbing vapors. A measurement is made from the amount of gas adsorbed on the powder surface versus the partial pressure. The measurement is often referred to as the BET specific surface area after Brunauer, Emmett and Teller who developed the concept in 1938.

Under equilibrium, the rate of adsorption equals the rate of evaporation. Letting P equal the partial pressure of adsorbate, P_0 equal the saturation pressure of adsorbate (which depends on the gas and temperature), X equal the amount of gas adsorbed at a pressure P, X_m equal the monolayer capacity of the powder (the amount of gas nescessary to form a uniform surface coating one atomic layer thick), and C equal a constant relating to the adsorption enthalpy, gives

$$\frac{P}{X(P_0-P)} = \frac{1}{X_m C} + \frac{C-1}{X_m C}\frac{P}{P_0} \qquad .....(15)$$

The linear relation between the term on the left of the equal sign and the partial pressure ratio P/P_0 is noted. This is the BET equation , and is generally valid for powders in the range P/P_0 from 0.05 to 0.30. Equation (15) can be rewritten in a general form as,

$$\frac{P}{X(P_0-P)} = B + A\frac{P}{P_0} \qquad .....(16)$$

where

$$X_m = \frac{1}{A+B} \qquad .....(17)$$

Giving A as the slope and B as the intercept of the linear equation. Finally, the surface area is calculated as

$$S = \frac{X_m N_o A_o}{wM} \quad \text{.....(18)}$$

using M as the molecular weight of adsorbate, A_o as the average occupational area of an adsorbate molecule, N_o as Avogadro's number, and w as the sample weight (German, 1984).

The surface area of all synthesized Al-doped TiO_2 samples and B-doped TiO_2 samples are shown in Table 12 and Table 13, respectively.The other data of porosity of trivalent (Al, B)-doped TiO_2 samples are shown in Table 14 and Table 15. These data were compared between as-prepared undoped TiO_2 and commercial P25-TiO_2 product. Moreover, the porosity study of synthesized samples are in Figures 20-25.

Table 12 Surface area of undoped TiO_2, P25-TiO_2, and Al-doped TiO_2 samples

Al doped TiO_2 samples	Surface area[a] (m^2/g)
undoped TiO_2	115.90
P25-TiO_2	51.41
a)amount_Al/TiO_2	
1_Al/TiO_2	229.55
2_Al/TiO_2	191.10
3_Al/TiO_2	223.97
4_Al/TiO_2	219.26
b)water_Al/TiO_2	
50w_Al/TiO_2	227.50
100w_Al/TiO_2	229.55
150w_Al/TiO_2	266.91
200w_Al/TiO_2	266.56
c)acid_Al/TiO_2	
CH_3COOH_Al/TiO_2	225.22
HCl_Al/TiO_2	229.55
HNO_3_Al/TiO_2	232.46
H_2SO_4_Al/TiO_2	191.50
H_3PO_4_Al/TiO_2	260.74
d)calcined_Al/TiO_2	
400c_Al/TiO_2	80.27
500c_Al/TiO_2	63.38
600c_Al/TiO_2	55.60
700c_Al/TiO_2	45.53
800c_Al/TiO_2	23.77

a Data were determined by using SA3100,Coulter.

Table 13 Surface area of undoped TiO_2, P25-TiO_2, and B-doped TiO_2 samples

B doped TiO_2 samples	Surface area[a] (m^2/g)
undoped TiO_2	115.90
P25-TiO_2	51.41
a)amount_B/TiO_2	
0.50wt_B/TiO_2	190.94
1.0wt_B/TiO_2	197.65
2.0wt_B/TiO_2	192.89
3.0wt_B/TiO_2	173.69
4.0wt_B/TiO_2	200.07
5.0wt_B/TiO_2	186.00
10.0wt_B/TiO_2	198.54
b)water_B/TiO_2	
50w_B/TiO_2	109.36
100w_B/TiO_2	190.94
150w_B/TiO_2	188.58
200w_B/TiO_2	204.00
c)acid_B/TiO_2	
CH_3COOH_B/TiO_2	206.94
HCl_B/TiO_2	190.94
HNO_3_B/TiO_2	186.20
H_2SO_4_B/TiO_2	229.21
H_3PO_4_B/TiO_2	310.98
d)calcined_B/TiO_2	
400c_B/TiO_2	63.01
500c_B/TiO_2	44.84
600c_B/TiO_2	31.42
700c_B/TiO_2	22.52
800c_B/TiO_2	14.25

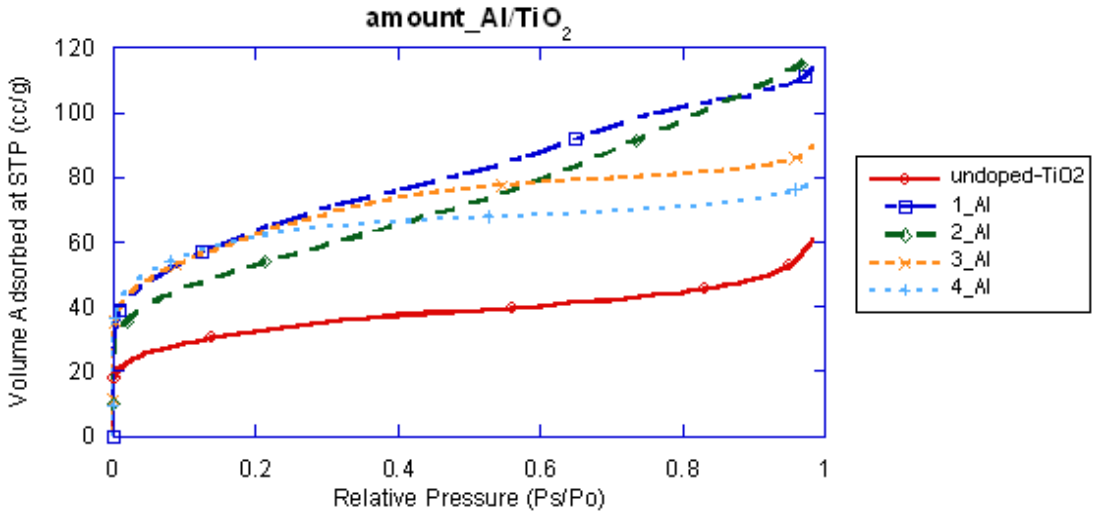
Table 14 Porosity of undoped TiO_2, P25-TiO_2, and A-doped TiO_2 samples

Sample	Pore volume (%) for pore diameter								Porosity
	<6	6-8	8-10	10-12	12-16	16-20	20-80	＞80	(ml/g)
Undoped-TiO_2	15.20	7.17	4.24	5.13	6.05	7.10	39.53	15.57	0.0454
P25-TiO_2	5.00	3.00	2.00	2.00	3.00	4.00	38.00	43.00	0.2350
a)amount_Al/TiO_2									
1_Al/TiO_2	41.55	16.87	6.52	4.72	4.27	3.34	14.11	8.62	0.0826
2_Al/TiO_2	35.72	15.33	7.70	7.26	7.44	6.49	15.58	4.12	0.1084
3_Al/TiO_2	35.01	7.06	3.36	4.08	4.54	5.07	26.20	14.68	0.0315
4_Al/TiO_2	18.09	7.62	4.40	5.54	6.23	7.30	33.66	17.17	0.0257
b)water_Al/TiO_2									
50w_Al/TiO_2	41.18	19.01	8.35	7.61	5.53	3.39	11.00	3.93	0.0565
100w_Al/TiO_2	41.55	16.87	6.52	4.72	4.27	3.34	14.11	8.62	0.0826
150w_Al/TiO_2	32.02	15.96	10.15	10.80	10.19	6.56	11.72	2.60	0.1844
200w_Al/TiO_2	26.47	17.15	11.32	13.26	12.25	8.50	9.74	1.30	0.3366
c)acid_Al/TiO_2									
CH_3COOH_Al/TiO_2	32.44	15.67	7.42	6.54	5.81	5.80	18.42	7.89	0.0839
HCl_Al/TiO_2	41.55	16.87	6.52	4.72	4.27	3.34	14.11	8.62	0.0826
HNO_3_Al/TiO_2	28.49	17.89	11.34	11.95	9.97	4.90	10.88	4.57	0.0848
H_2SO_4_Al/TiO_2	34.97	10.56	4.69	4.71	4.74	4.73	23.79	11.82	0.0662
H_3PO_4_Al/TiO_2	25.33	11.52	6.44	7.49	7.95	7.82	24.51	8.95	0.2665
d)calcined_Al/TiO_2									
400c_Al/TiO_2	20.05	20.21	9.86	8.06	11.57	18.22	10.56	1.47	0.1674
500c_Al/TiO_2	8.96	12.63	12.20	12.57	13.67	19.39	16.23	4.36	0.1753
600c_Al/TiO_2	5.49	8.28	9.81	14.10	14.83	12.55	31.58	3.36	0.1749
700c_Al/TiO_2	3.24	3.96	4.37	9.20	20.57	14.73	41.88	2.04	0.1682
800c_Al/TiO_2	2.00	1.49	1.25	2.11	3.88	7.80	75.82	5.64	0.1362

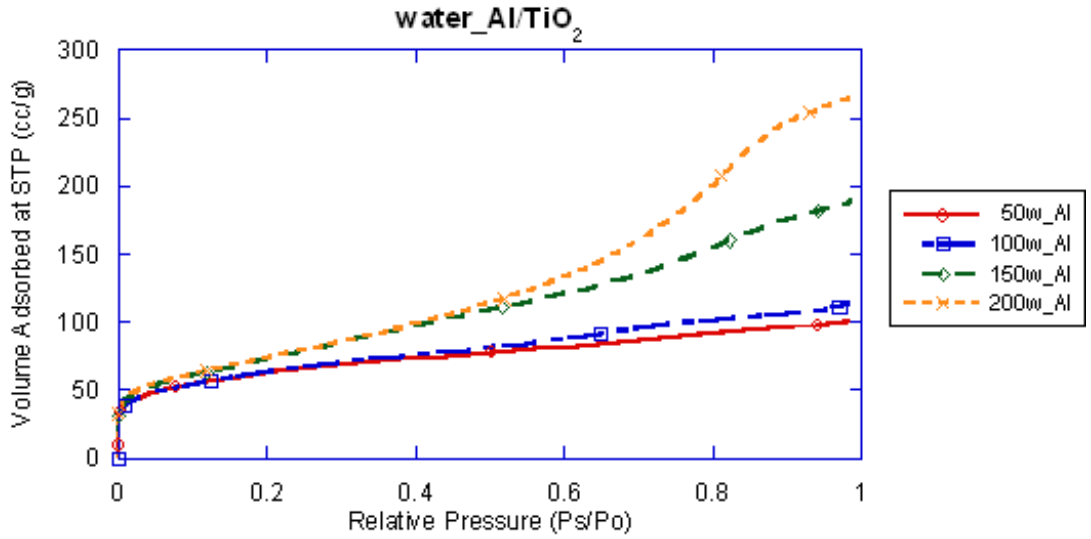
Table 15 Porosity of undoped TiO_2, P25-TiO_2, and B-doped TiO_2 samples

Sample	Pore volume (%) for pore diameter								Porosity (ml/g)
	<6	6-8	8-10	10-12	12-16	16-20	20-80	＞80	
Undoped-TiO_2	15.20	7.17	4.24	5.13	6.05	7.10	39.53	15.57	0.0454
P25-TiO_2	5.00	3.00	2.00	2.00	3.00	4.00	38.00	43.00	0.2350
a)amount_B/TiO_2									
0.5wt_B/TiO_2	31.07	6.56	3.51	3.95	4.86	5.99	34.68	9.38	0.1875
1.0wt_B/TiO_2	26.32	5.95	3.40	4.03	4.68	6.11	36.04	13.47	0.2385
2.0wt_B/TiO_2	28.07	5.51	3.12	3.96	4.78	6.33	35.76	12.47	0.2270
3.0wt_B/TiO_2	33.99	6.33	3.17	3.79	4.54	5.15	30.52	12.51	0.1907
4.0wt_B/TiO_2	24.69	5.54	3.10	3.81	4.88	6.25	36.22	15.50	0.2515
5.0wt_B/TiO_2	27.58	5.64	3.12	3.63	4.56	5.62	35.97	13.89	0.2129
10.0wt_B/TiO_2	28.71	6.50	3.60	4.31	5.45	6.32	33.39	11.74	0.1457
b)water_B/TiO_2									
50w_B/TiO_2	17.17	8.66	5.52	6.08	7.29	7.92	31.83	15.53	0.0401
100w_B/TiO_2	31.07	6.56	3.51	3.95	4.86	5.99	34.68	9.38	0.1875
150w_B/TiO_2	16.16	6.76	3.55	5.05	6.39	9.00	48.09	5.01	0.4217
200w_B/TiO_2	14.35	8.73	5.79	7.40	10.56	13.61	35.17	4.39	0.4603
c)acid_B/TiO_2									
CH_3COOH_B/TiO_2	20.44	4.83	2.71	3.52	4.52	6.06	41.61	16.31	0.3615
HCl_B/TiO_2	31.07	6.56	3.51	3.95	4.86	5.99	34.68	9.38	0.1875
HNO_3_B/TiO_2	23.28	6.48	3.44	4.00	5.26	6.93	42.82	7.79	0.3134
H_2SO_4_B/TiO_2	21.78	11.01	6.52	7.83	6.38	9.63	29.49	4.37	0.1332
H_3PO_4_B/TiO_2	67.65	15.12	4.92	3.07	1.79	1.36	4.60	1.49	0.0914
d)calcined_B/TiO_2									
400c_B/TiO_2	1.86	1.93	2.60	4.10	8.08	7.90	62.19	11.34	0.3832
500c_B/TiO_2	1.30	1.09	0.96	1.71	3.11	5.66	70.70	15.47	0.3524
600c_B/TiO_2	1.63	1.10	0.83	1.36	2.18	5.15	61.07	26.68	0.2282
700c_B/TiO_2	1.88	1.11	0.79	1.12	1.83	2.93	55.635	34.70	0.1686
800c_B/TiO_2	2.72	1.53	1.01	1.33	2.00	3.10	8.97	29.35	0.0876

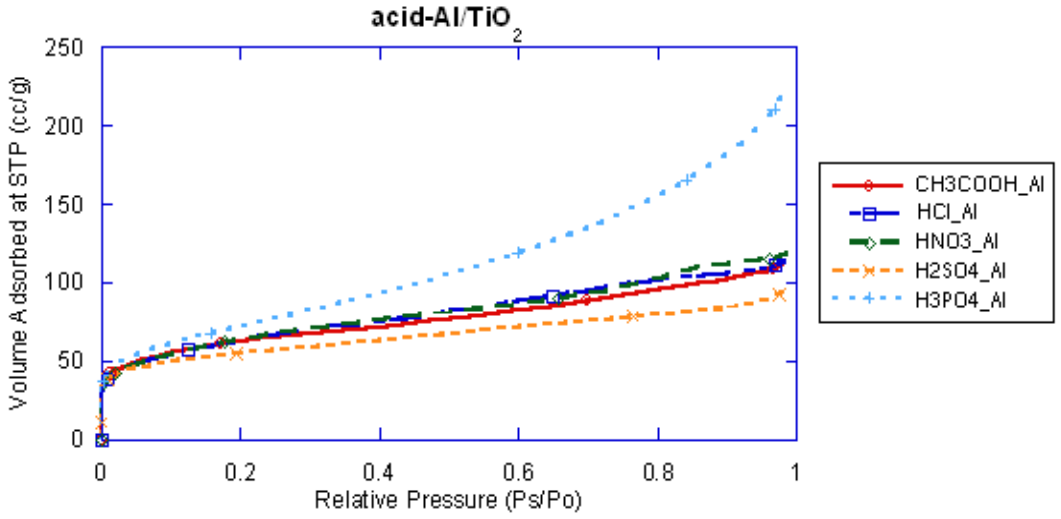
a) amount_ Al doped TiO_2



b) water_ Al doped TiO_2



c) acid_ Al doped TiO_2



d) calcined_ Al doped TiO_2

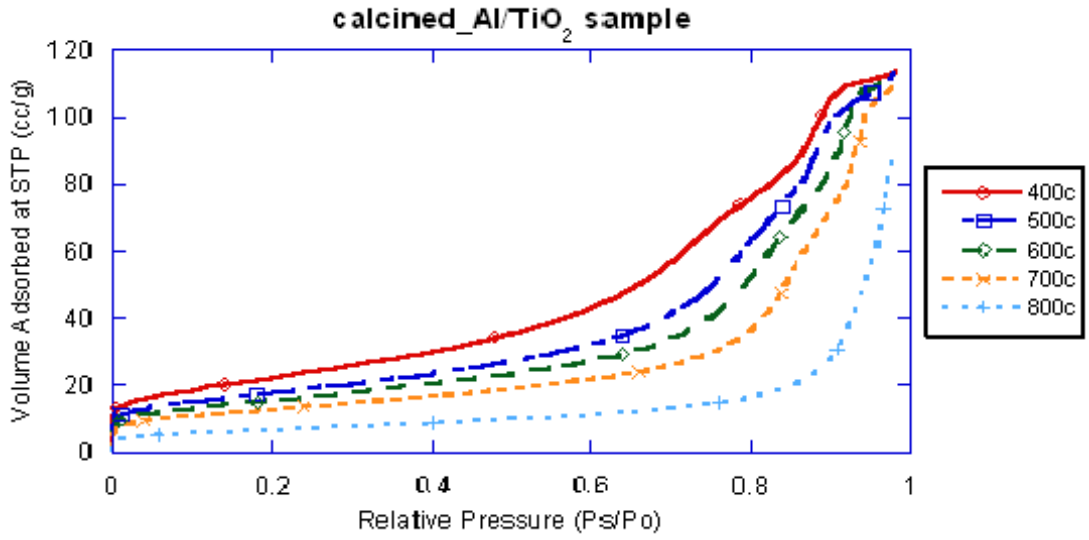
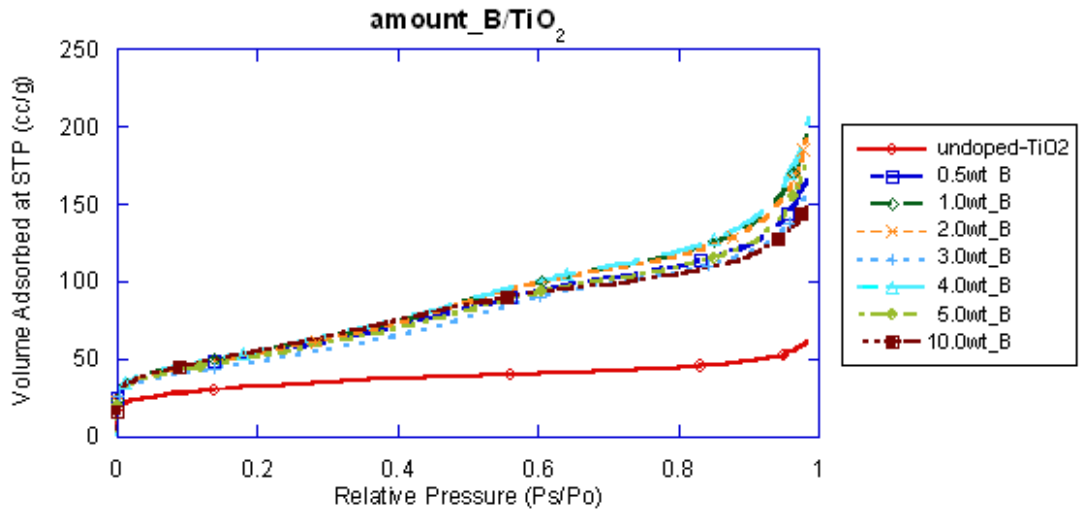
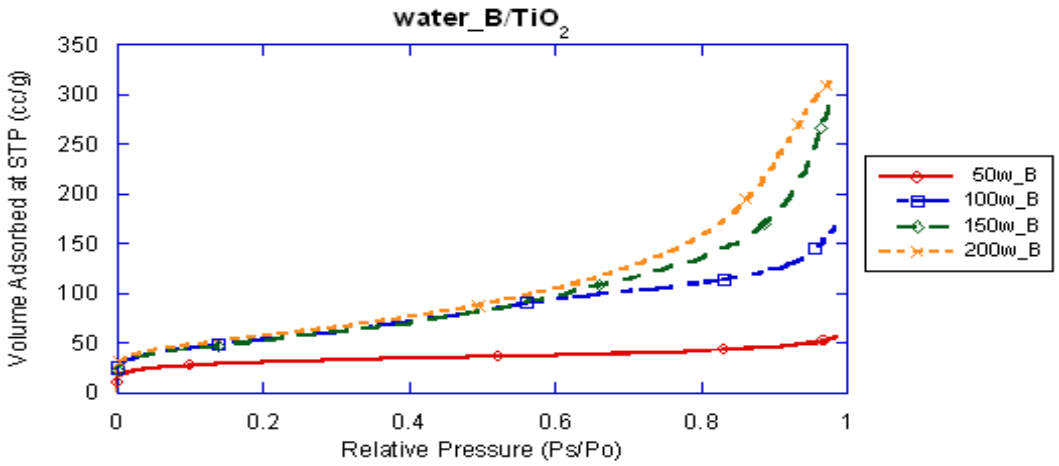


Figure 20 Nitrogen adsorption isotherm of Al-doped TiO_2 samples : a) amount_ Al doped TiO_2, b) water_ Al doped TiO_2, c) acid_ Al doped TiO_2, and d) calcined_ Al doped TiO_2 samples.

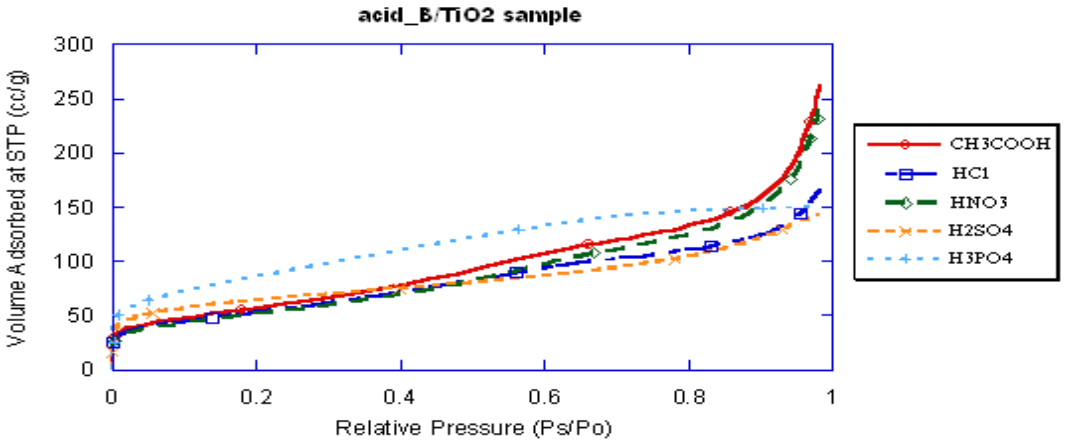
a) amount_ B doped TiO_2



b) water_ B doped TiO_2



c) acid_ B doped TiO_2



d) calcined_ B doped TiO_2

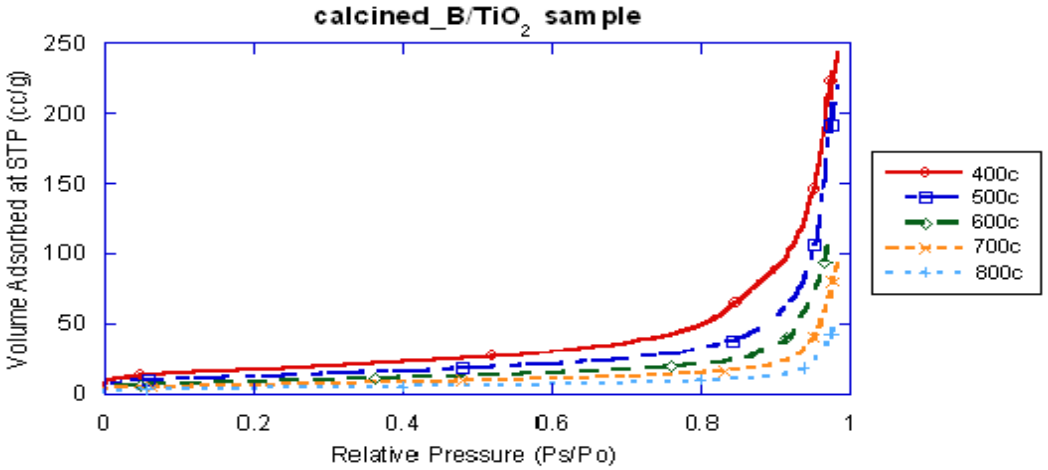
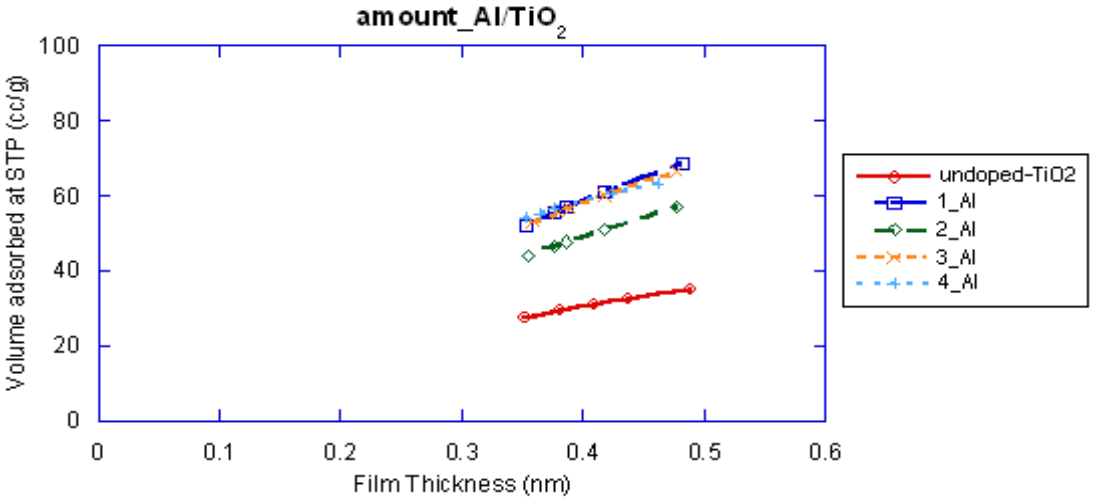
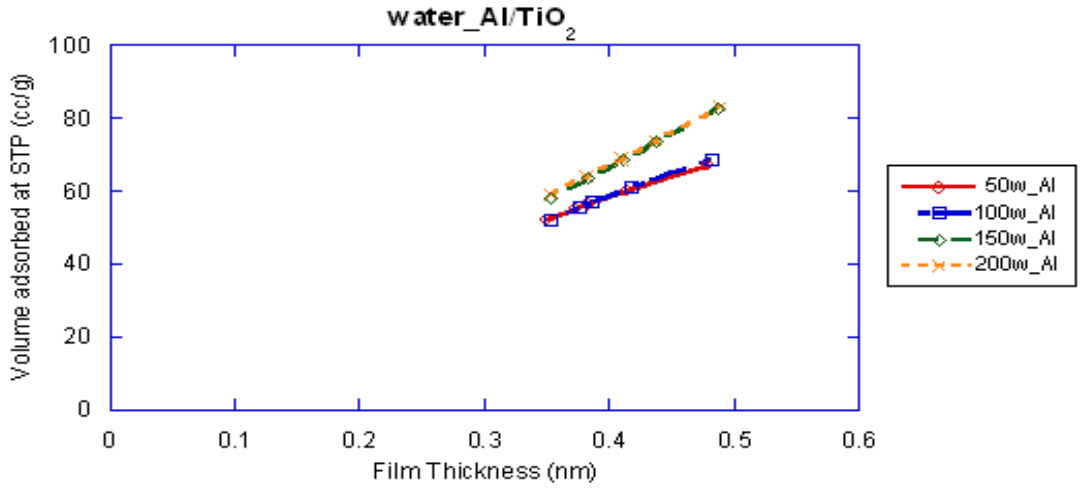


Figure 21 Nitrogen adsorption isotherm of B-doped TiO_2 samples : a) amount_ B doped TiO_2, b) water_ B doped TiO_2, c) acid_ B doped TiO_2, and d) calcined_ B doped TiO_2 samples.

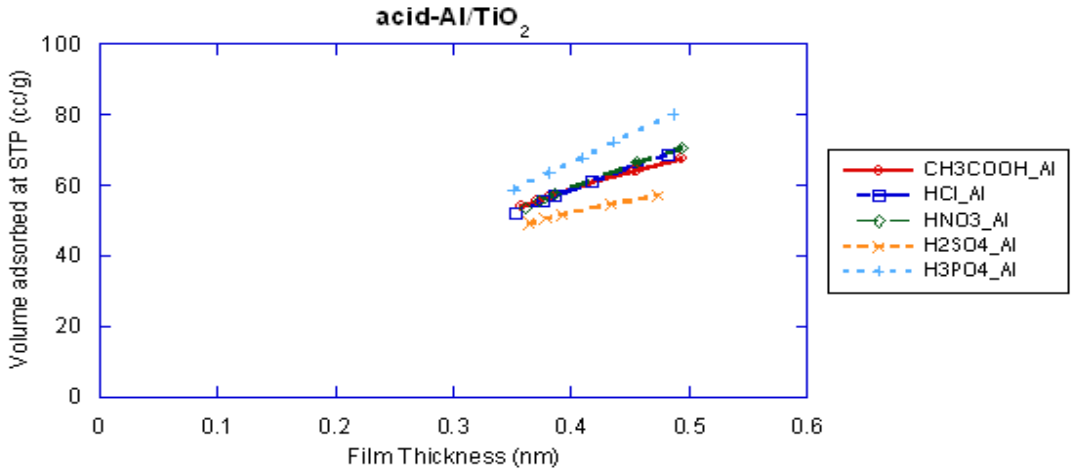
a) amount_ Al doped TiO_2



b) water_ Al doped TiO_2



c) acid_ Al doped TiO_2



d) calcined_ Al doped TiO_2

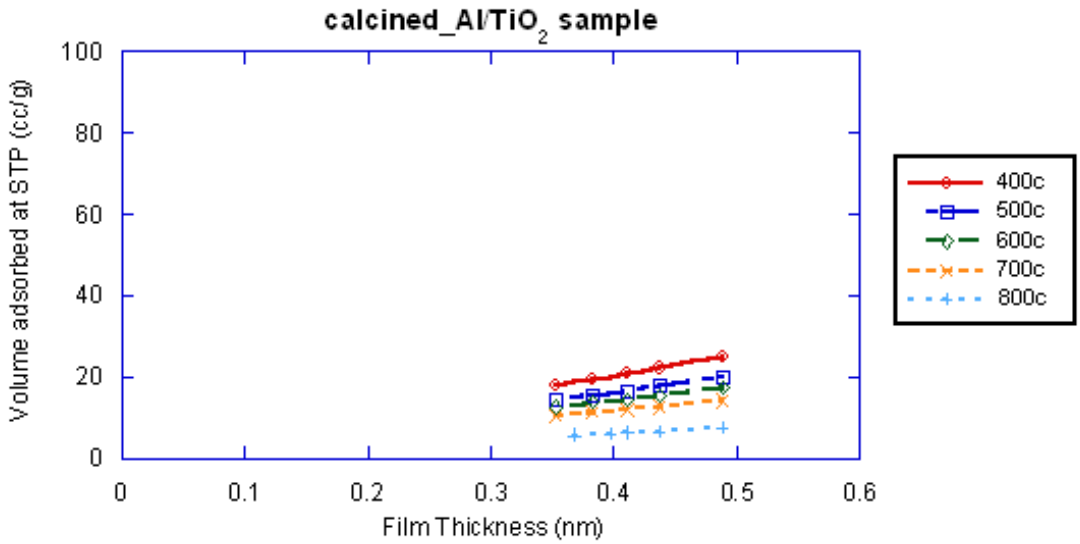
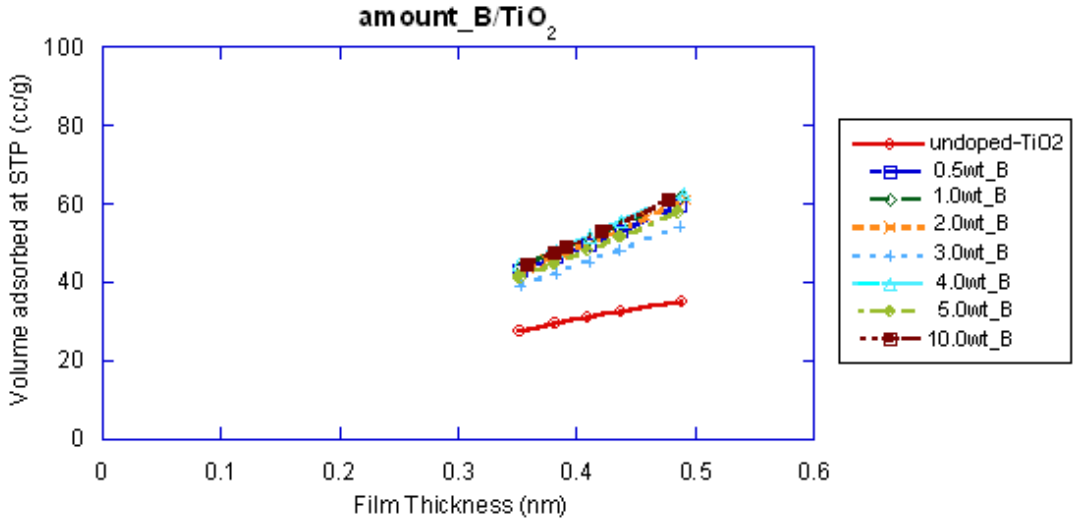
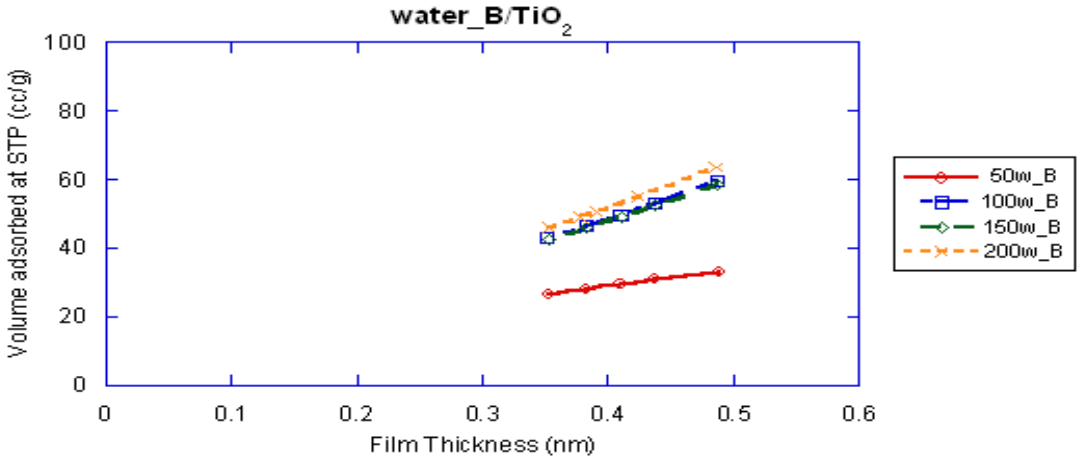


Figure 22 t-plot of nitrogen adsorption isotherm of Al-doped TiO_2 samples : a) amount_ Al doped TiO_2, b) water_ Al doped TiO_2, c) acid_ Al doped TiO_2, and d) calcined_ Al doped TiO_2 samples.

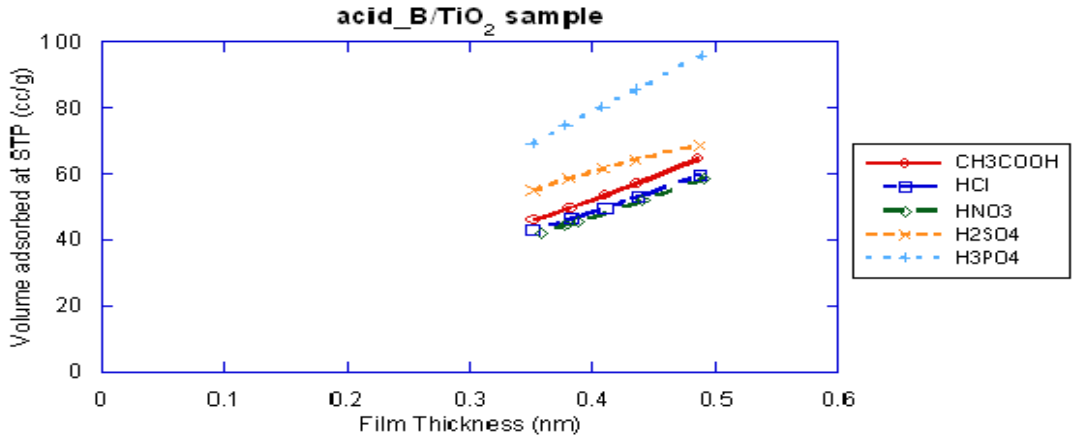
a) amount_ B doped TiO_2



b) water_ B doped TiO_2



c) acid_ B doped TiO_2



d) calcined_ B doped TiO_2

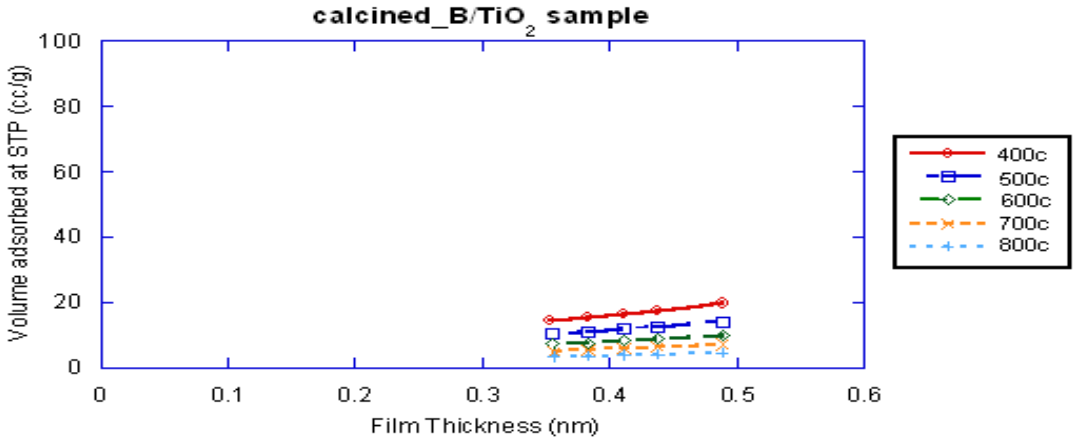
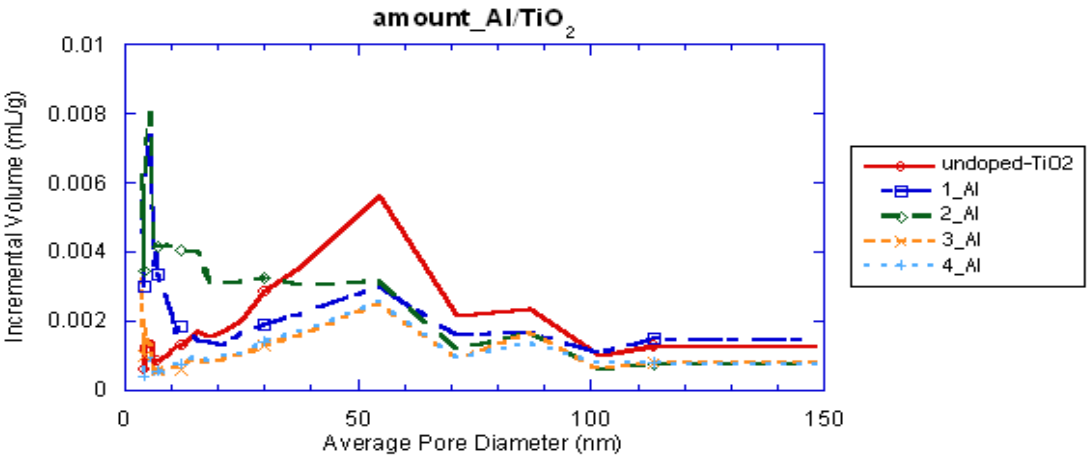
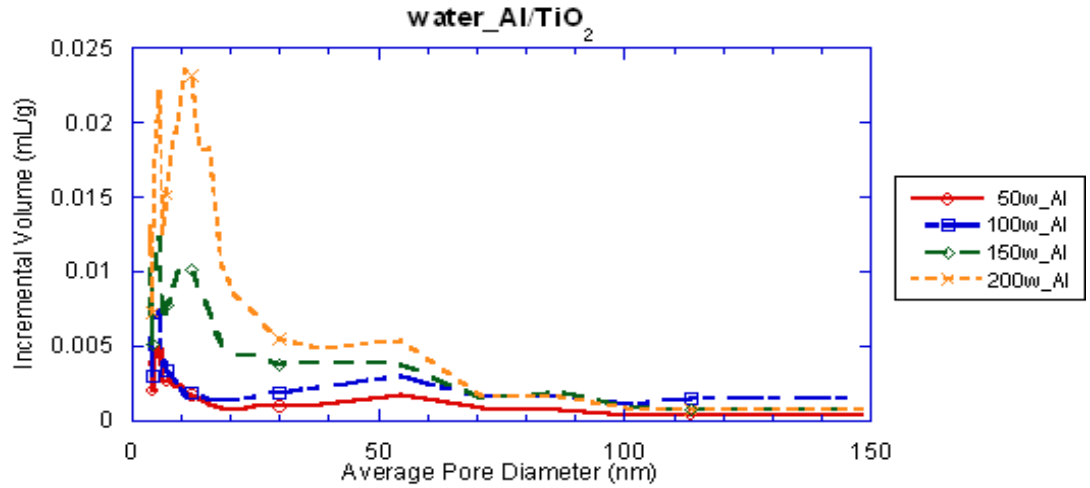


Figure 23 t-plot of nitrogen adsorption isotherm of B-doped TiO_2 samples :a) amount_ B doped TiO_2, b) water_ B doped TiO_2, c) acid_ B doped TiO_2, and d) calcined_ B doped TiO_2 samples.

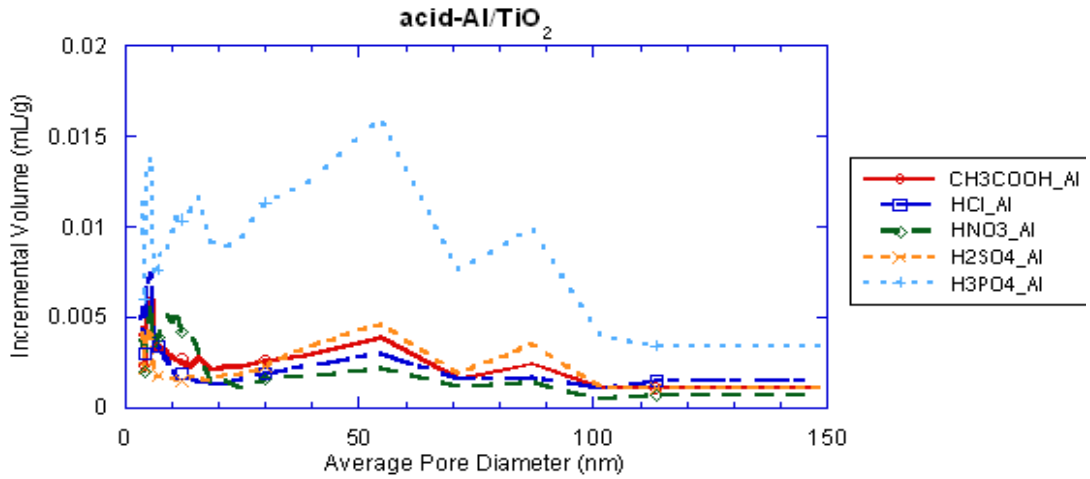
a) amount_ Al doped TiO_2



b) water_ Al doped TiO_2



c) acid_ Al doped TiO_2



d) calcined_ Al doped TiO_2

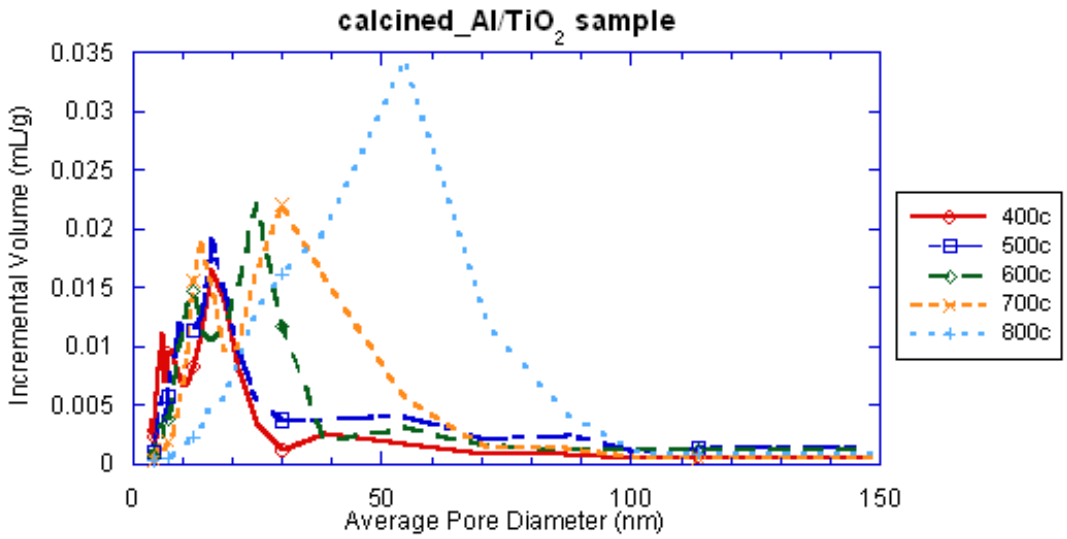
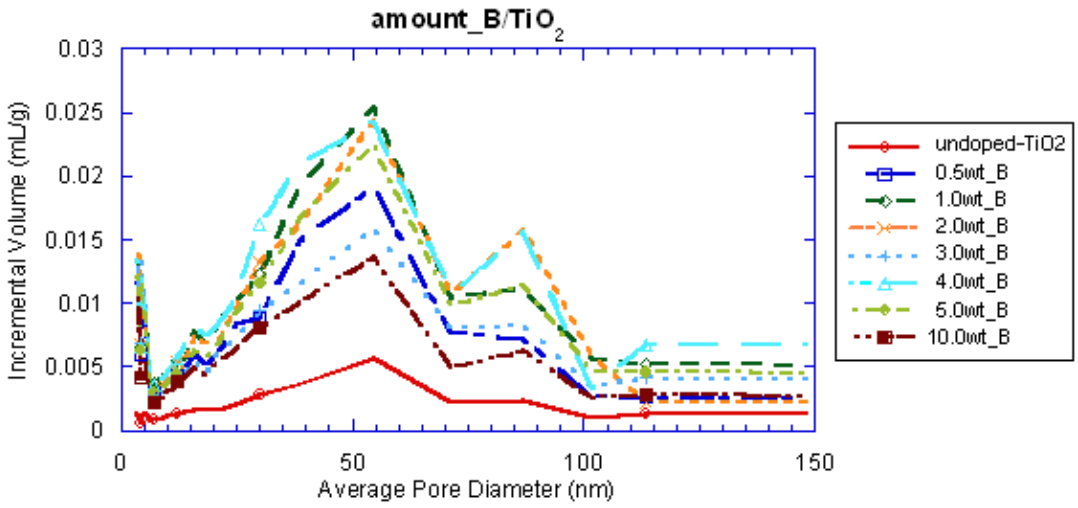
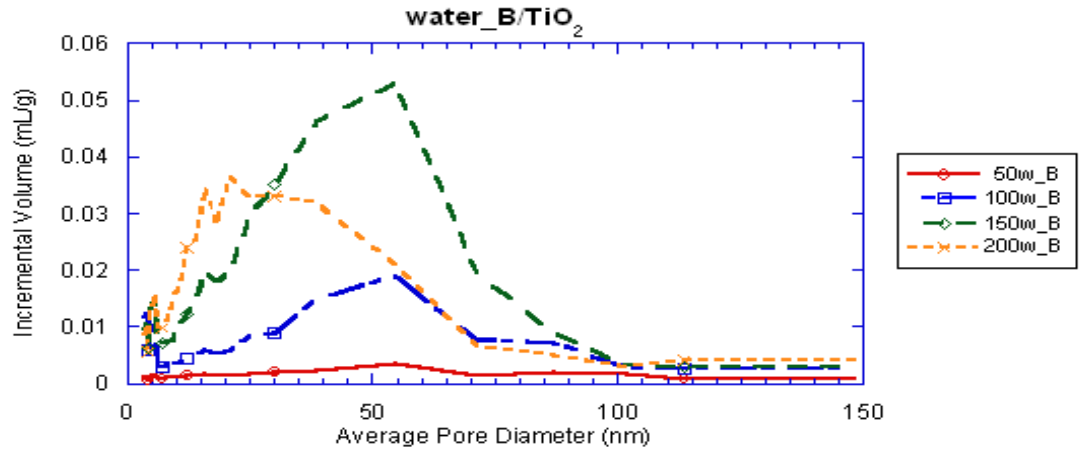


Figure 24 Pore size distribution curve of Al-doped TiO_2 samples : a) amount_ Al doped TiO_2, b) water_ Al doped TiO_2, c) acid_ Al doped TiO_2, and d) calcined_ Al doped TiO_2 samples.

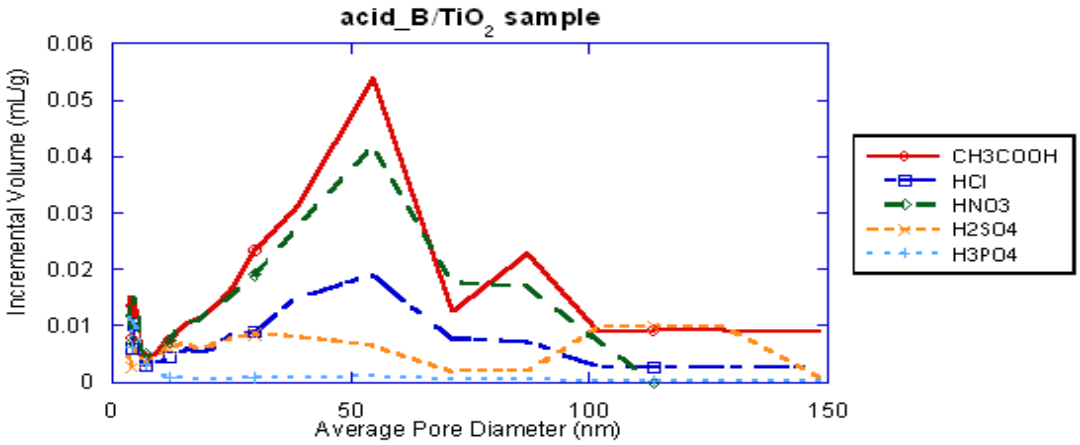
a) amount_ B doped TiO_2



b) water_ B doped TiO_2



c) acid_ B doped TiO_2



d) calcined_ B doped TiO_2

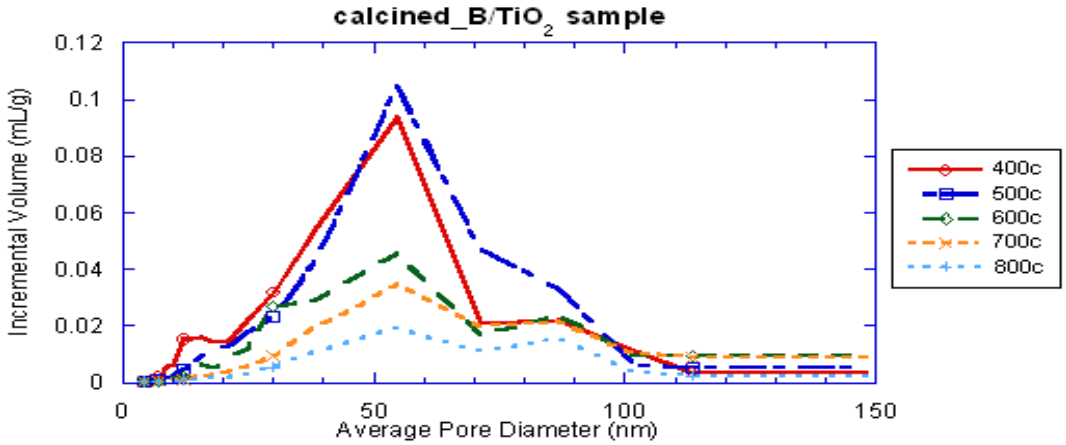
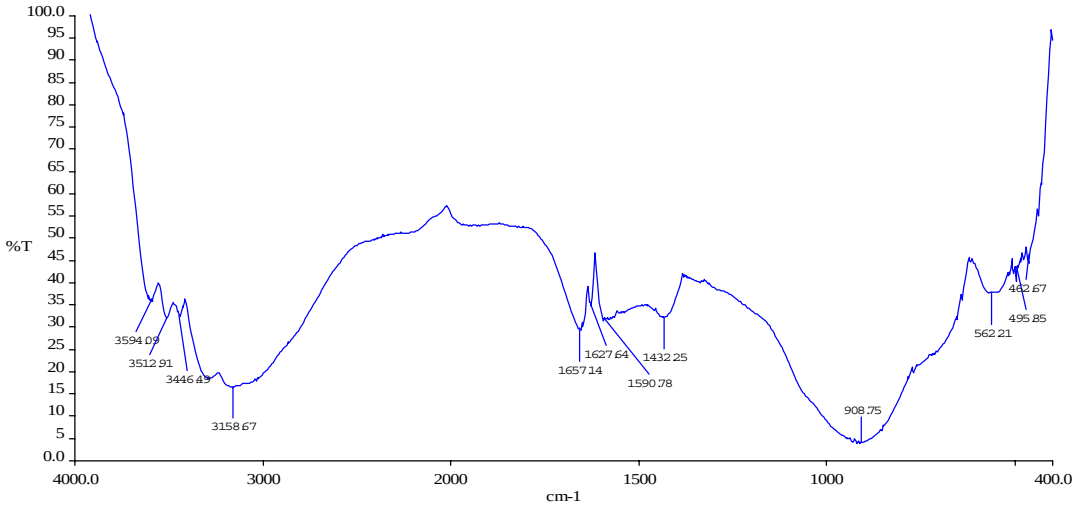


Figure 25 Pore size distribution curve of B-doped TiO_2 samples : a) amount_ B doped TiO_2, b) water_ B doped TiO_2, c) acid_ B doped TiO_2, and d) calcined_ B doped TiO_2 samples.

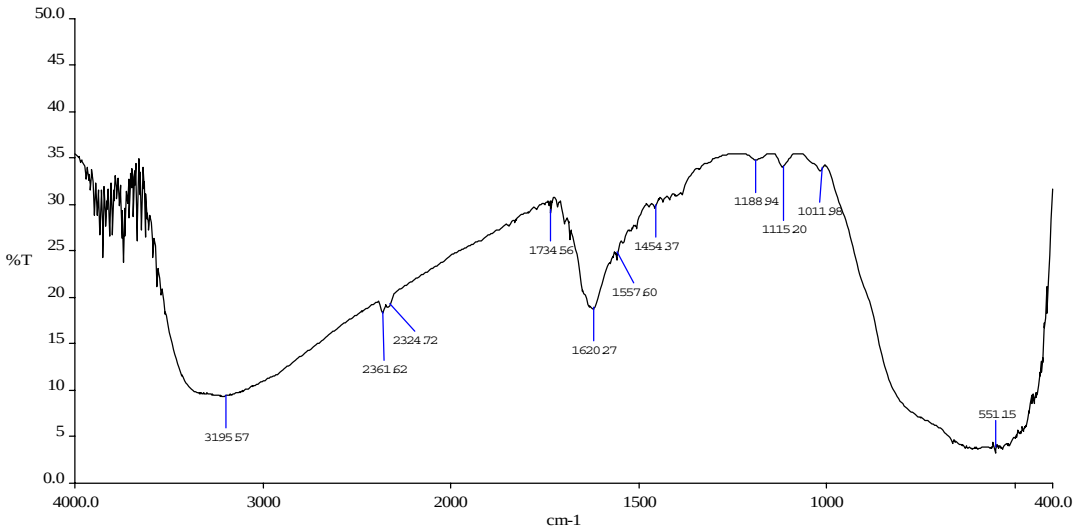
3.1.2.3 Fourier-transformed infrared spectroscopy (FT-IR)

Infrared spectroscopy is a technique for determining the functional groups within the compounds. The FT-IR spectrum range of the usage in the mid-infrared region, which covers the frequency from 400 to 4,000 cm^{-1}. In Figures 26 and 27 show the FT-IR spectrum of Al-doped TiO_2 samples and B-doped TiO_2 samples, respectively. The assigned modes of the functional groups corresponding to Figures 19 and 20 are listed in Tables 26 and 27, respectively.

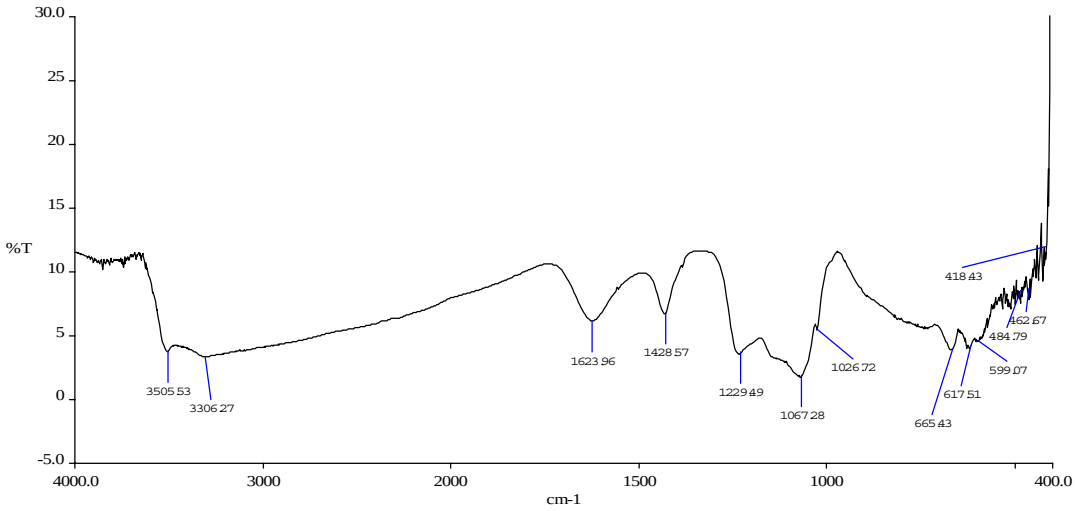
a) undoped TiO_2



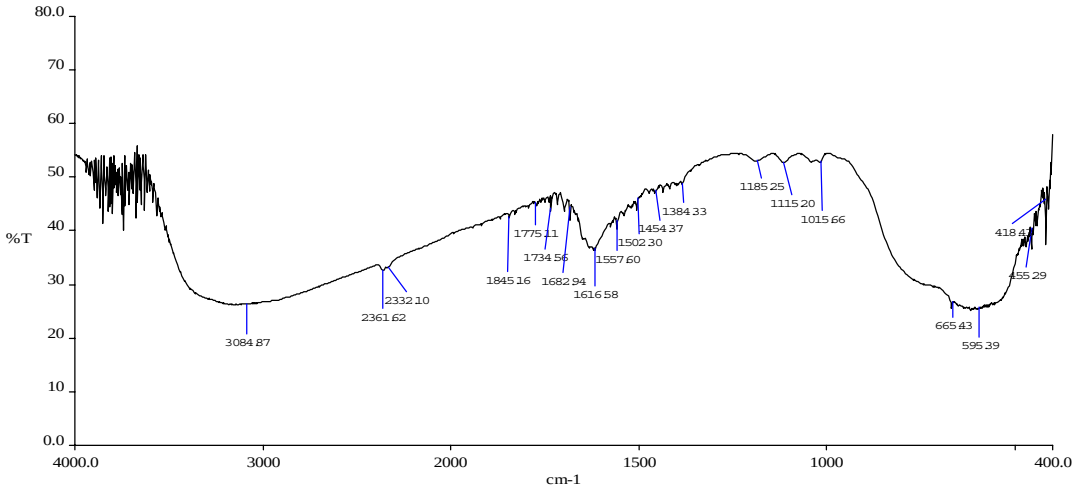
b) 1_Al/TiO_2



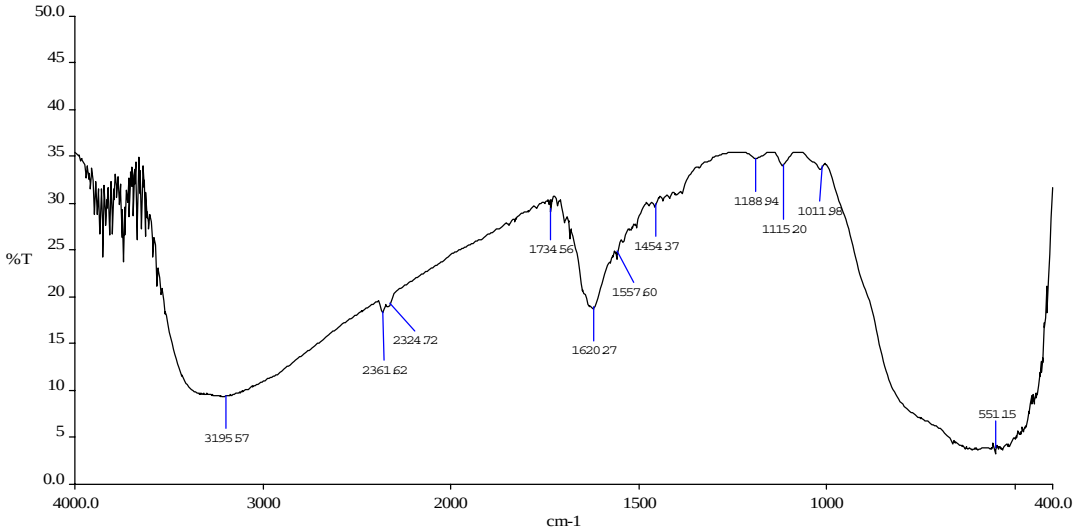
c) 4_ Al/TiO_2



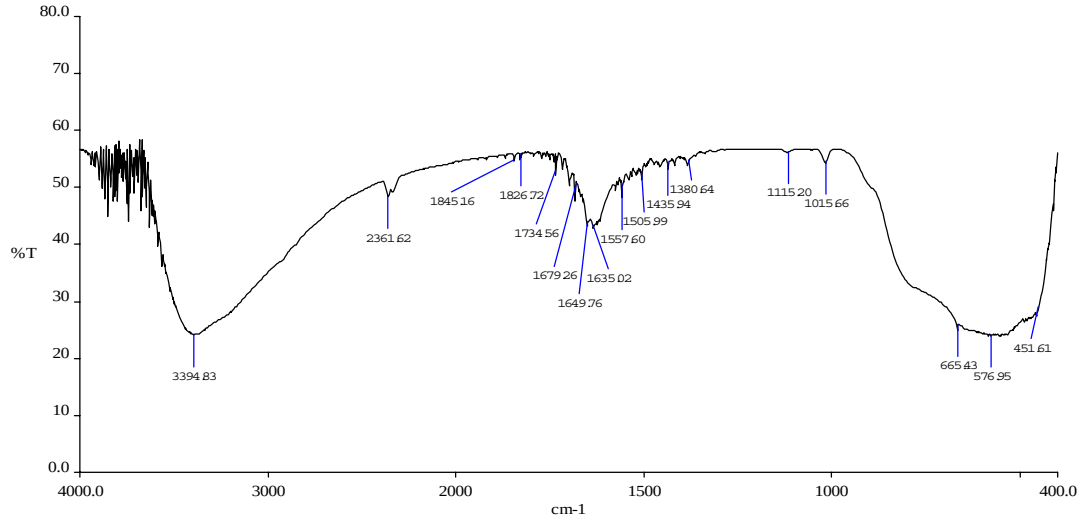
d) 50w_ Al/TiO_2



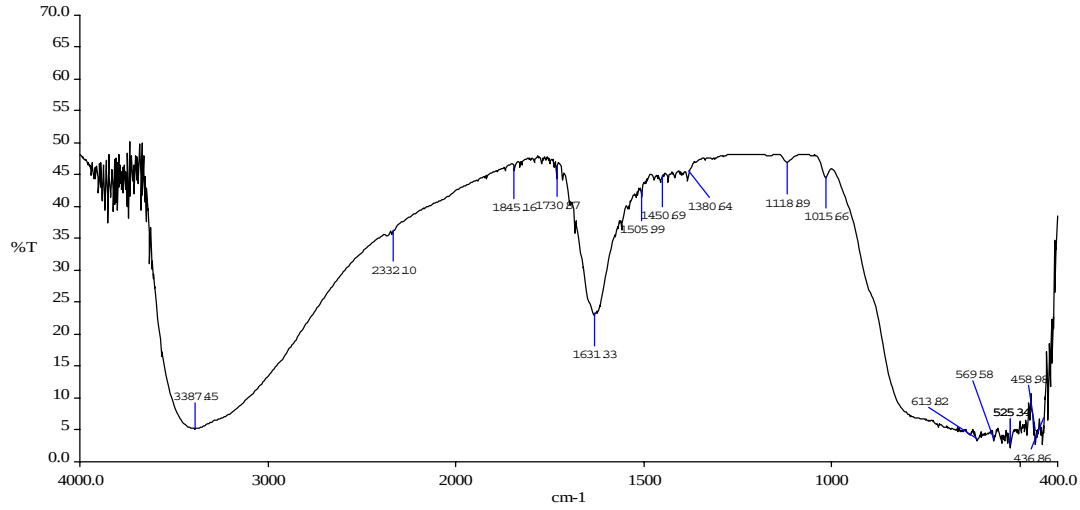
e) 100w_ Al/TiO_2



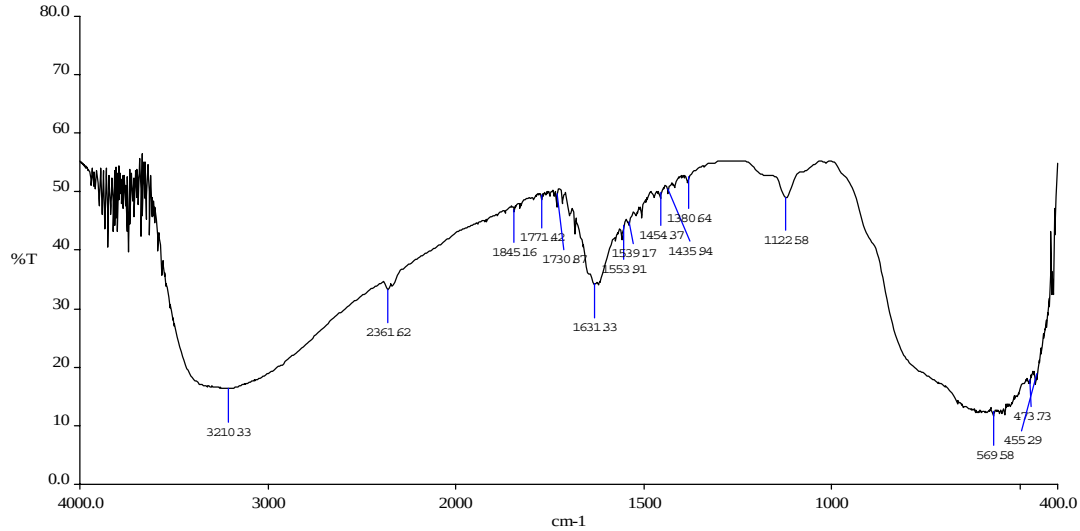
f) 150w_ Al/TiO_2



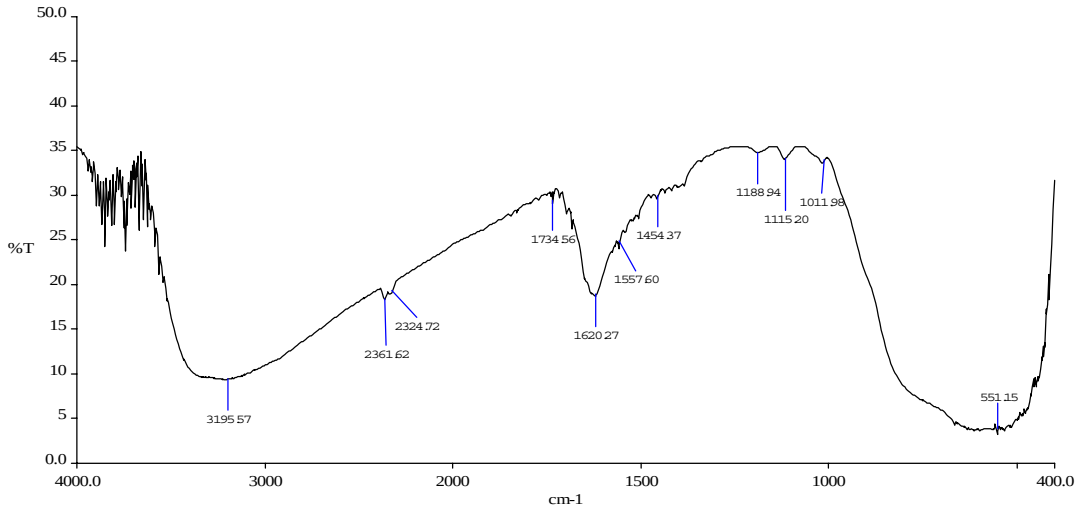
g) 200w_ Al/TiO_2



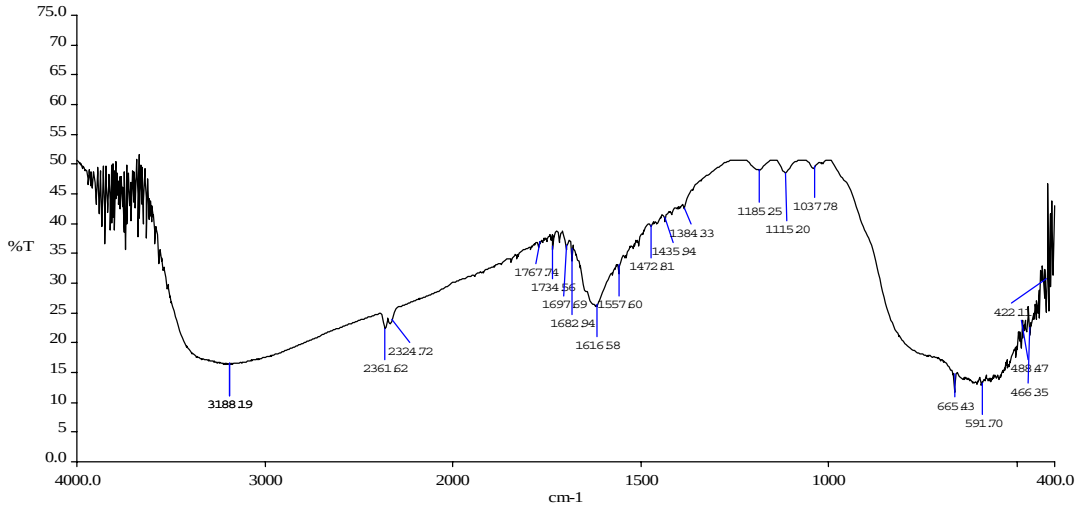
h) CH_3COOH_ Al/TiO_2



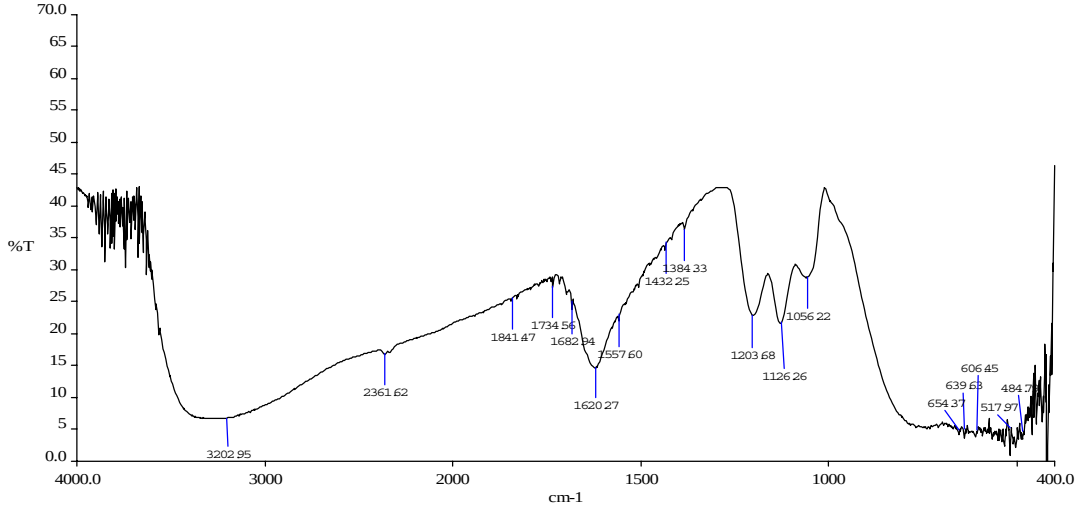
i) HCl_ Al/TiO_2



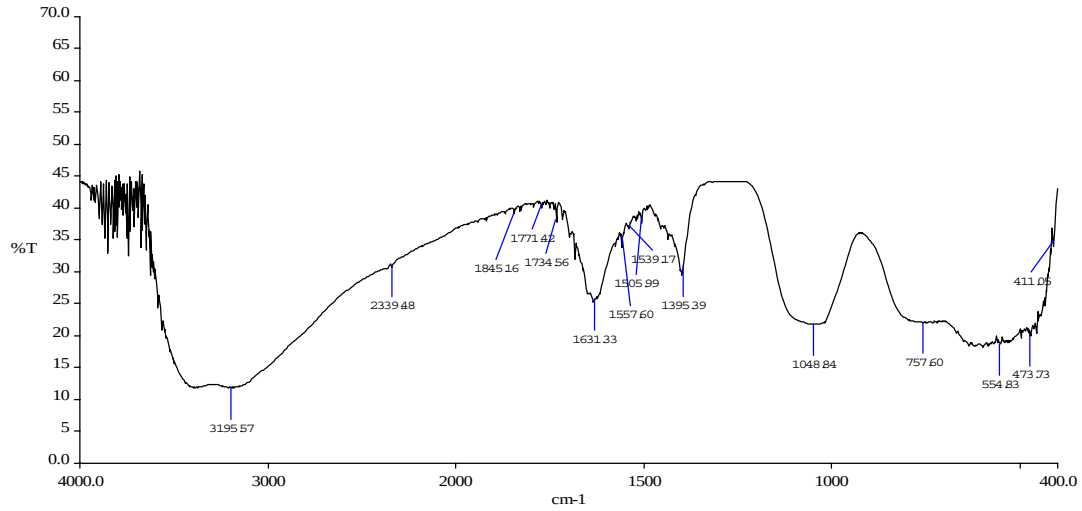
j) HNO_3_ Al/TiO_2



k) H_2SO_4_ Al/TiO_2



l) H_3PO_4_ Al/TiO_2



m) 500c_ Al/TiO_2

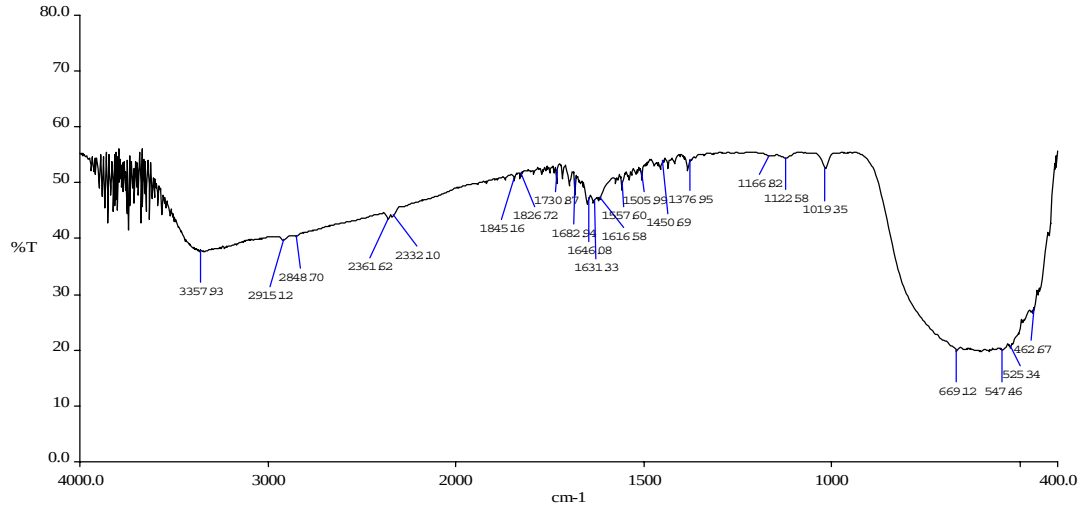
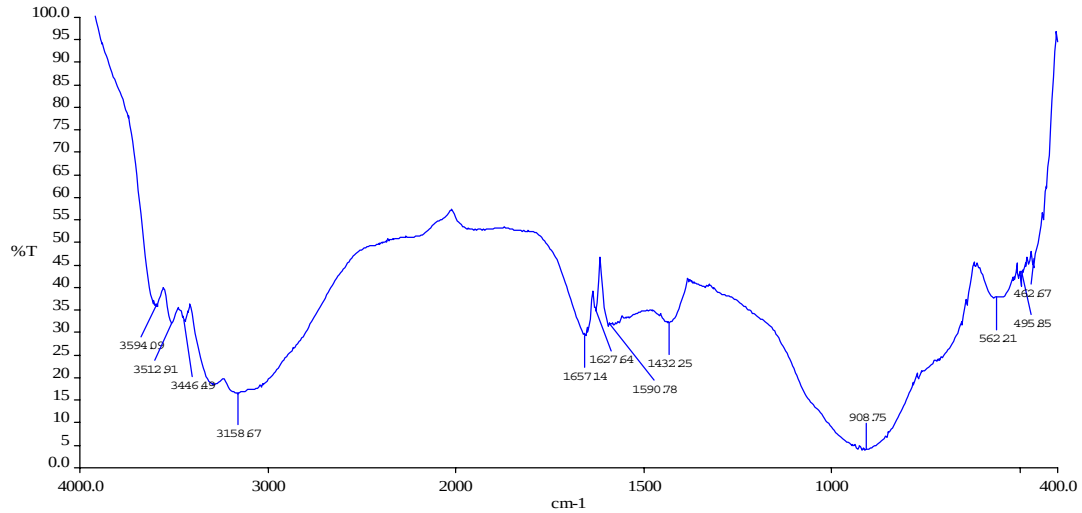
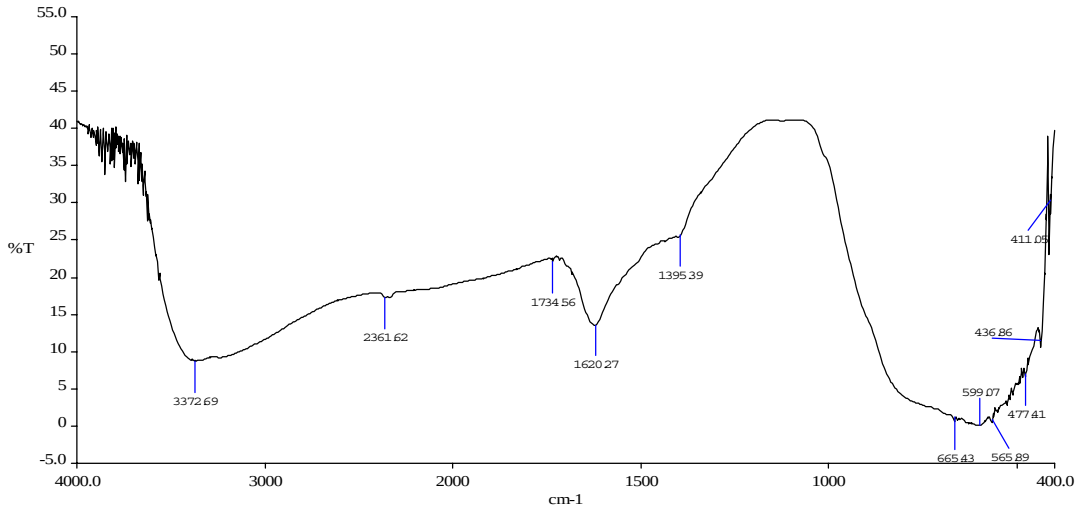


Figure 26 FT-IR spectrum of Al-doped TiO_2 samples in the range 4,000 – 400 cm^{-1}.

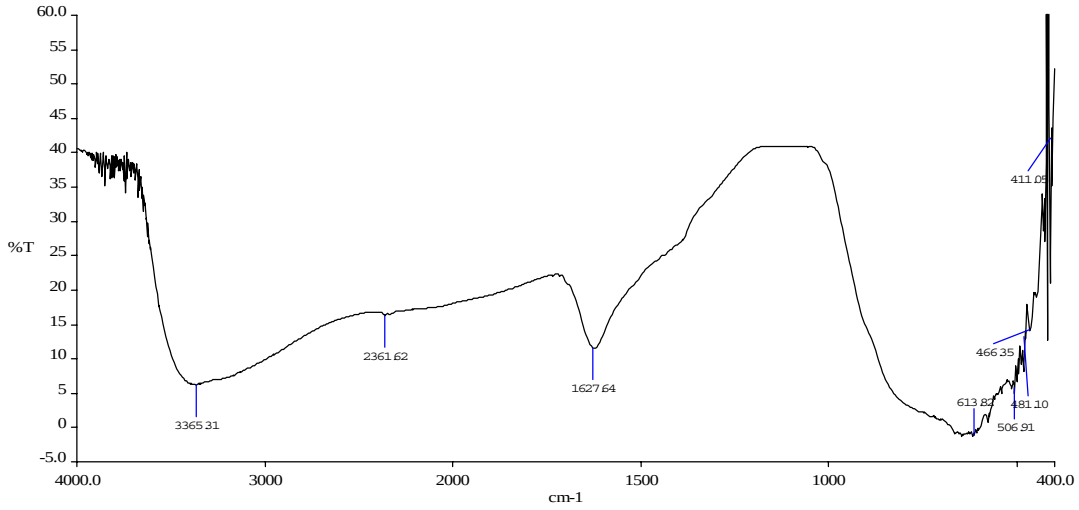
a) undoped TiO_2



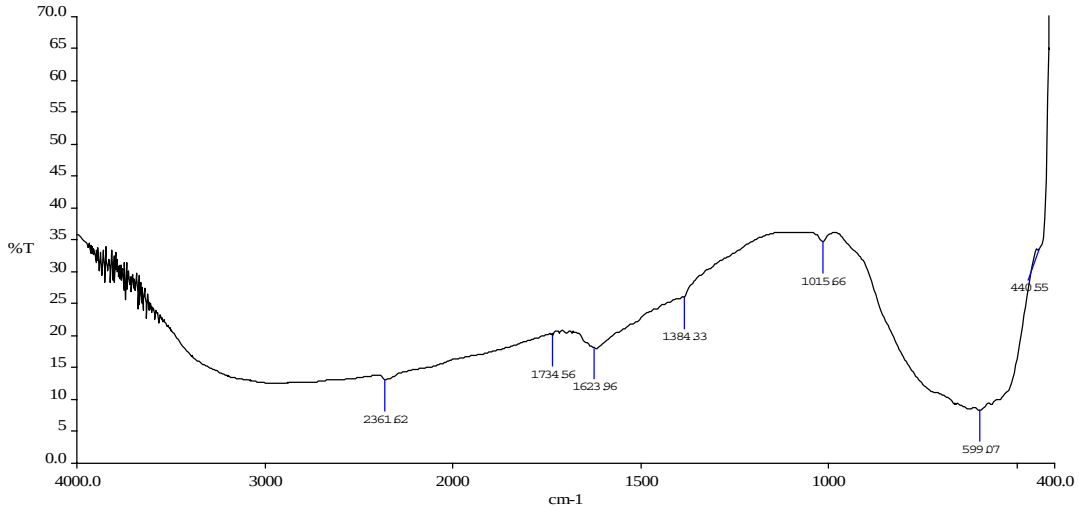
b) 0.5wt_B/TiO_2



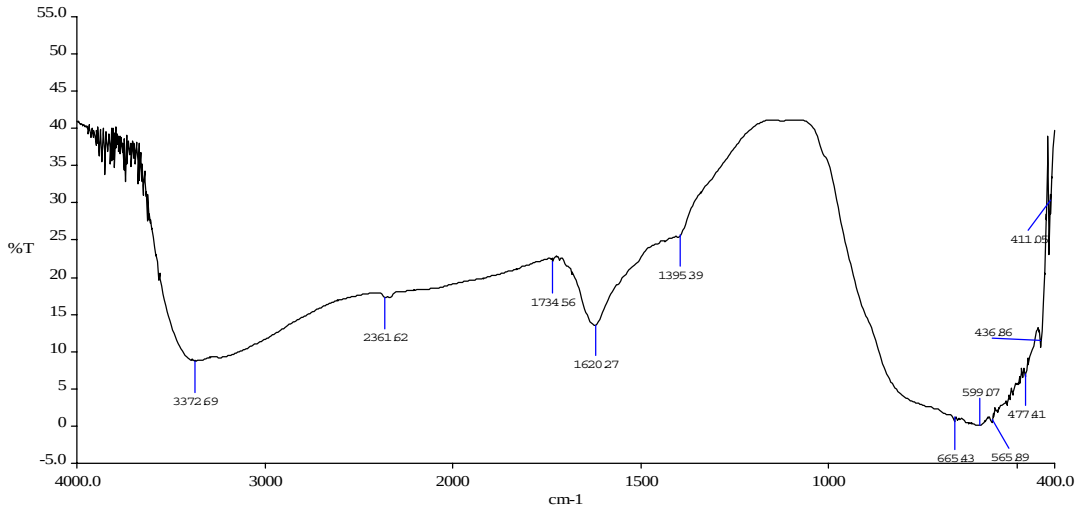
c) 10.0wt_ B/TiO_2



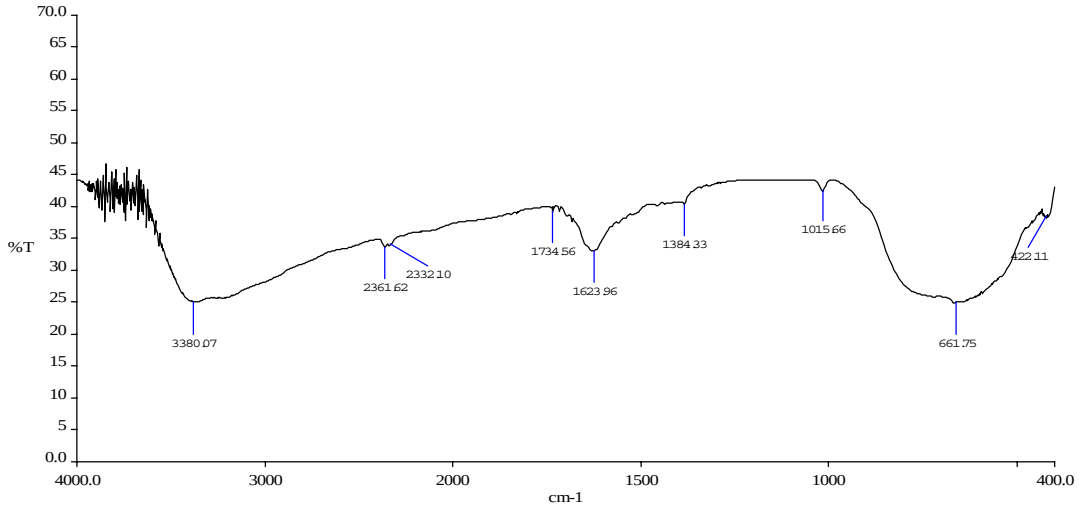
d) 50w_ B/TiO_2



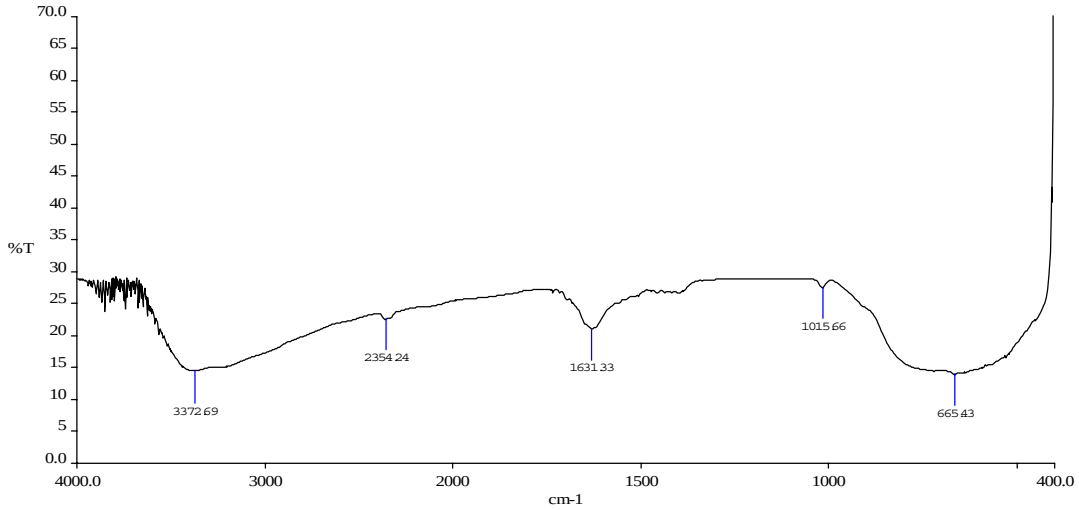
e) 100w_ B/TiO_2



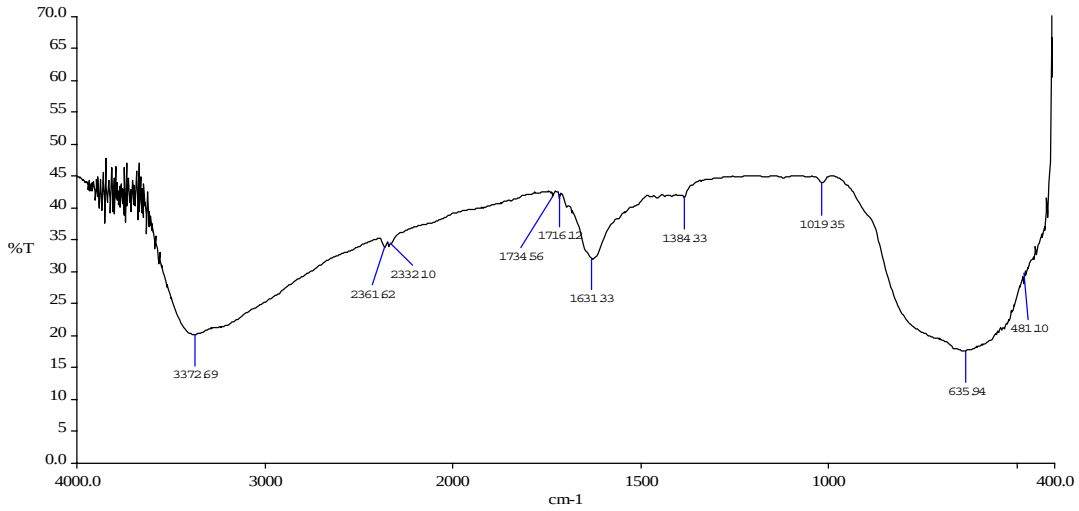
f) 150w_ B/TiO_2



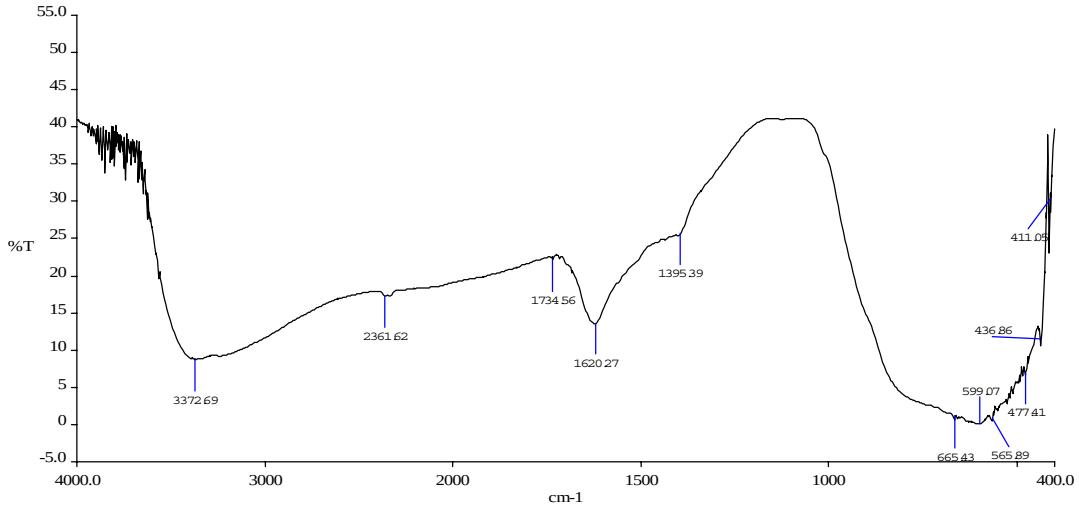
g) 200w_ B/TiO_2



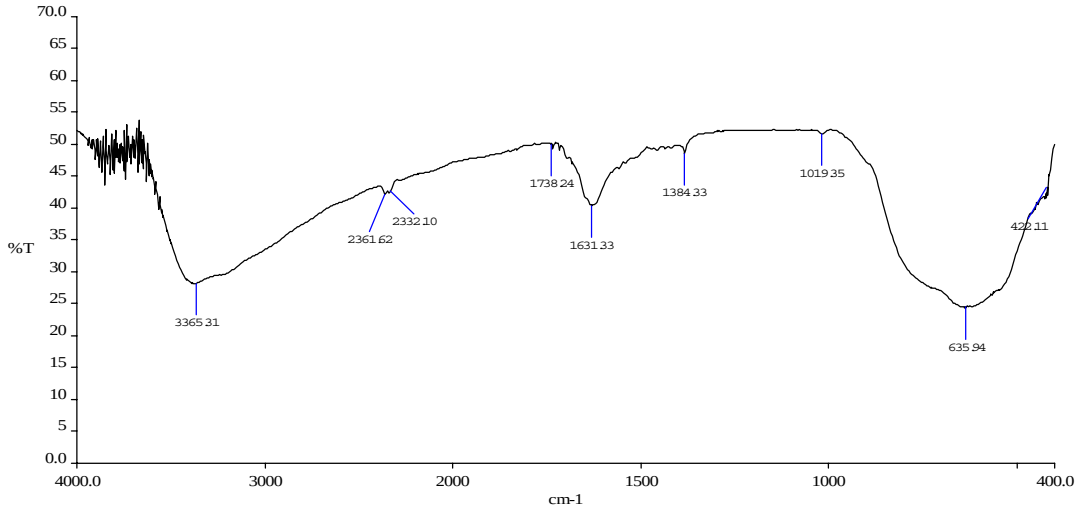
h) CH_3COOH_ B/TiO_2



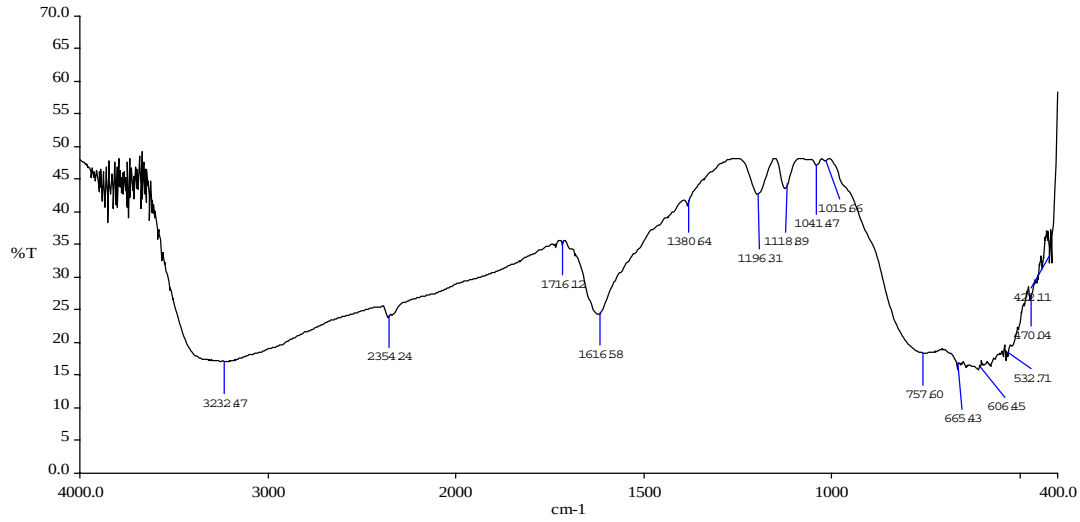
i) HCl_ B/TiO_2



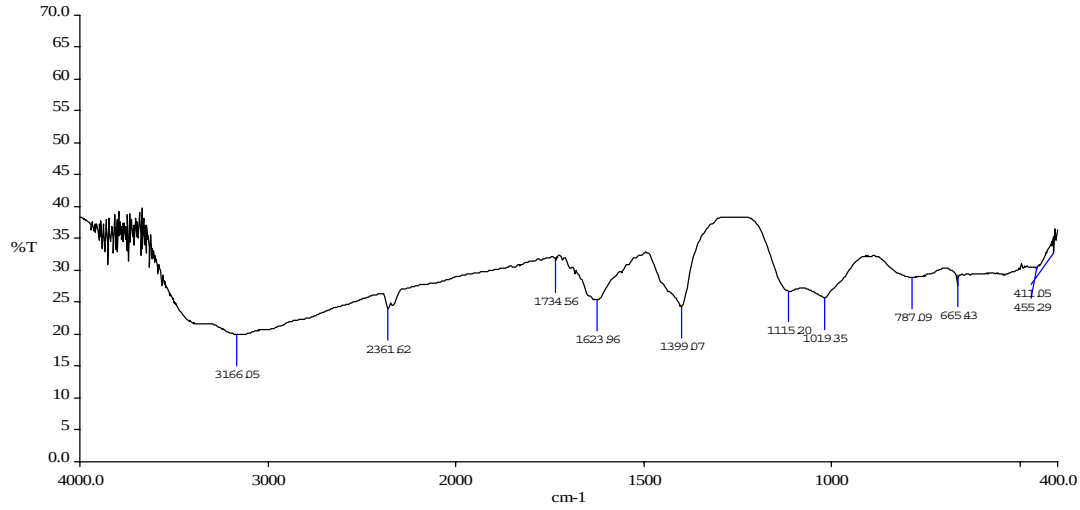
j) HNO_3_ B/TiO_2



k) H_2SO_4_ B/TiO_2



l) H_3PO_4_ B/TiO_2



m) 500c_ B/TiO_2

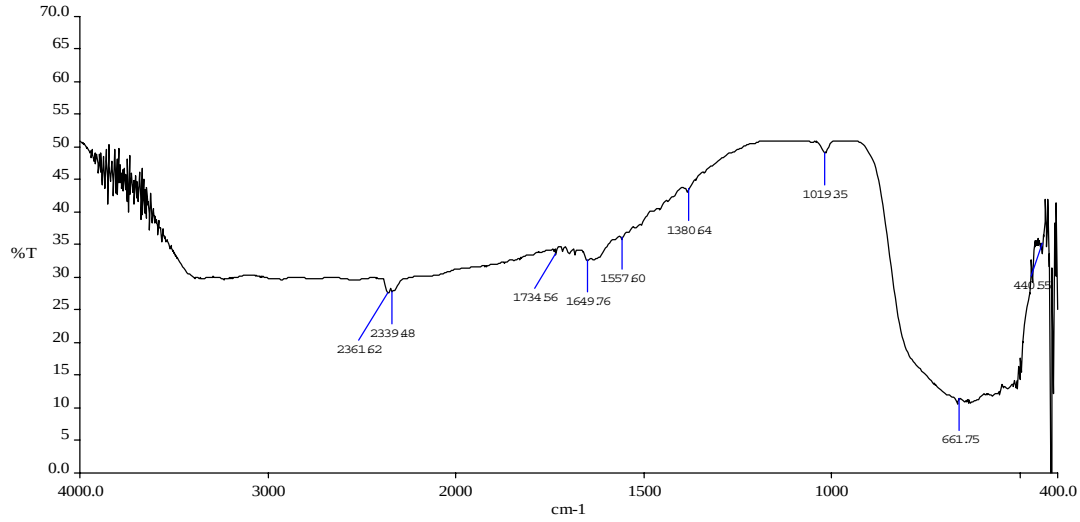


Figure 27 FT-IR spectrum of B-doped TiO_2 samples in the range 4,000 – 400 cm^{-1}.

Table 16 Assignment of the FT-IR bands of all Al-doped TiO_2 samples

Al-doped TiO_2 samples	Wave number (cm^{-1})	Assignment	Functional groups/molecule	Reference
Undoped TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	1,637	O-H bending	OH groups	Velasco et al., 1999
	1,432	N-H bending	NH_4^+ (composite)	Sanobez et al., 1999
	908	OH out of plane	H_2O or OH groups	Sanobez et al., 1999
	462	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
1_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	O-H bending	OH groups	Velasco et al., 1999
	1,115	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	552	Ti-O stretching	TiO_2	Harizannov et al., 2001
4_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	1,623	O-H bending	OH groups	Velasco et al., 1999
	1,428	N-H bending	NH_4^+ (composite)	Sanobez et al., 1999
	1,229 - 1,067	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	599	Ti-O stretching	TiO_2	Harizannov et al., 2001
50w_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,616	O-H bending	OH groups	Velasco et al., 1999
	1,185-1,015	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	595	Ti-O stretching	TiO_2	Harizannov et al., 2001
100w_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	O-H bending	OH groups	Velasco et al., 1999
	1,115	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	552	Ti-O stretching	TiO_2	Harizannov et al., 2001

Al-dopedTiO2 samples	Wave number (cm-1)	Assignment	Functional groups/molecule	Reference
150w_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,635	O-H bending	OH groups	Velasco et al., 1999
	1,015	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	576	Ti-O stretching	TiO_2	Harizannov et al., 2001
	455	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
200w_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,332	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,631	O-H bending	OH groups	Velasco et al., 1999
	1,015	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	525	Ti-O stretching	TiO_2	Harizannov et al., 2001
	436	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
CH_3COOH_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,631	O-H bending	OH groups	Velasco et al., 1999
	1,122	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	569	Ti-O stretching	TiO_2	Harizannov et al., 2001
	455	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
HCl_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	O-H bending	OH groups	Velasco et al., 1999
	1,115	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	552	Ti-O stretching	TiO_2	Harizannov et al., 2001
HNO_3_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,616	O-H bending	OH groups	Velasco et al., 1999
	1,185 - 1,036	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	591	Ti-O stretching	TiO_2	Harizannov et al., 2001
	484	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001

Al-doped TiO2 samples	Wave number (cm-1)	Assignment	Functional groups/molecule	Reference
H_2SO_4_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	O-H bending	OH groups	Velasco et al., 1999
	1,2031 - 1,056	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	639	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	517	Ti-O stretching	TiO_2	Harizannov et al., 2001
	484	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
H_3PO_4_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,339	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,631	O-H bending	OH groups	Velasco et al., 1999
	1,395	P=O stretching	PO_4^{3-}	John R. Dyer, 1965
	1,048	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	554	Ti-O stretching	TiO_2	Harizannov et al., 2001
	473	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
500c_Al/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,646 , 1,631	O-H bending	OH groups	Velasco et al., 1999
	1,376	C=O stretching	CO_3^{2-}, HCO_3^-	Harizanov et al., 2001
	1,116 - 1,019	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	547	Ti-O stretching	TiO_2	Harizannov et al., 2001
	462	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001

Table 17 Assignment of the FT-IR bands of all B-doped TiO_2 samples

B-doped TiO_2 samples	Wave number (cm^{-1})	Assignment	Functional groups/molecule	Reference
Undoped TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	1,637	O-H bending	OH groups	Velasco et al., 1999
	1,432	N-H bending	NH_4^+ (composite)	Sanobez et al., 1999
	908	OH out of plane	H_2O or OH groups	Sanobez et al., 1999
	462	Ti-O streching	TiO_2(rutile)	Zhang et al., 2001
0.5wt_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	O-H bending	OH groups	Velasco et al., 1999
	1,395	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	565	Ti-O stretching	TiO_2	Harizannov et al., 2001
	436 , 411	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
10.0wt_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,627	O-H bending	OH groups	Velasco et al., 1999
	613	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	506	Ti-O stretching	TiO_2	Harizannov et al., 2001
	466 , 411	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
50w_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,623	O-H bending	OH groups	Velasco et al., 1999
	1,384-1,015	S=O stretching	TiO_2(anatase)	John R. Dyer, 1965
	599	Ti-O stretching	TiO_2	Harizannov et al., 2001
	440	Ti-O stretching	TiO_2(rutile	Zhang et al., 2001
100w_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	O-H bending	OH groups	Velasco et al., 1999
	1,395	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	565	Ti-O stretching	TiO_2	Harizannov et al., 2001
	436 , 411	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001

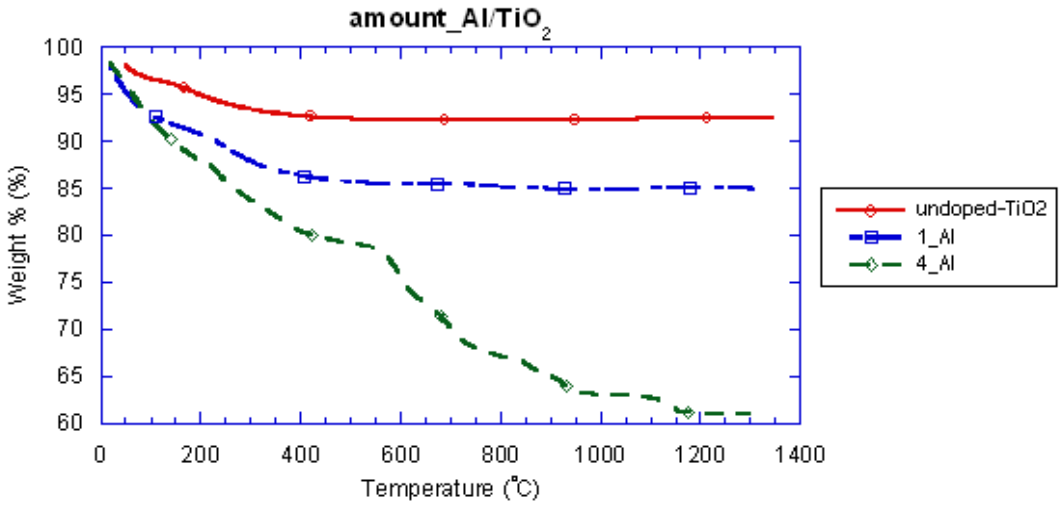
B-doped TiO2 samples	Wave number (cm-1)	Assignment	Functional groups/molecule	Reference
150w_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,623	O-H bending	OH groups	Velasco et al., 1999
	1,384 - 1,015	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	661	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	422	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
200w_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,354	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,631	O-H bending	OH groups	Velasco et al., 1999
	1,015	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
CH_3COOH_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching,	CO_2	John R. Dyer, 1965
	1,631	C ≡N stretching	OH groups	Velasco et al., 1999
	1,384 - 1,019	O-H bending	SO_4^{2-}	John R. Dyer, 1965
	665	S=O stretching	TiO_2(anatase)	Zhang et al., 2001
	481	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
HCl_B/TiO_2	3,500-3,000	Ti-O stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,620	S-H stretching	OH groups	Velasco et al., 1999
	1,395	O-H bending	SO_4^{2-}	John R. Dyer, 1965
	665	S=O stretching	TiO_2(anatase)	Zhang et al., 2001
	565	Ti-O stretching	TiO_2	Harizannov et al., 2001
	436 , 411	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
HNO_3_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,631	O-H bending	OH groups	Velasco et al., 1999
	1,384-1,019	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	635	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	422	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001

B-doped TiO2 samples	Wave number (cm-1)	Assignment	Functional groups/molecule	Reference
H_2SO_4_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,354	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,616	O-H bending	OH groups	Velasco et al., 1999
	1,380-1,015	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	606 , 632	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	470 , 422	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
H_3PO_4_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	2,361	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,623	O-H bending	OH groups	Velasco et al., 1999
	1,399 - 1,019	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	665	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	455 , 411	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001
500c_B/TiO_2	3,500-3,000	-OH and –NH stretching	H_2O, Ti-OH and NH_4^+	Wang et al., 2000
	1,649	O=C=O stretching	CO_2	John R. Dyer, 1965
	1,380	C=O stretching	CO_3^{2-}, HCO_3^-	Harizannov et al., 2001
	1,019	S=O stretching	SO_4^{2-}	John R. Dyer, 1965
	661	Ti-O stretching	TiO_2(anatase)	Zhang et al., 2001
	440	Ti-O stretching	TiO_2(rutile)	Zhang et al., 2001

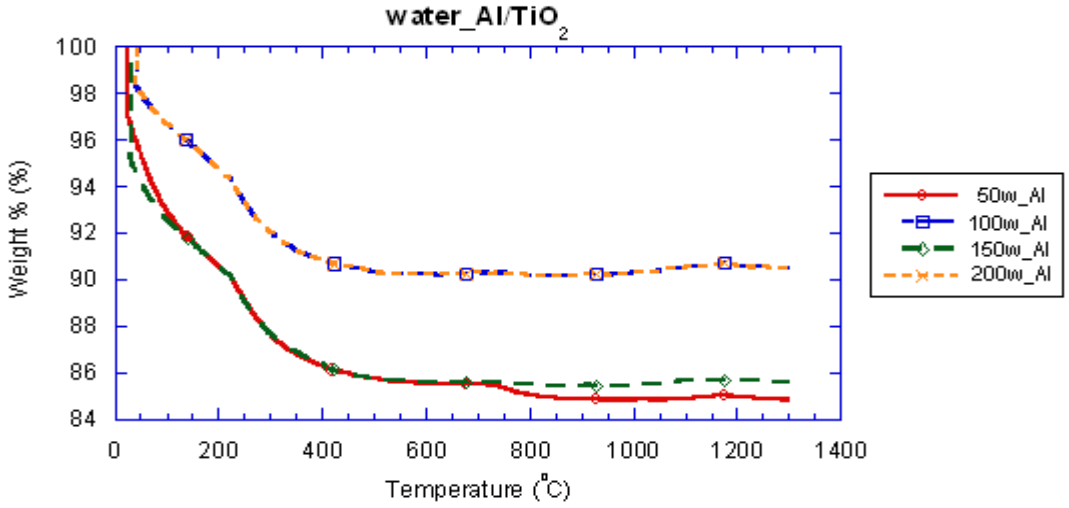
3.1.2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is used to measure variations in mass which recorded the loss in weight with time or temperature due to desorption, dehydration or desolvation, sublimation, decomposition, and solid-solid reactions. The TG curve of Al-doped TiO_2 samples and B-doped TiO_2 samples are shown in Figures 28 and 29, respectively.

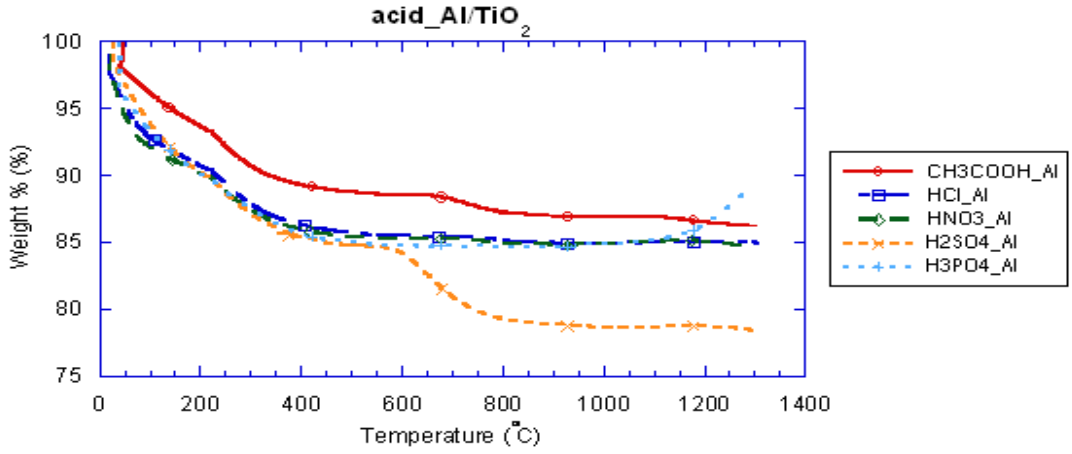
a) amount_Al/TiO_2



b) water_ Al/TiO_2



c) acid_ Al/TiO_2



d) calcined_ Al/TiO_2

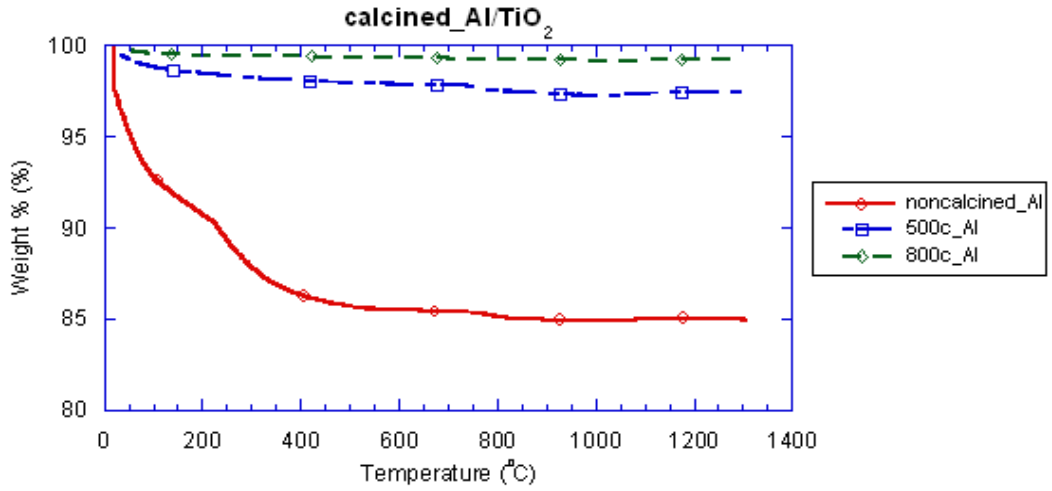
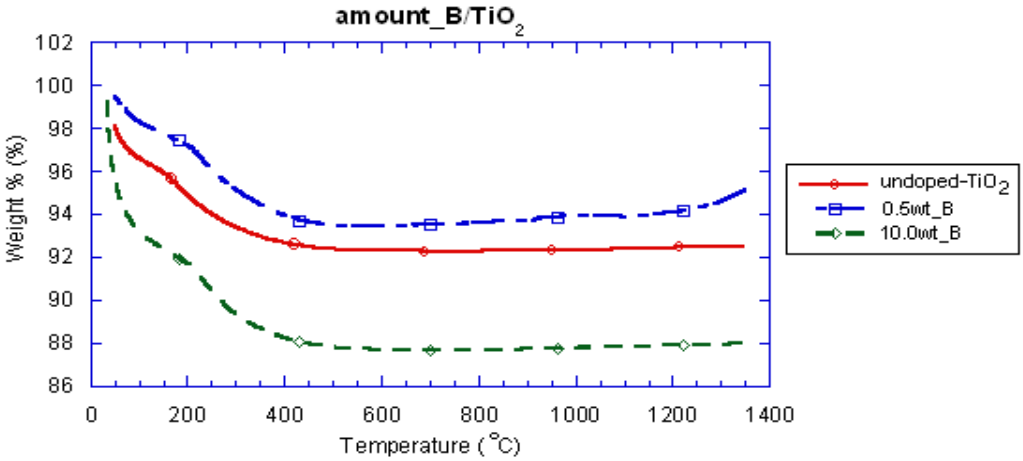
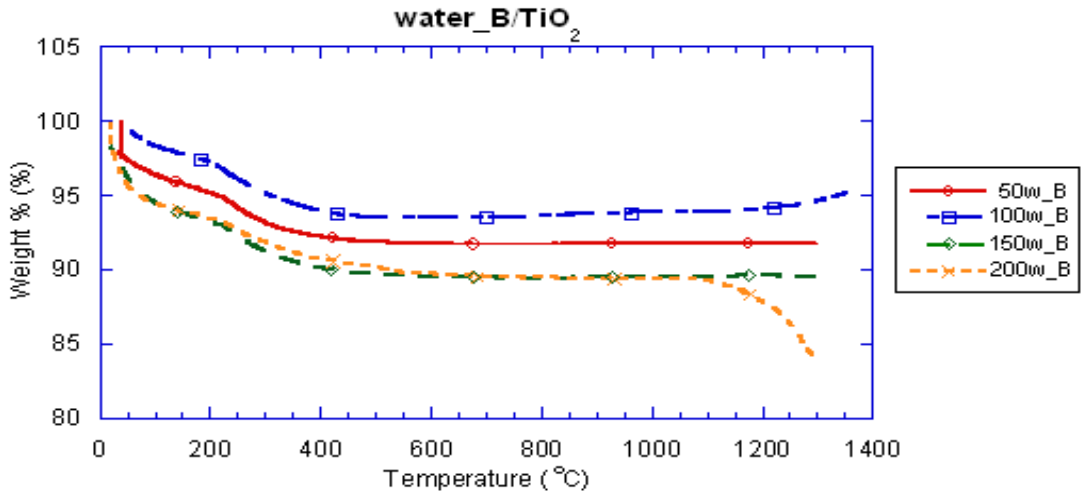


Figure 28 TGA curve of Al-doped TiO_2 samples

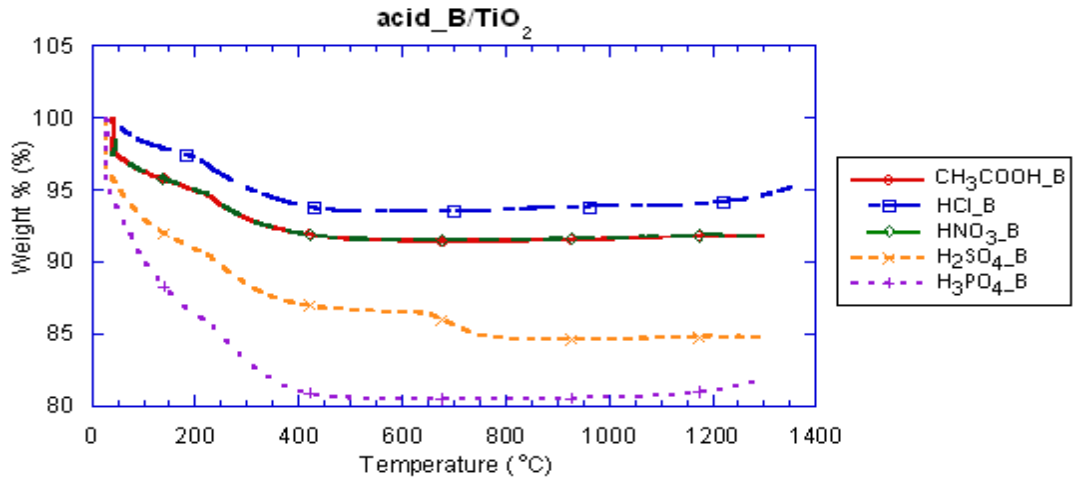
a) amount_ B/TiO_2



b) water_ B/TiO_2



c) acid_ B/TiO_2



d) calcined_ B/TiO_2

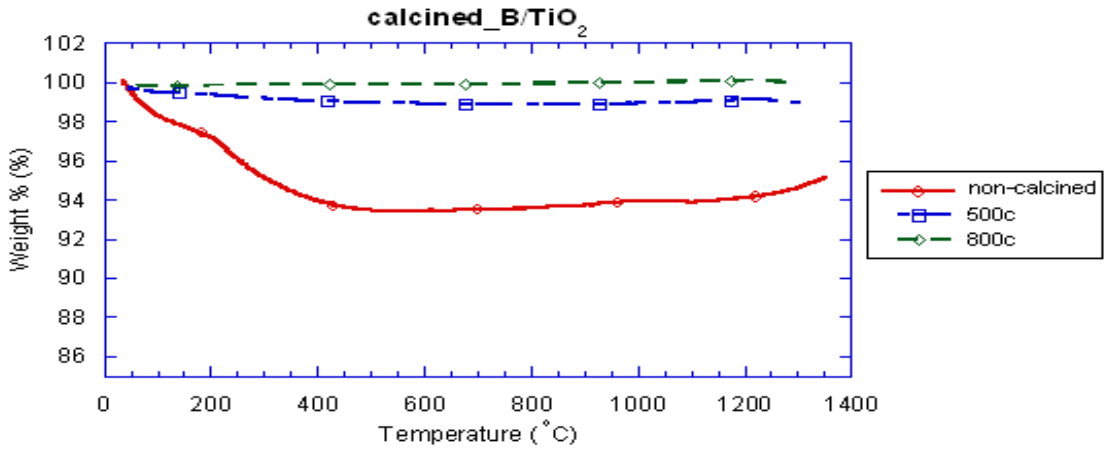


Figure 29 TGA curve of B-doped TiO_2 samples

The weight loss of Al-doped TiO_2 and B-doped TiO_2 samples are shown in Table 18 and Table 19, respectively

Table 18 The data of weight loss of Al-doped TiO_2 samples

Al doped TiO_2 samples	Temperature (°C)	Weight loss (%)
undoped TiO_2	room temp. – 700	5.84
	> 700	-
a) amount_Al/TiO_2		
1_Al/TiO_2	room temp. – 165	8.50
	165-600	6.04
	> 600	0.53
4_Al/TiO_2	room temp. – 500	20.55
	500-650	6.50
	650-850	5.75
	850-970	3.77
	> 970	1.95
b) water_Al/TiO_2		
50w_Al/TiO_2	room temp. – 650	14.46
	> 650	0.65
100w_Al/TiO_2	room temp. – 165	8.50
	165-600	6.04
	> 600	0.53
150w_Al/TiO_2	room temp. – 620	14.27
	> 620	0.16
200w_Al/TiO_2	room temp. – 600	9.71
	> 600	-

Al doped TiO_2 samples	Temperature ($^{\circ}C$)	Weight loss (%)
c) acid_Al/TiO_2		
CH_3COOH_Al/TiO_2	room temp. – 600	11.42
	600-1,000	1.68
	> 1,000	0.65
HCl_Al/TiO_2	room temp. – 165	8.50
	165-600	6.04
	> 600	0.53
HNO_3_Al/TiO_2	room temp. – 650	14.84
	> 650	0.94
H_2SO_4_Al/TiO_2	room temp. – 550	15.30
	> 550	6.05
H_3PO_4_Al/TiO_2	room temp. –500	14.83
	> 500	0.30
d) calcined_Al/TiO_2		
500c_Al/TiO_2	room temp. – 620	2.10
	> 620	0.60
800c_Al/TiO_2	room temp. – 550	0.65
	> 550	-

Table 19 The data of weight loss of B-doped TiO_2 samples

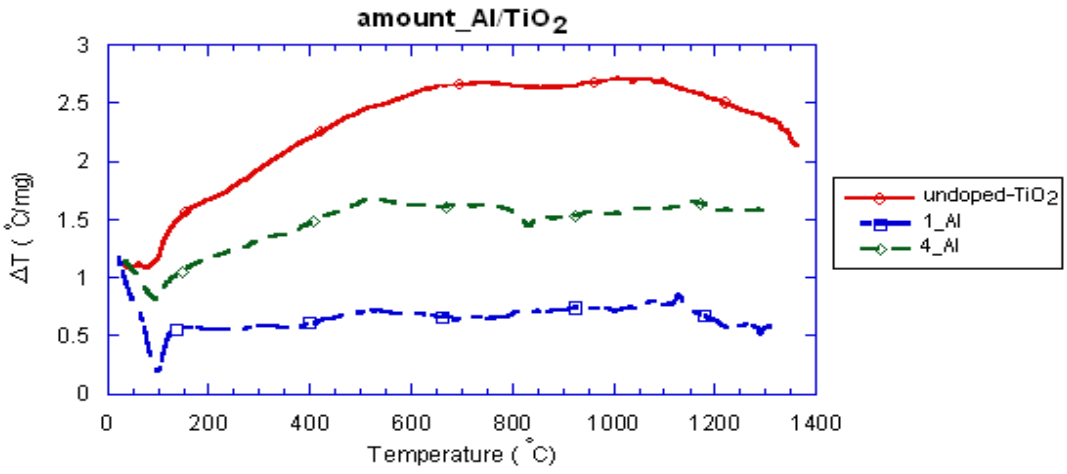
B doped TiO_2 samples	Temperature (°C)	Weight loss (%)
undoped TiO_2	room temp. – 700	5.84
	> 700	-
a) amount_B/TiO_2		
0.5wt_B/TiO_2	room temp. – 800	8.08
	> 800	-
10.0wt_B/TiO_2	room temp. – 600	12.00
	> 600	-
b) water_B/TiO_2		
50w_B/TiO_2	room temp. – 700	8.25
	> 700	-
100w_B/TiO_2	room temp. – 800	8.08
	> 800	-
150w_B/TiO_2	room temp. – 760	10.53
	> 760	-
200w_B/TiO_2	room temp. – 900	10.52
	> 900	-
c) acid_B/TiO_2		
CH_3COOH_B/TiO_2	room temp. – 700	8.47
	> 700	-
HCl_B/TiO_2	room temp. – 800	8.08
	> 800	-
HNO_3_B/TiO_2	room temp. – 600	7.98
	> 600	-
H_2SO_4_B/TiO_2	room temp. – 600	13.45
	600-900	1.81
	> 800	-

B doped TiO_2 samples	Temperature (°C)	Weight loss (%)
H_3PO_4_B/TiO_2	room temp. – 700	19.51
	> 700	-
d) calcined_B/TiO_2		
500c_B/TiO_2	room temp. – 700	1.13
	> 700	-
800c_B/TiO_2	-	-

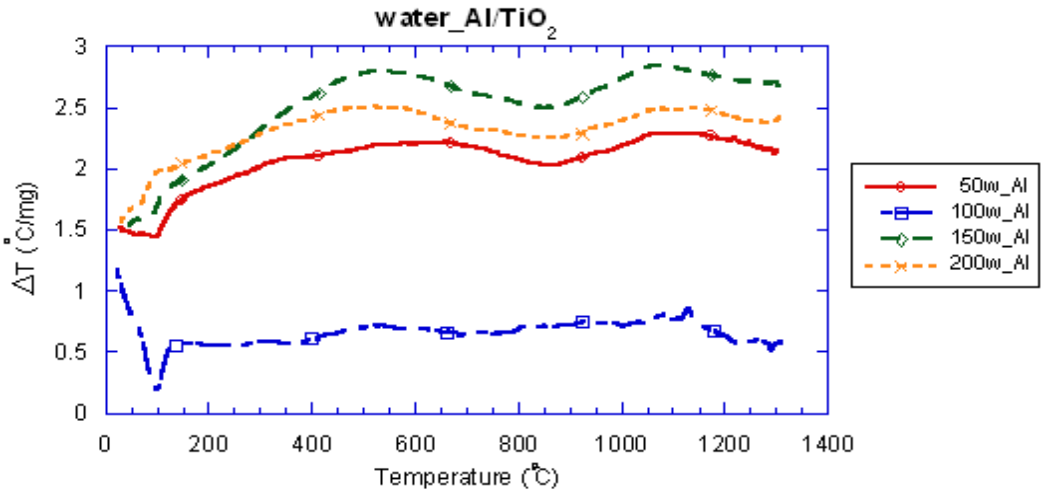
3.1.2.5 Differential thermal analysis (DTA)

Differential thermal analysis is a thermal technique which determining the temperatures of possible decomposition and phase changes (Reddy, et al, 2000). The DTA curve records these differences during reactions in the sample, showing thermal effects as deviations from the zero line. Figures 30 and 31 show the DTA curves of Al-doped TiO_2 and B-doped TiO_2 samples, respectively.

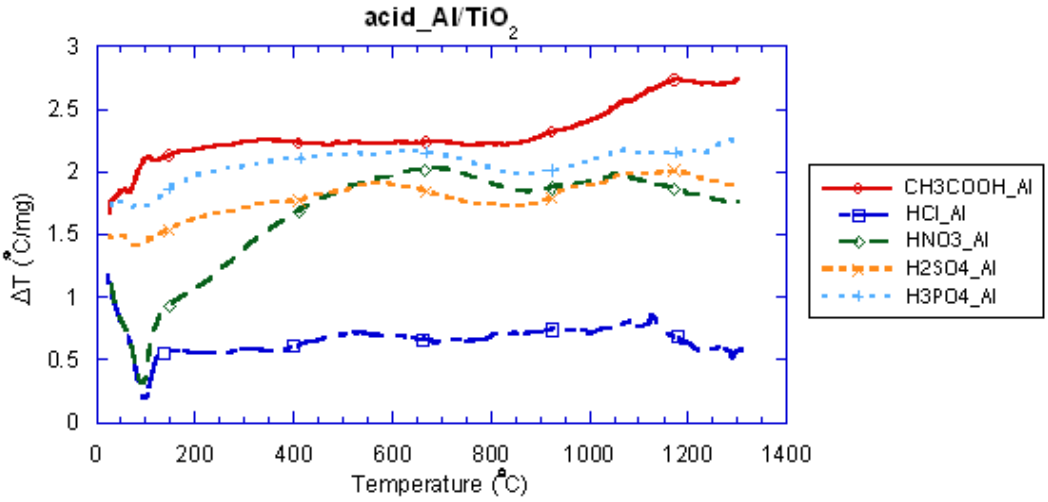
a) amount_Al/TiO_2



b) water_ Al/TiO_2



c) acid_ Al/TiO_2



d) calcined_ Al/TiO_2

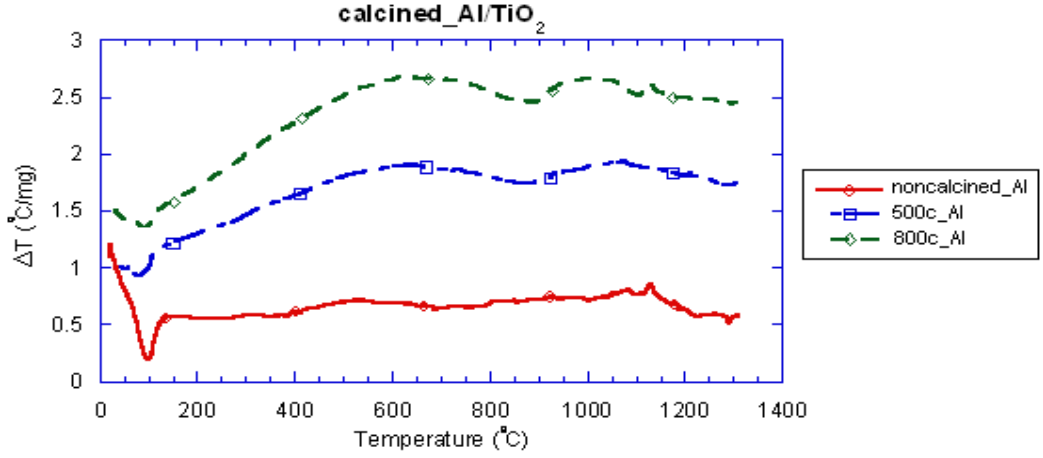
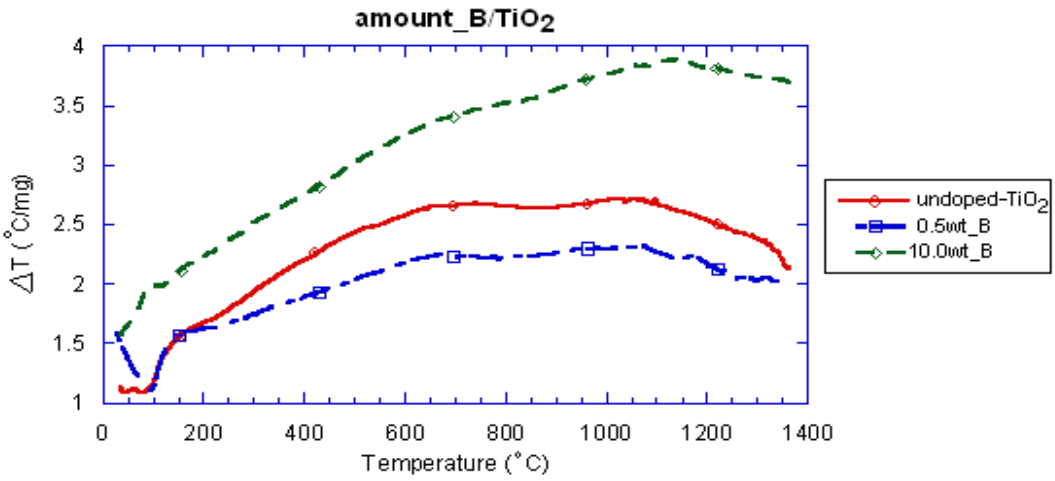
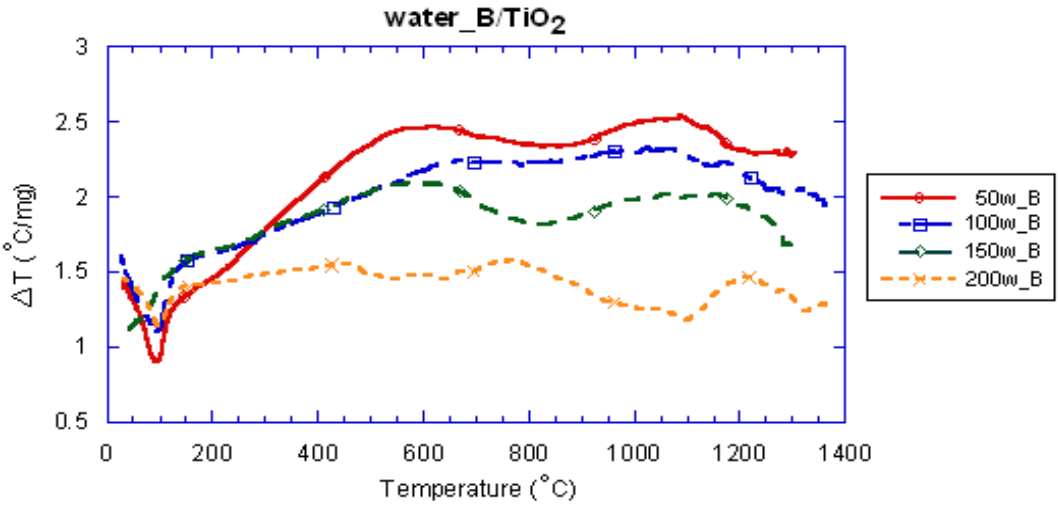


Figure 30 DTA curve of Al-doped TiO_2 samples

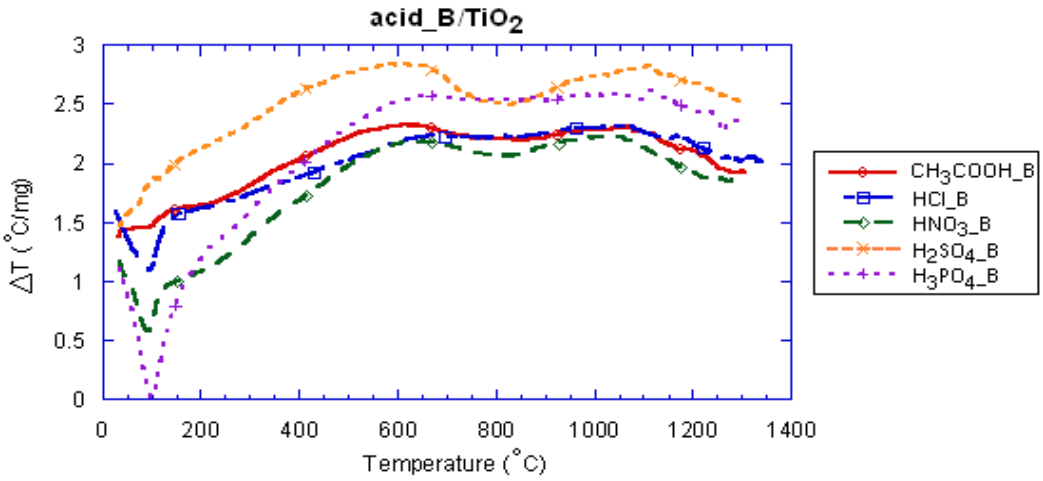
a) amount_B/TiO_2



b) water_ B/TiO_2



c) acid_ B/TiO_2



d) calcined_ B/TiO_2

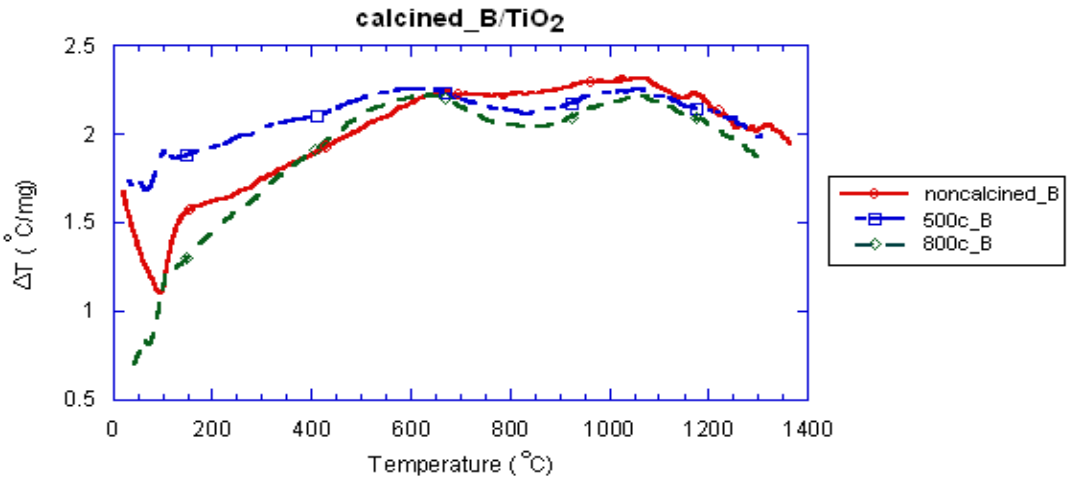


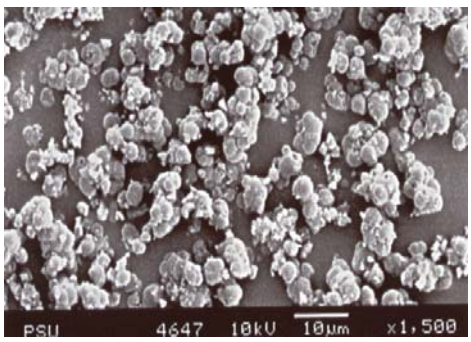
Figure 31 DTA curve of B-doped TiO_2 samples

3.1.2.6 Scanning electron microscope (SEM)

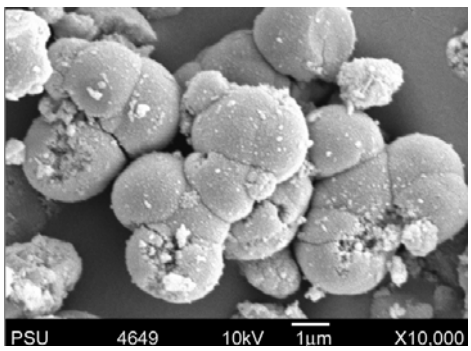
Scanning electron microscope is a technique which used to investigate the network structure and the texture of sample as shown in Figures 32 and 33 for the synthesized trivalent ion (Al, B)-doped titanium dioxide samples.

a) amount_ Al/TiO_2

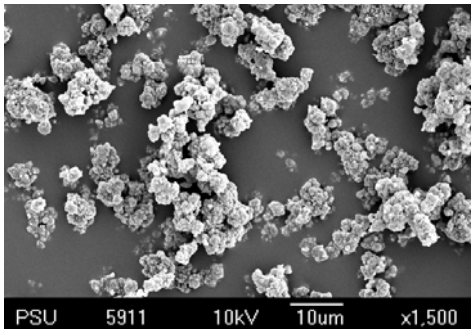
1a) undoped TiO_2×1,500



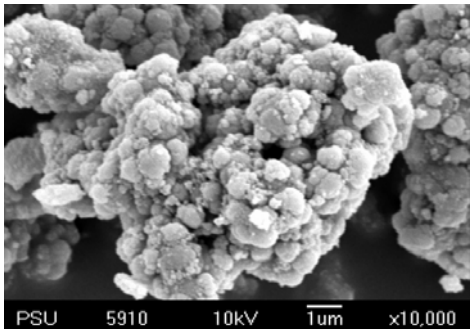
1b) undoped TiO_2×10,000



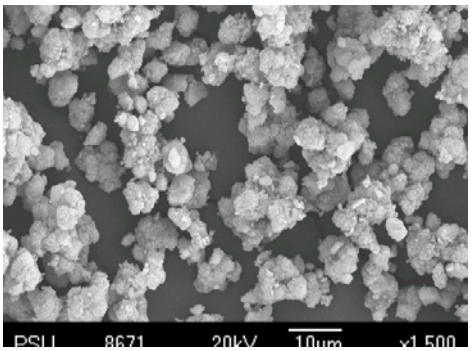
2a) 1_ Al/TiO_2 ×1,500



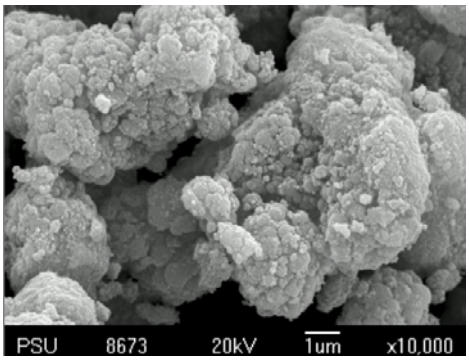
2b) 1_ Al/TiO_2×10,000



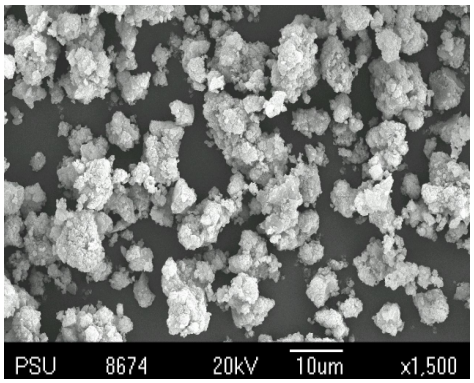
3a) 2_ Al/TiO_2×1,500



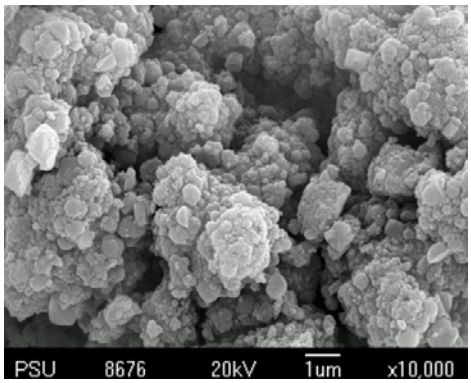
3b) 2_ Al/TiO_2×10,000



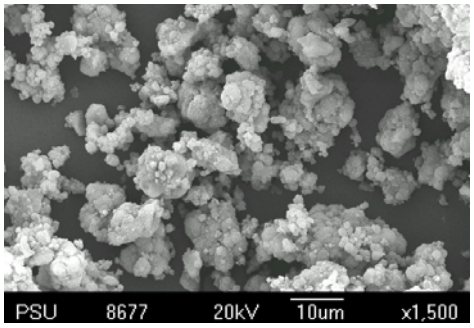
4a) 3_ Al/TiO_2 ×1,500



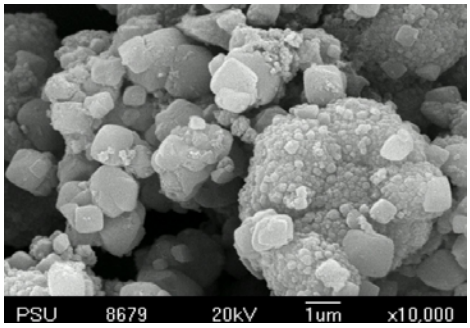
4b) 3_ Al/TiO_2×10,000



5a) 4_ Al/TiO_2 ×1,500

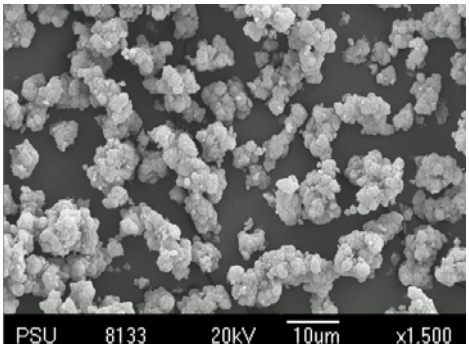


5b) 4_ Al/TiO_2×10,000

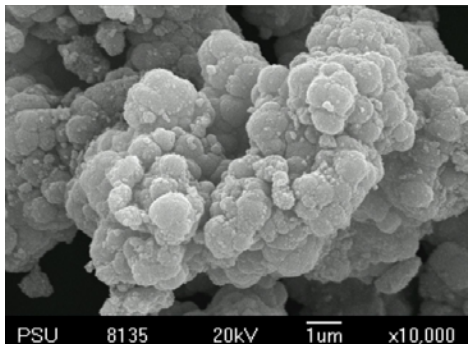


b) water_ Al/TiO_2

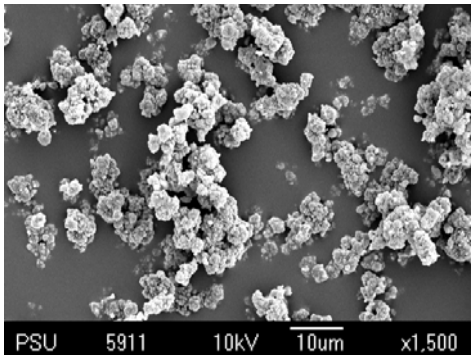
1a) 50w_ Al/TiO_2×1,500



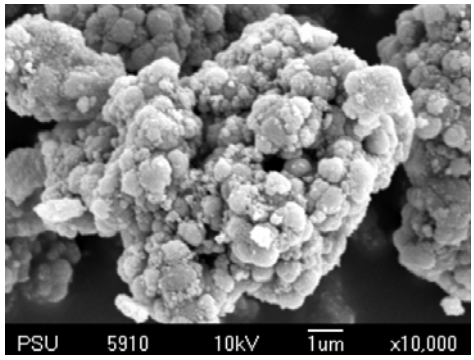
1b) 50w_ Al/TiO_2×10,000



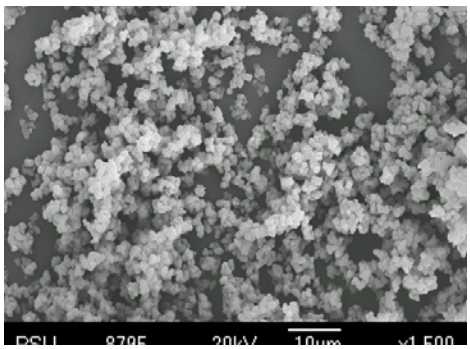
2a) 100w_ Al/TiO_2×1,500



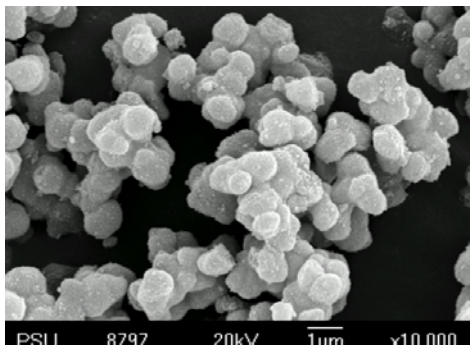
2b) 100w_ Al/TiO_2×10,000



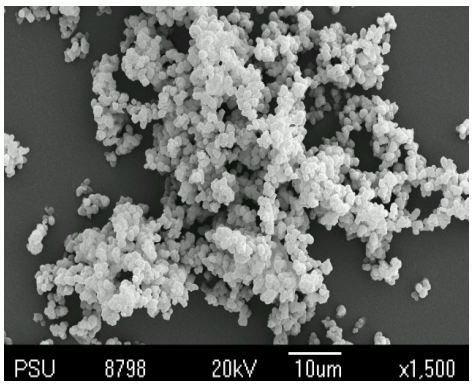
3a) 150w_ Al/TiO_2×1,500



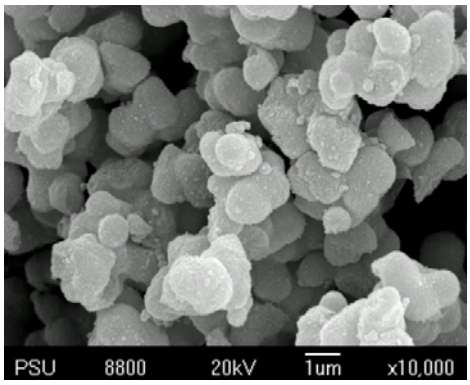
3b) 150w_ Al/TiO_2 ×10,000



4a) 200w_ Al/TiO_2 ×1,500

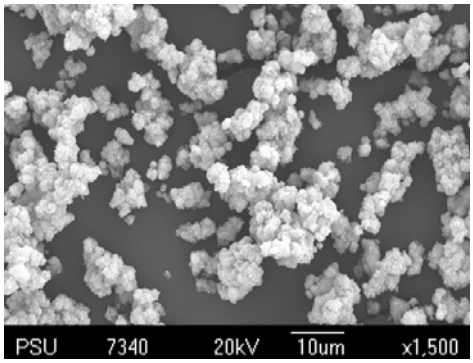


4b) 200w_ Al/TiO_2 ×10,000

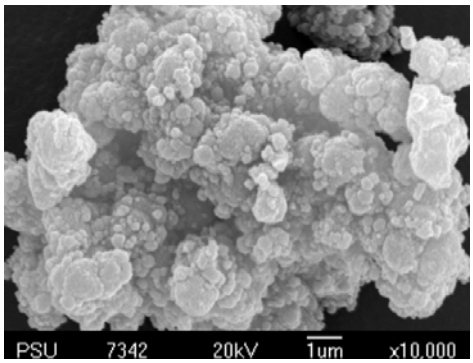


c) acid_ Al/TiO_2

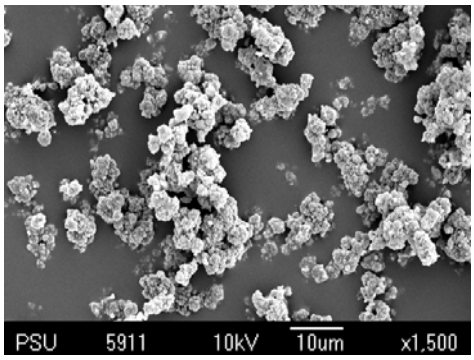
1a) CH_3COOH_ Al/TiO_2×1,500



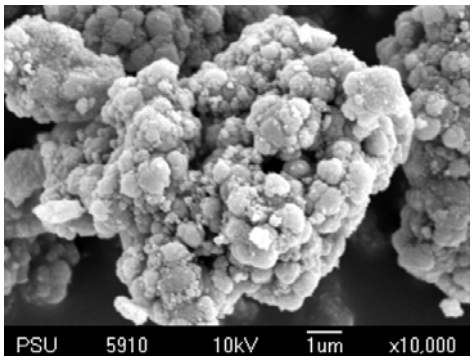
1b) CH_3COOH_ Al/TiO_2×10,000



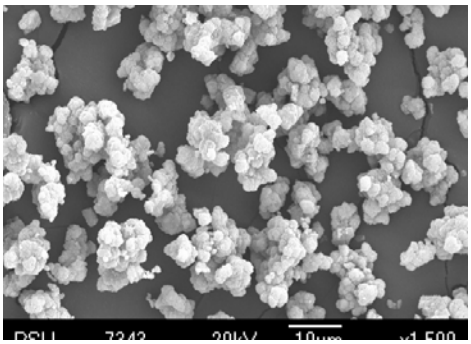
2a) HCl_ Al/TiO_2×1,500



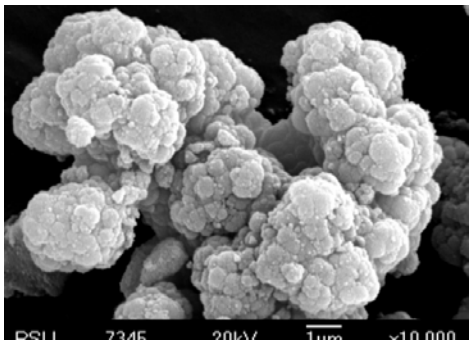
2b) HCl_ Al/TiO_2×10,000



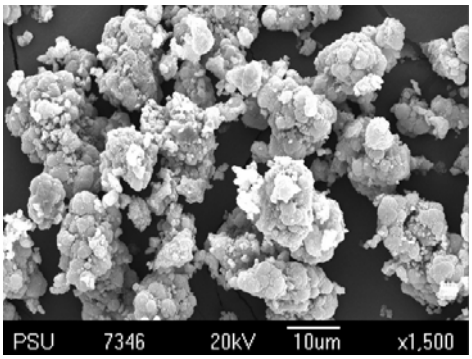
3a) HNO_3_ Al/TiO_2 ×1,500



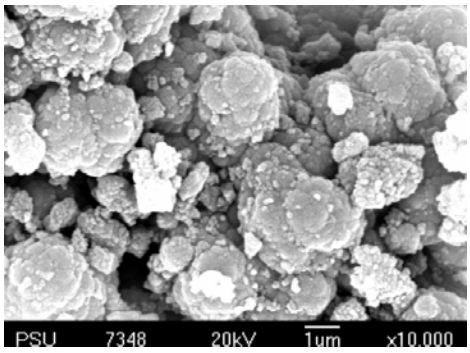
3b) HNO_3_ Al/TiO_2 ×10,000



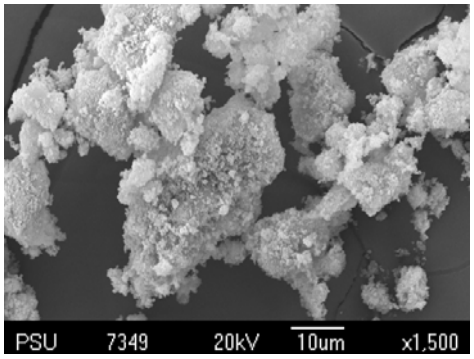
4a) H_2SO_4_ Al/TiO_2×1,500



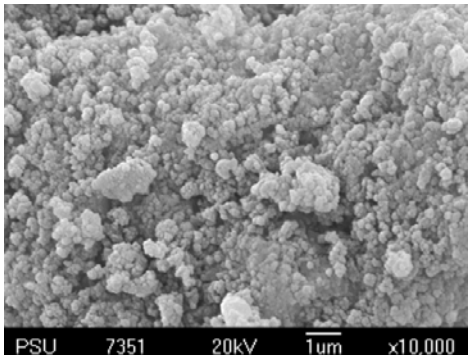
4b) H_2SO_4_ Al/TiO_2×10,000



5a) H_3PO_4_ Al/TiO_2×1,500

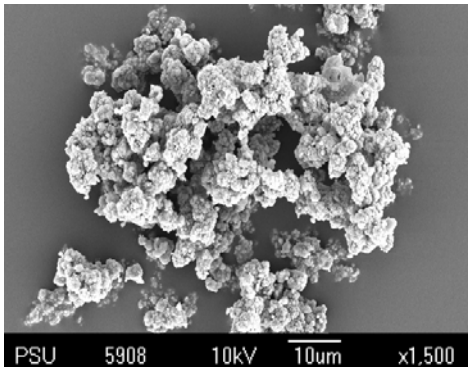


5b) H_3PO_4_ Al/TiO_2×10,000

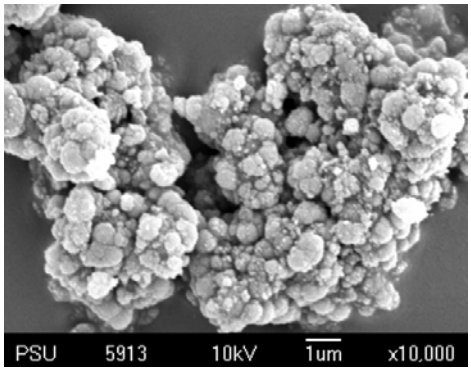


d) calcined_ Al/TiO_2

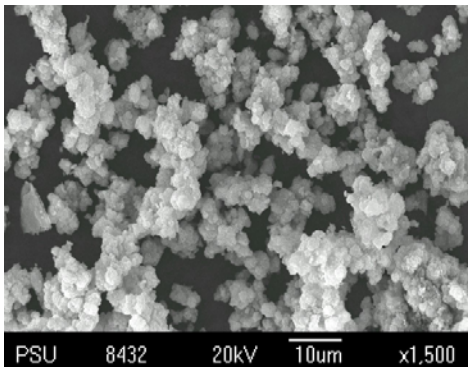
1a) 500c_ Al/TiO_2×1,500



1b) 500c_ Al/TiO_2×10,000



2a) 800c_ Al/TiO_2×1,500



2b) 800c_ Al/TiO_2×10,000

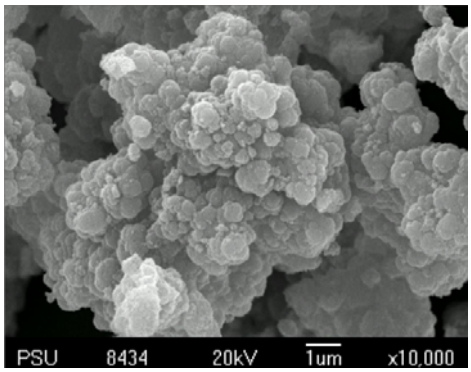
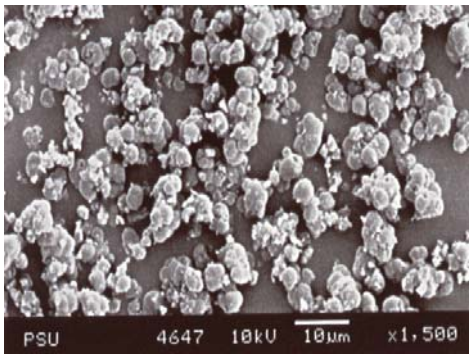


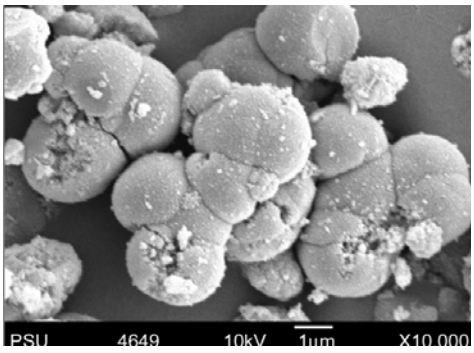
Figure 32 SEM image of Al-doped TiO_2 samples

a) amount_ B/TiO_2

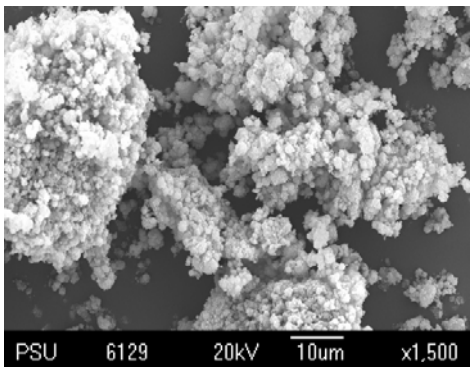
1a) undoped TiO_2×1,500



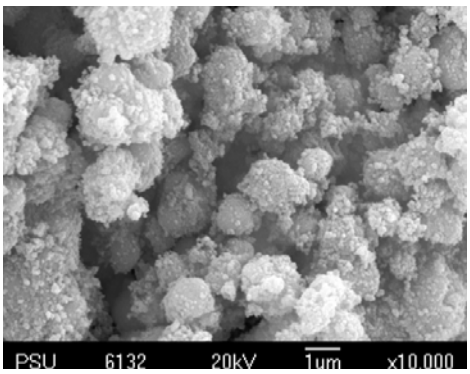
1b) undoped TiO_2×10,000



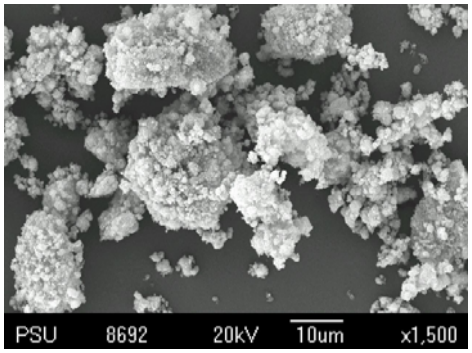
2a) 0.5wt_ B/TiO_2×1,500



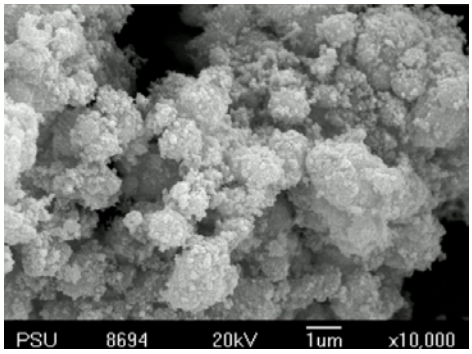
2b) 0.5wt_ B/TiO_2×10,000



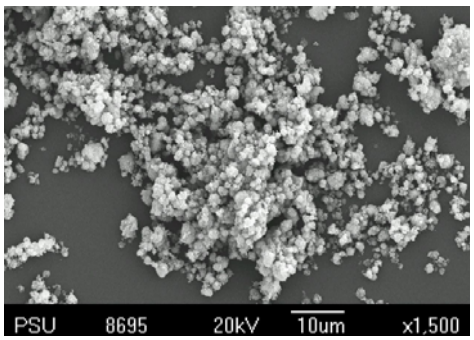
3a) 1.0wt_ B/TiO_2×1,500



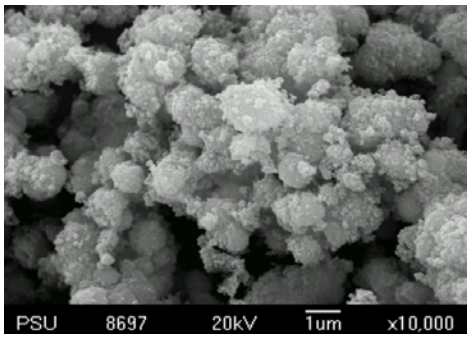
3b) 1.0wt_ B/TiO_2×10,000



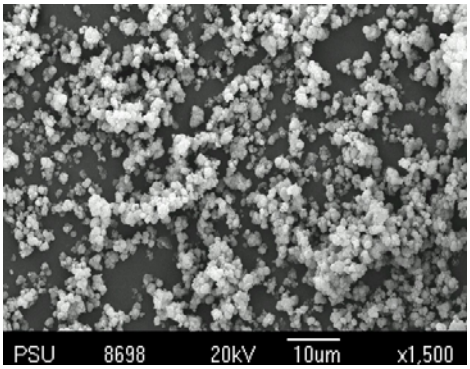
4a) 5.0wt_ B/TiO_2×1,500



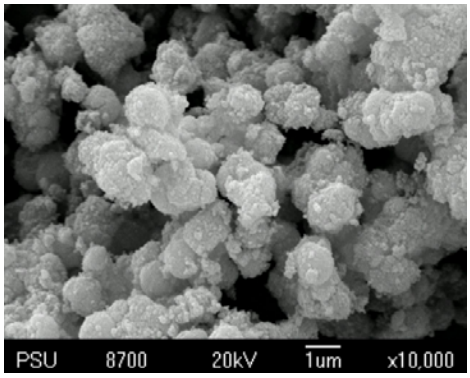
4b) 5.0wt_ B/TiO_2×10,000



5a) 10.0wt_ B/TiO_2 ×1,500

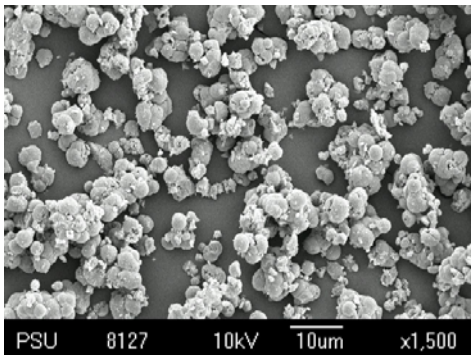


5b) 10.0wt_ B/TiO_2 ×10,000

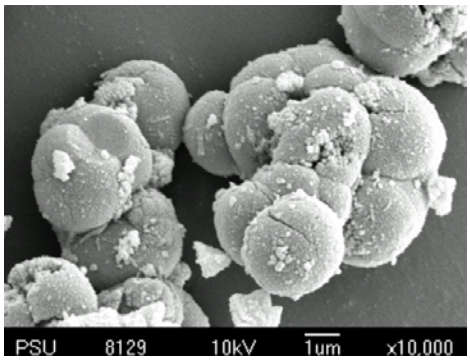


b) water_ B/TiO_2

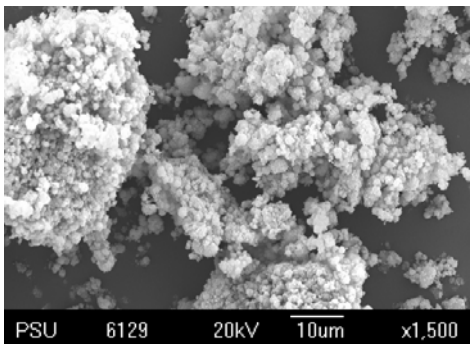
1a) 50w_ B/TiO_2×1,500



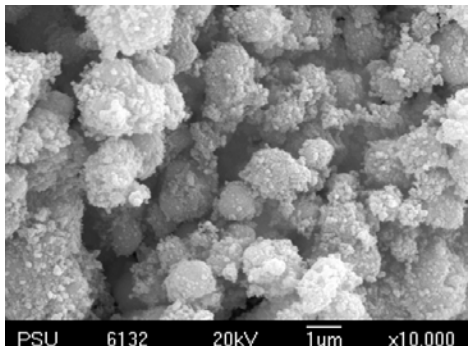
1b) 50w_ B/TiO_2×10,000



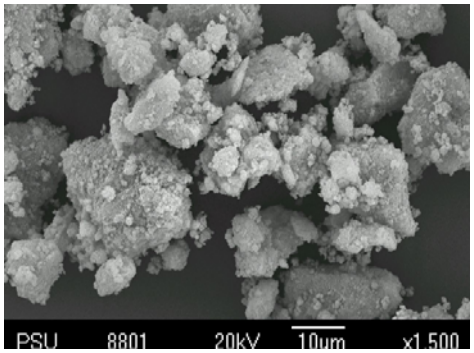
2a) 100w_ B/TiO_2×1,500



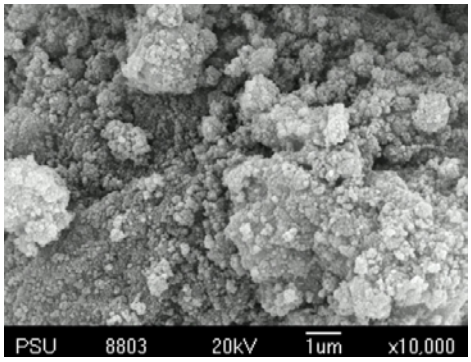
2b) 100w_ B/TiO_2×10,000



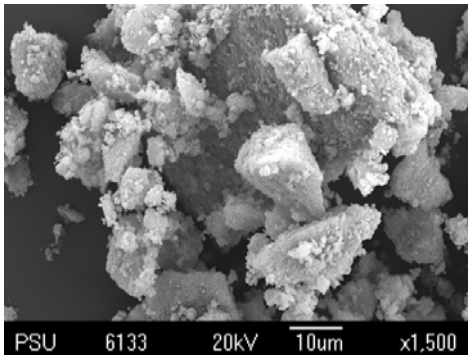
3a) 150w_ B/TiO_2×1,500



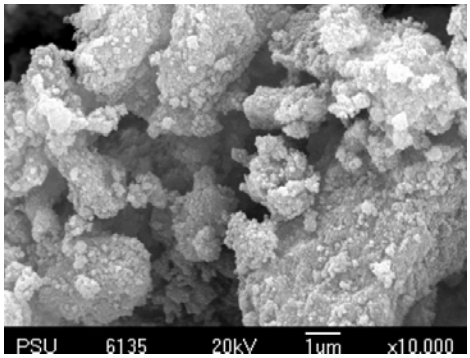
3b) 150w_ B/TiO_2×10,000



4a) 200w_ B/TiO_2×1,500

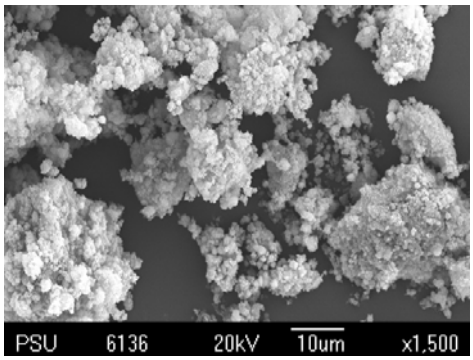


4b) 200w_ B/TiO_2×10,000

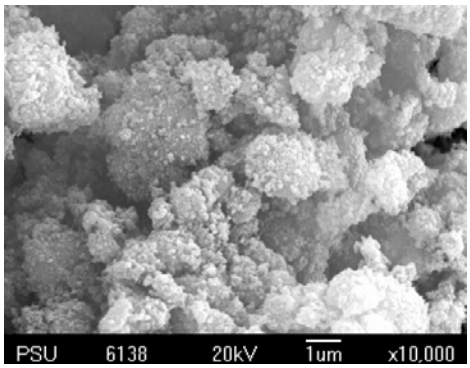


c) acid_ B/TiO_2

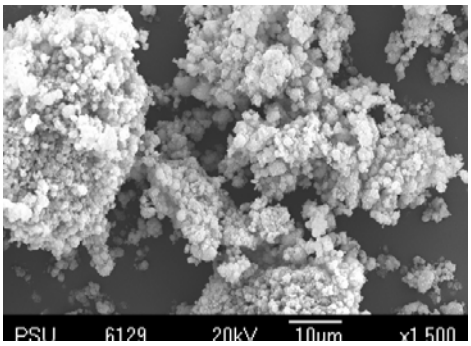
1a) CH_3COOH_ B/TiO_2×1,500



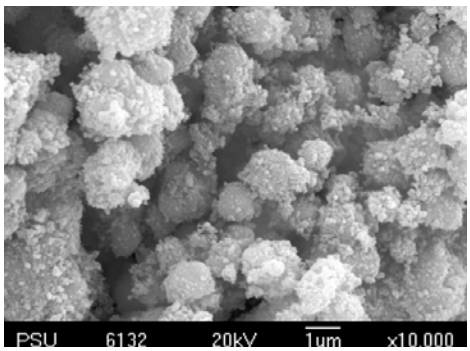
1b) CH_3COOH_ B/TiO_2×10,000



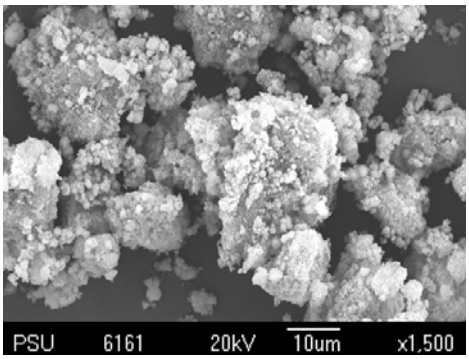
2a) HCl_ B/TiO_2×1,500



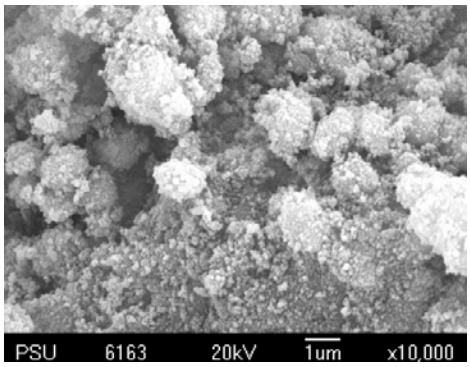
2b) HCl_ B/TiO_2×10,000



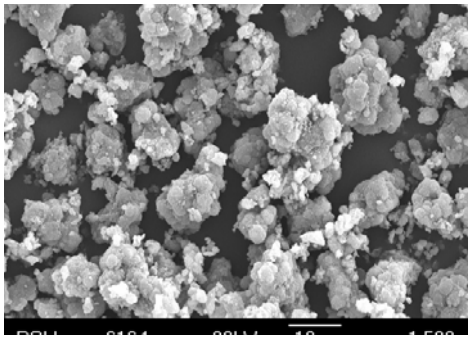
3a) HNO_3_ B/TiO_2×1,500



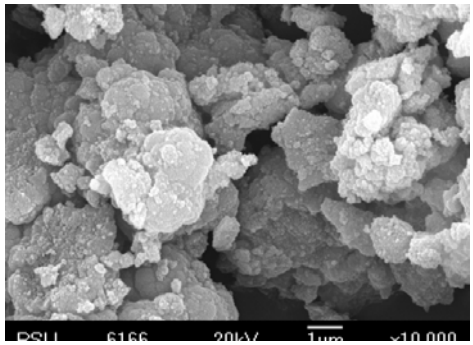
3b) HNO_3_ B/TiO_2×10,000



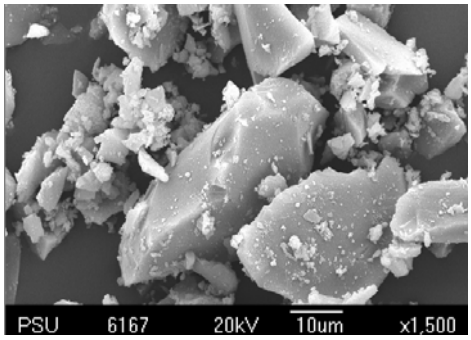
4a) H_2SO_4_ B/TiO_2×1,500



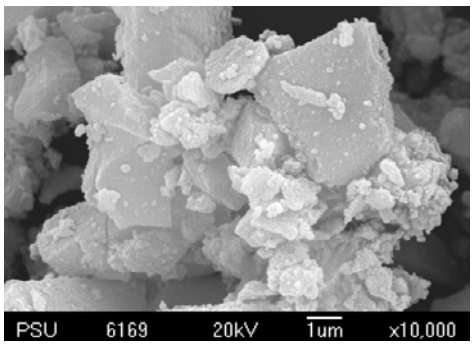
4b) H_2SO_4_ B/TiO_2×10,000



5a) H_3PO_4_B/TiO_2 ×1,500

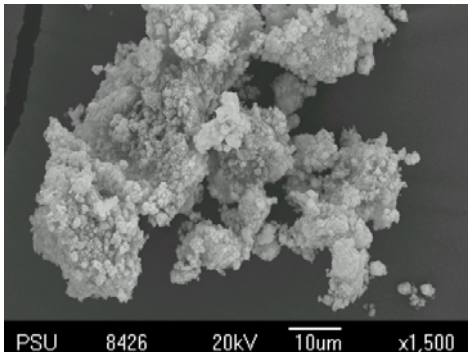


5b) H_3PO_4_B/TiO_2 ×10,000

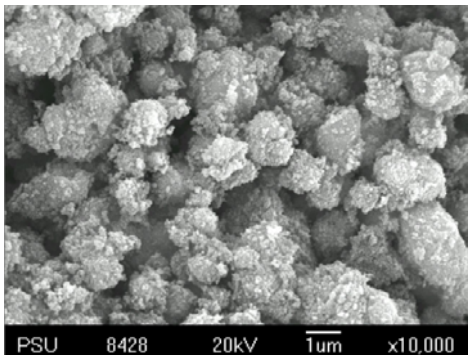


d) calcined_ B/TiO_2

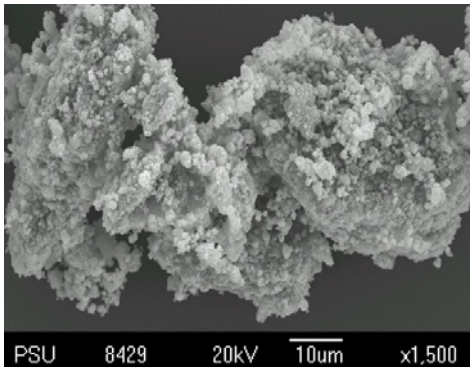
1a) 500c_ B/TiO_2×1,500



1b) 500c_ B/TiO_2×10,000



2a) 800c_ B/TiO_2 ×1,500



2a) 800c_ B/TiO_2 ×10,000

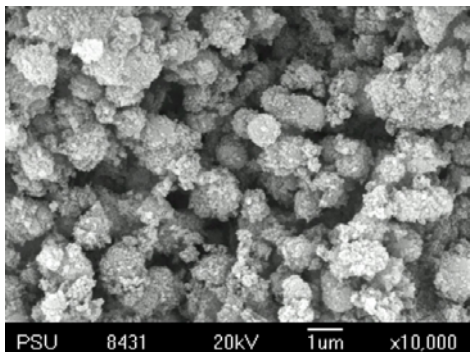


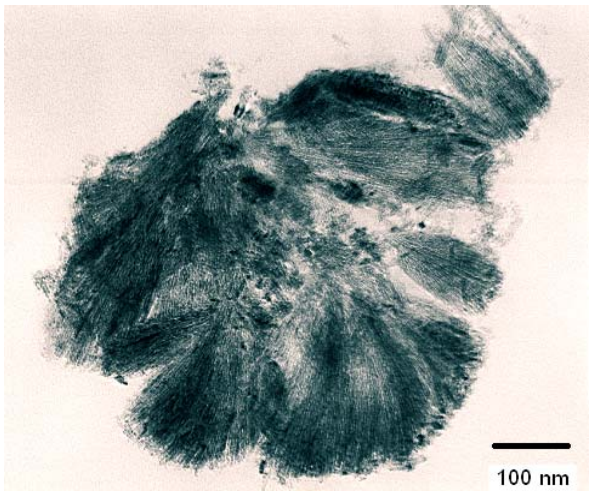
Figure 33 SEM image of B-doped TiO_2 samples

It can be seen that the photograph of the undoped TiO_2 sample appears regularly aggregated and uniform nearly spherical particles. For all case of Al-doped TiO_2 samples show dense of uniform spherical particle with higher aggregate than undoped TiO_2 sample. In the case of B-doped TiO_2 samples found that almost B-doped TiO_2 samples also have dense of uniform nearly spherical particle with higher aggregate than undoped TiO_2 sample. But for the H_3PO_4_B/TiO_2 sample shows non-uniform structure and the case of 50w_B/TiO_2 sample has similar appearance of the undoped TiO_2 sample.

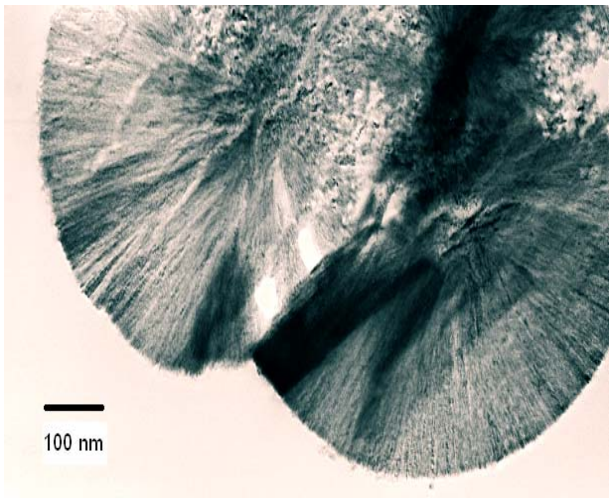
3.1.2.7 Transmission electron microscope (TEM)

Transmission electron microscope technique is used to estimate the particle size and the texture of crossed section particles. The TEM micrograph of synthesized undoped TiO_2, Al-doped TiO_2 and B-doped TiO_2 samples are shown in Figure 34.

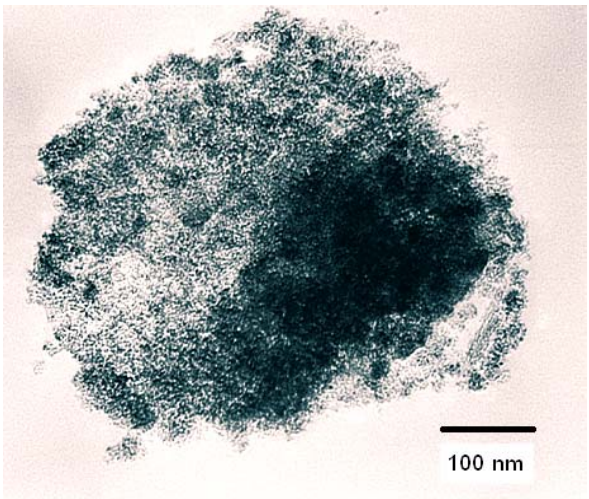
a) undoped TiO_2



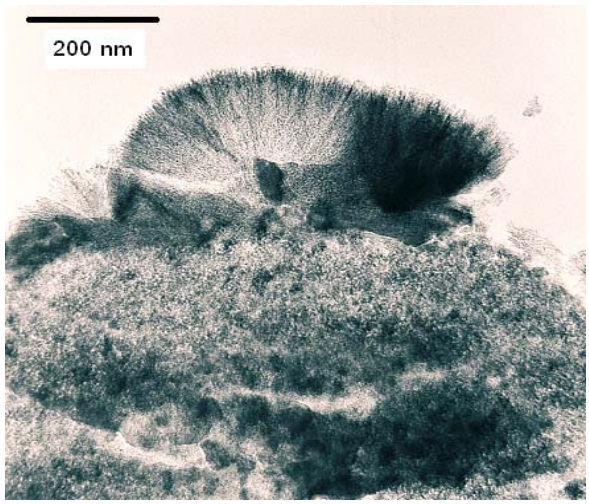
b) undoped TiO_2



c) Al-doped TiO_2



d) Al-doped TiO_2



e) B-doped TiO_2 f) B-doped TiO_2

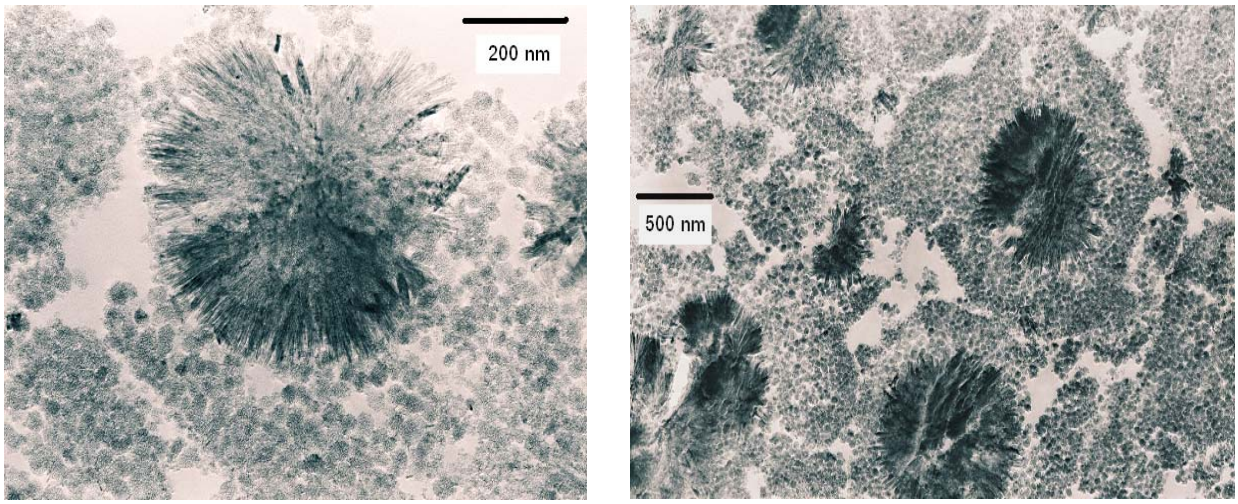


Figure 34 TEM images of synthesized TiO_2 samples (undoped TiO_2 sample : 27a and 27b, Al-doped TiO_2 sample : 27c and 27d and B-doped TiO_2 sample : 27e and 27f)

In Figure 34a and 34b, a TEM picture of the undoped TiO_2 consisted of tenuous fibers and the dark areas in these pictures were the result of aggregation of fibers. The TEM pictures of Al-doped TiO_2 sample that shown in Figure 34c and 34d appeared as highly aggregate of particles while the TEM picture in Figure 34d have small fibers of rutile particles. The B-doped TiO_2 structure consisted of rod-like rutile particles and also have small spherical particles.

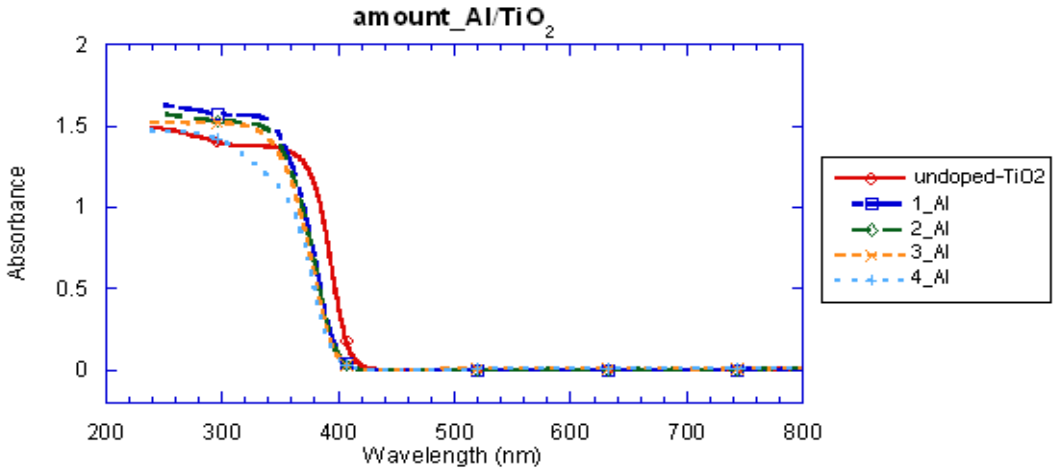
3.1.2.8 Ultraviolet-Visible spectrophotometry (UV-Vis)

UV-Vis spectroscopy has been used to characterize the bulk structure of crystalline and amorphous titanium dioxide. TiO_2 is a semiconductor oxide with easily measured optical band-gap. UV-Vis diffused reflectance spectroscopy is used to probe the band structure or molecular energy levels in the materials since UV-Vis light excitation creates photogenerated electrons and holes (Q. Zhang et al., 2000). Figure 35 and Figure 36 show the UV absorption edge which determined by the linear extrapolation of the steep part of the UV absorption toward the baseline. The corresponding band gap energy of each titanium dioxide sample can be calculated from the following Plank' s equation :

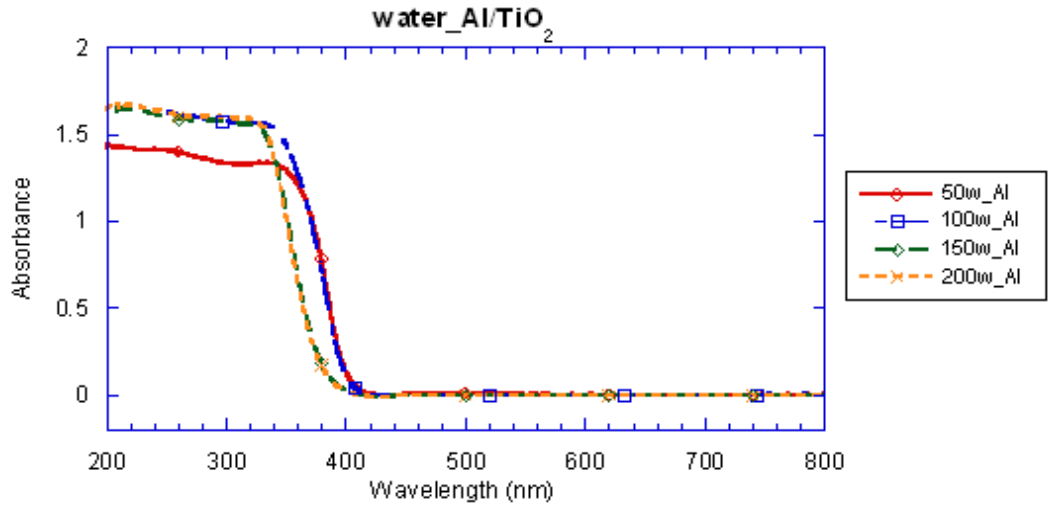
$$E_g = \frac{hc}{\lambda} = \frac{1240}{\lambda} \quad \text{.....(19)}$$

where E_g is the band gap energy (eV), h is the Plank' s constant (6.67×10^{-34} J.S), c is the velocity of light (3×10^{8} m.s^{-1}) and λ is the onset of absorption. The data of the onset of absorption and the band gap energy of Al-doped TiO_2 and B-doped TiO_2 samples are shown in Table 20 and Table 21, respectively. The diffused UV-Vis absorption spectra of Al doped TiO_2 and B-doped TiO_2 are shown in Figure 35 and Figure 36, respectively.

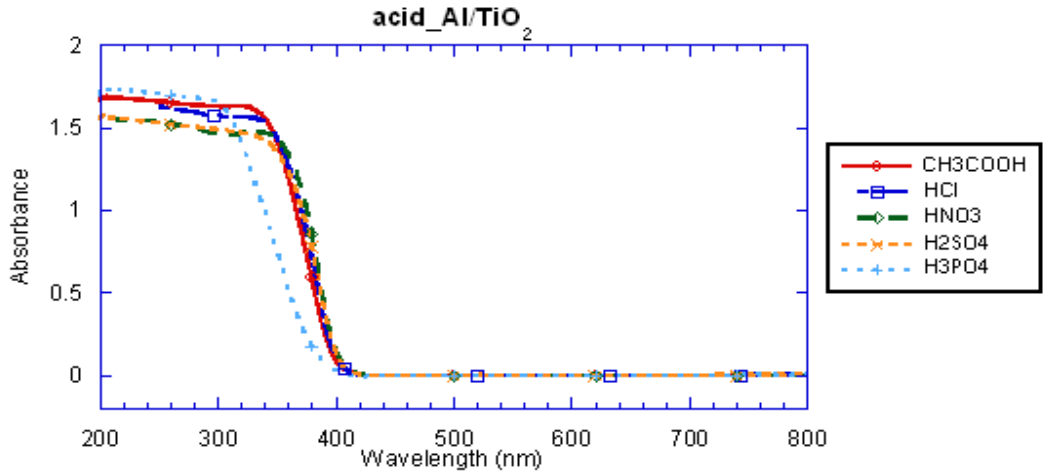
a) amount_Al/TiO_2



b) water_ Al/TiO_2



c) acid_ Al/TiO_2



d) calcined_ Al/TiO_2

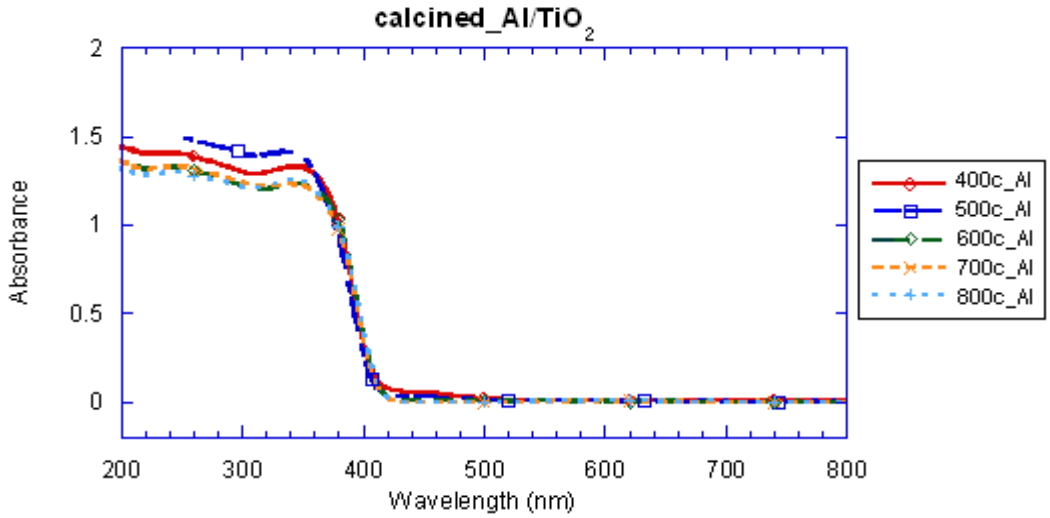
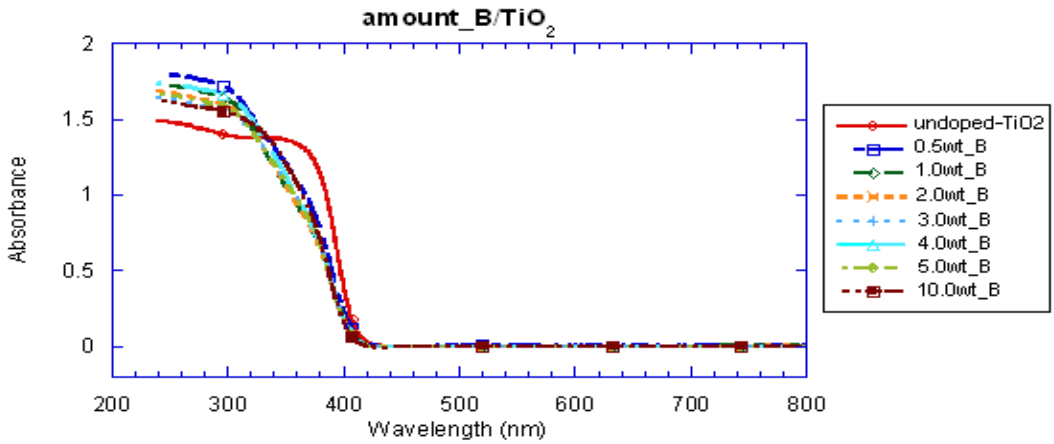
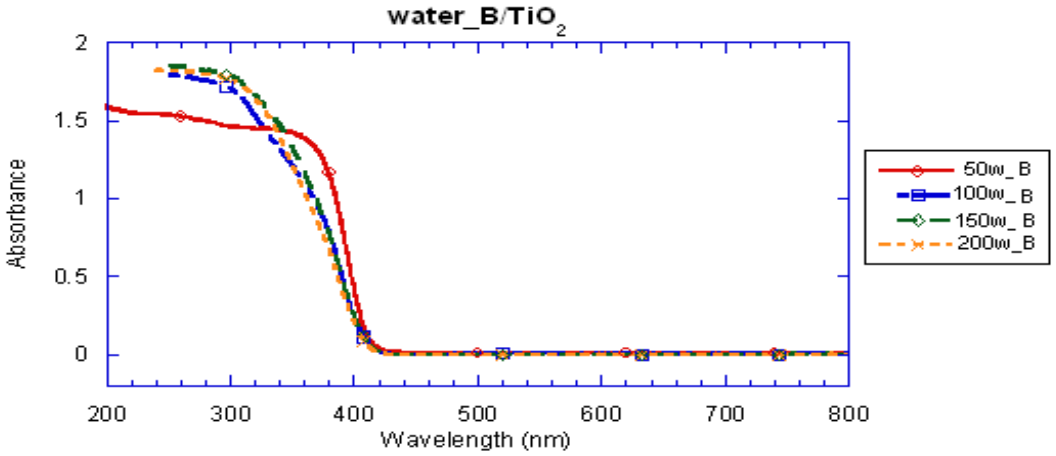


Figure 35 The diffused UV-Vis absorption spectra of Al-doped TiO_2 samples : a) amount_ Al/TiO_2 , b) water_ Al/TiO_2 , c) acid_ Al/TiO_2 and d) calcined_ Al/TiO_2 samples.

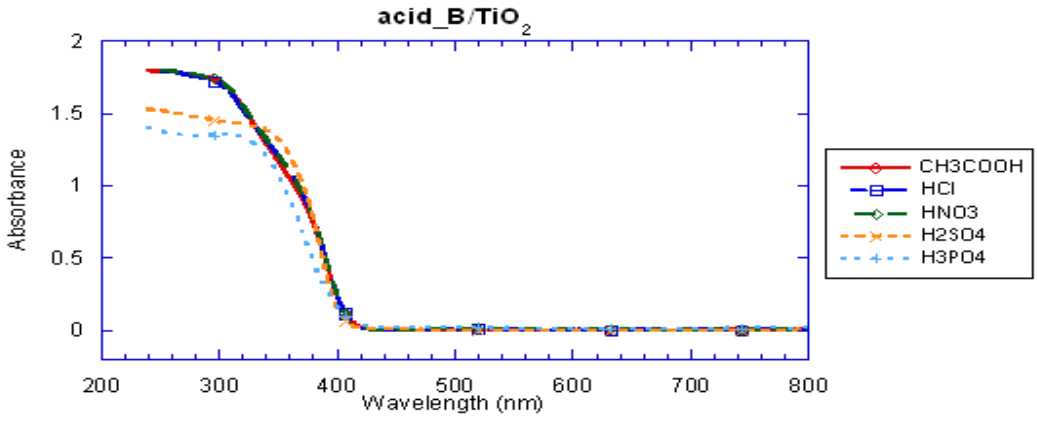
a) amount_ B/TiO_2



b) water_ B/TiO_2



c) acid_ B/TiO_2



d) calcined_ B/TiO_2

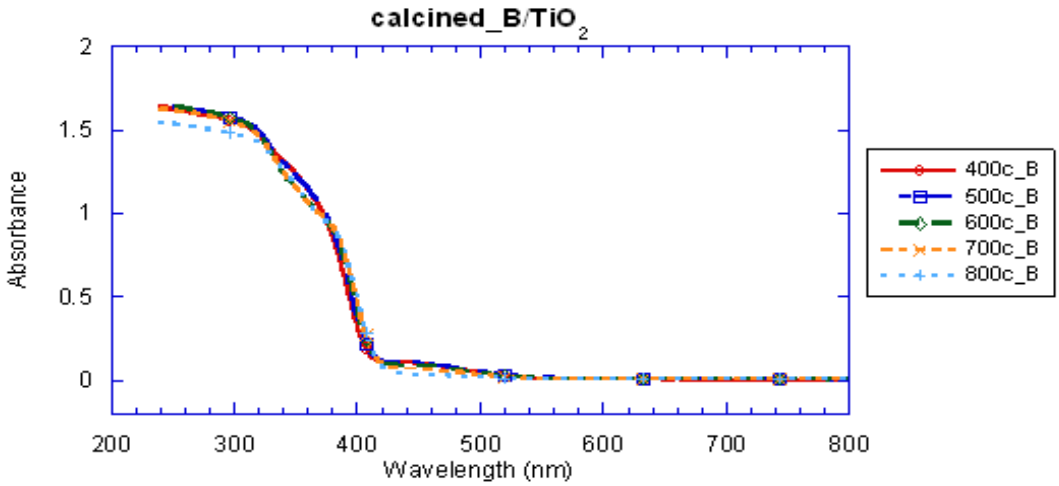


Figure 36 The diffused UV-Vis absorption spectra of B-doped TiO_2 samples : a) amount_ B/TiO_2 , b) water_ B/TiO_2 , c) acid_ B/TiO_2 and d) calcined_ B/TiO_2 samples.

Table 20 The onset of absorption and band gap energy of Al-doped TiO_2 samples

Al doped TiO_2 samples	Onset of absorption, λ (nm)	Band gap energy (eV)
undoped TiO_2	411	3.017
a)amount_Al/TiO_2		
1_Al/TiO_2	400	3.100
2_Al/TiO_2	398	3.116
3_Al/TiO_2	398	3.116
4_Al/TiO_2	397	3.123
b)water_Al/TiO_2		
50w_Al/TiO_2	402	3.085
100w_Al/TiO_2	400	3.100
150w_Al/TiO_2	380	3.623
200w_Al/TiO_2	378	3.280
c)acid_Al/TiO_2		
CH_3COOH_Al/TiO_2	399	3.108
HCl_Al/TiO_2	400	3.100
HNO_3_Al/TiO_2	403	3.077
H_2SO_4_Al/TiO_2	401	3.092
H_3PO_4_Al/TiO_2	383	3.238
d)calcined_Al/TiO_2		
400c_Al/TiO_2	411	3.017
500c_Al/TiO_2	407	3.050
600c_Al/TiO_2	412	3.010
700c_Al/TiO_2	412	3.010
800c_Al/TiO_2	411	3.017

Table 21 The onset of absorption and band gap energy of B-doped TiO_2 samples

B doped TiO_2 samples	Onset of absorption, λ (nm)	Band gap energy (eV)
undoped TiO_2	411	3.017
a)amount_B/TiO_2		
0.5wt_B/TiO_2	410	3.024
1.0wt_B/TiO_2	408	3.039
2.0wt_B/TiO_2	408	3.039
3.0wt_B/TiO_2	406	3.054
4.0wt_B/TiO_2	407	3.047
5.0wt_B/TiO_2	407	3.047
10.0wt_B/TiO_2	404	3.069
b)water_B/TiO_2		
50w_B/TiO_2	413	3.002
100w_B/TiO_2	410	3.024
150w_B/TiO_2	412	3.009
200w_B/TiO_2	411	3.017
c)acid_B/TiO_2		
CH_3COOH_B/TiO_2	407	3.047
HCl_B/TiO_2	410	3.024
HNO_3_B/TiO_2	410	3.024
H_2SO_4_B/TiO_2	405	3.062
H_3PO_4_B/TiO_2	405	3.062
d)calcined_B/TiO_2		
400c_B/TiO_2	413	3.002
500c_B/TiO_2	416	2.981
600c_B/TiO_2	415	2.988
700c_B/TiO_2	416	2.981
800c_B/TiO_2	419	2.959

In order to establish the type of band-to-band transition in these synthesized TiO_2 particles, the absorption data were fitted to equation for both indirect and direct band gap transitions (Kumar, et al., 2000).

Direct semiconductors are characterized by the minimum of the lowest conduction band positioned in k space directly under the maximum of the highest valence band. The optical absorption coefficient (α) near the absorption edge for direct interband transitions is given by equation (20) ;

$$\alpha = B_d(h\nu - E_g)^{1/2} / h\nu \qquad .....(20)$$

where B_d is the absorption constant for a direct transition.

For indirect semiconductors, the minimum of the lowest conduction band is shifted relative to the maximum of the highest valence band and the lowest-energy interband transition must then be accompanied by phonon excitation. Indirect interband transitions are characterized by the stronger energy dependence of the optical absorption coefficient (α) nearer the absorption edge than is otherwise the case for direct transitions. The equation of indirect transition given by the following equation ;

$$\alpha = B_i(h\nu - E_g)^2 / h\nu \qquad .....(21)$$

where B_i is the absorption constant for an indirect transition, $h\nu$ is the energy of excitation, E_g is the band gap energy (N. Serpone, et al.,1995).

The absorption coefficient (α) for reflectivity measurements could be calculated by the following equation (Zhao, et al., 1991) ;

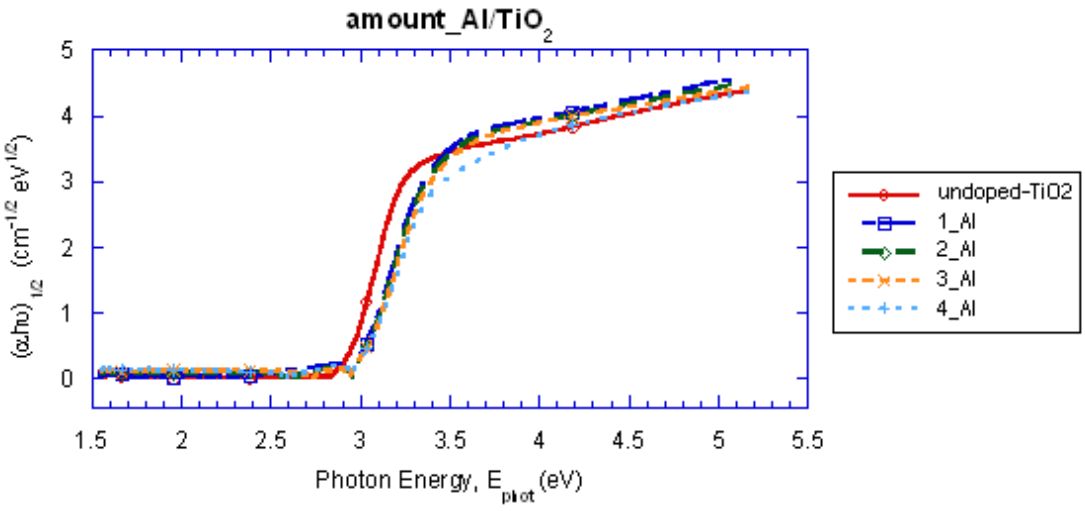
$$\alpha = \frac{A}{d_s'} \qquad .....(22)$$

where A is the measured absorbance and d_s' is the thickness of sample in UV-Vis cell (0.4 cm).

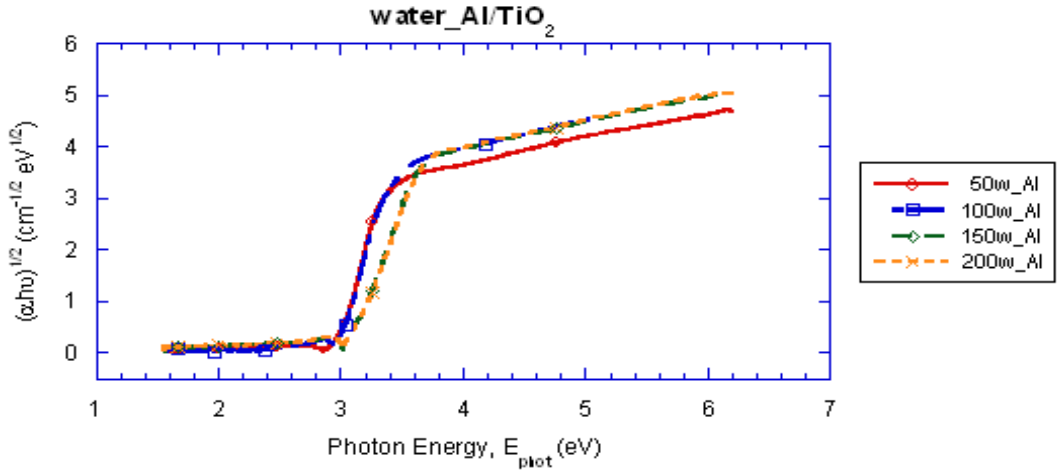
Figure 37 and Figure 38 show the $\alpha^{1/2}$ versus E_{phot} plot for an indirect transition of Al-doped TiO_2 samples and B-doped TiO_2 samples, respectively. The plot for an direct transition of

the $(\alpha E_{phot})^2$ versus E_{phot} are shown in Figure 39 and Figure 40 for synthesized trivalent (Al, B)-doped TiO_2 samples. Given that the α is the absorption coefficient and E_{phot} is the photon energy, $E_{phot} = (1239/\lambda)$ eV, where λ is the wavelength in nanometers. The value of E_{phot} extrapolated to $\alpha = 0$ gives an absorption energy, which corresponds to a band gap energy (K. Madhusudan Reddy, et al., 2002). The band gap values calculated from Figures 37 – 40 are shown in Table 22 and Table 23 for Al-doped TiO_2 samples and B-doped TiO_2 samples, respectively.

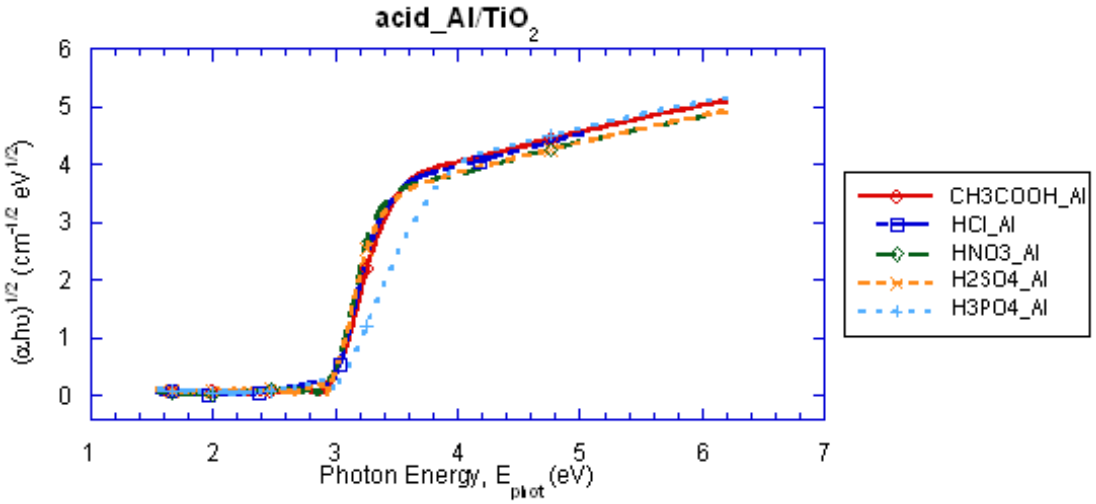
a) amount_ Al/TiO_2



b) water_ Al/TiO_2



c) acid_Al/ TiO_2



d) calcined_ Al/ TiO_2

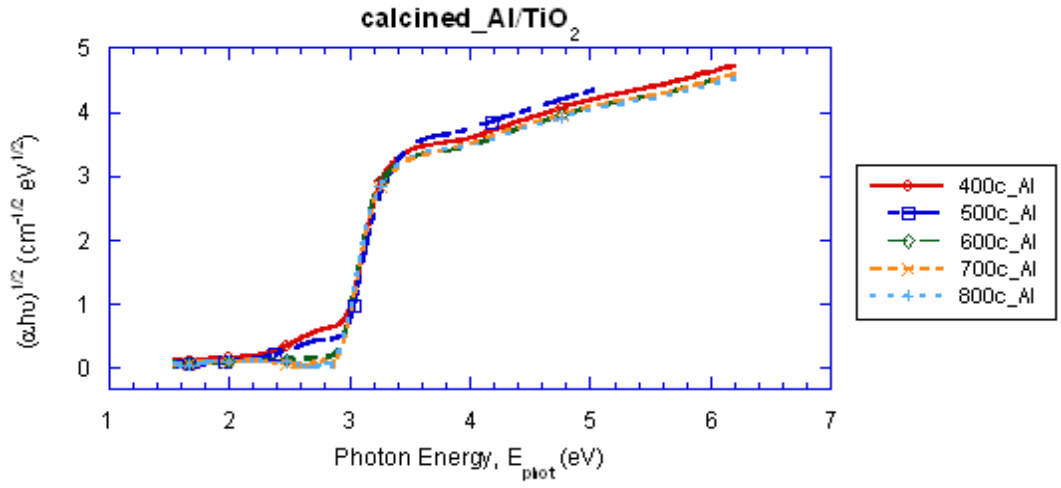
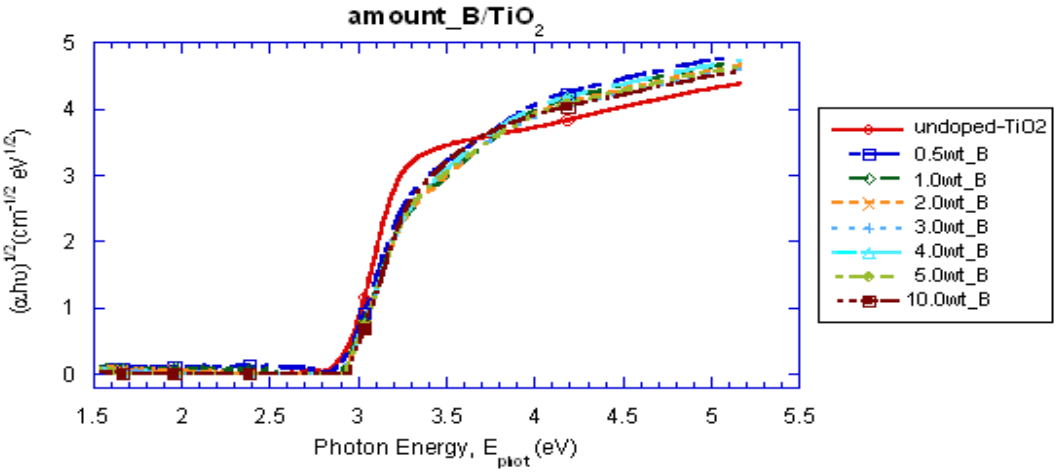
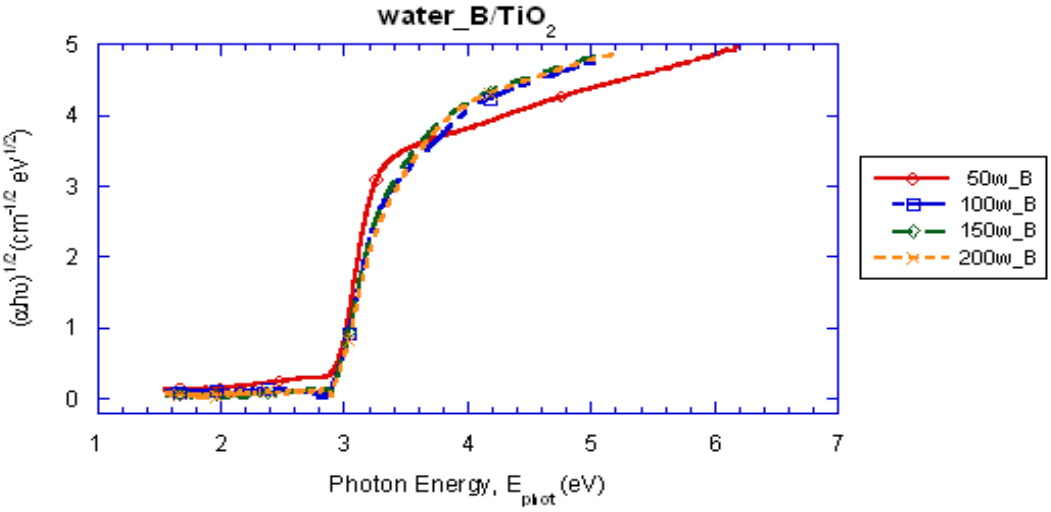


Figure 37 Plot of $(\alpha\ h\nu)^{1/2}$ versus E_{phot} for an indirect transition of Al-doped TiO_2 samples. The band gap (E_g) are obtained by extrapolation to $\alpha = 0$.

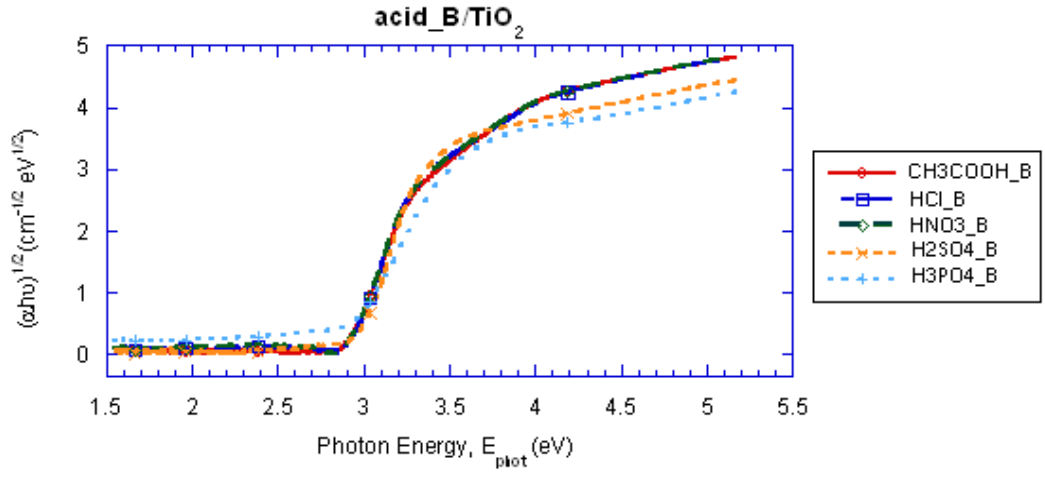
a) amount_ B/ TiO_2



b) water_ B/ TiO_2



c) acid_ B/ TiO_2



d) calcined_ B/ TiO_2

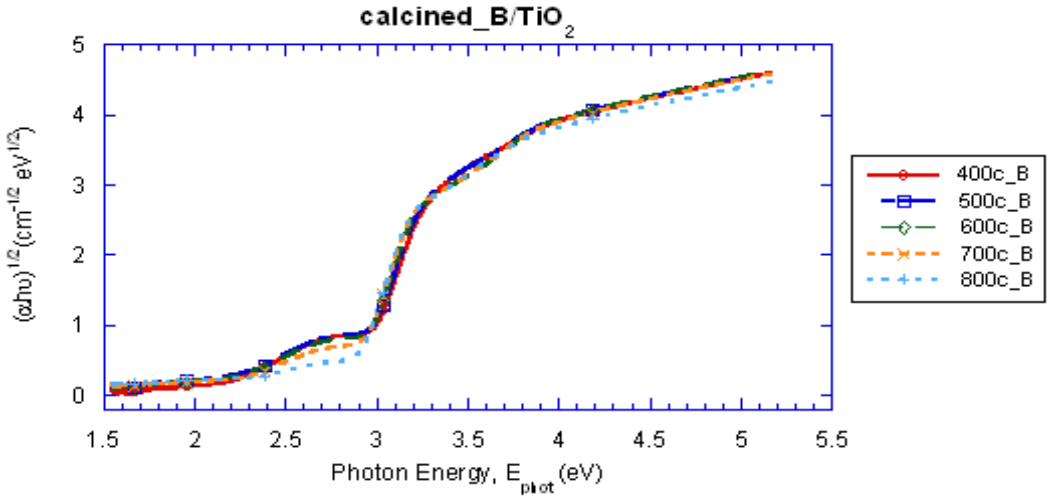
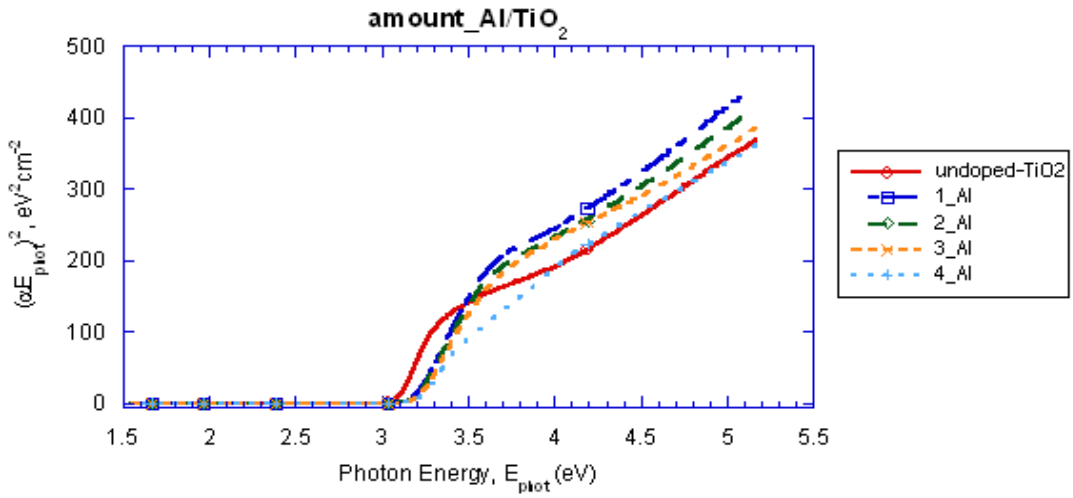
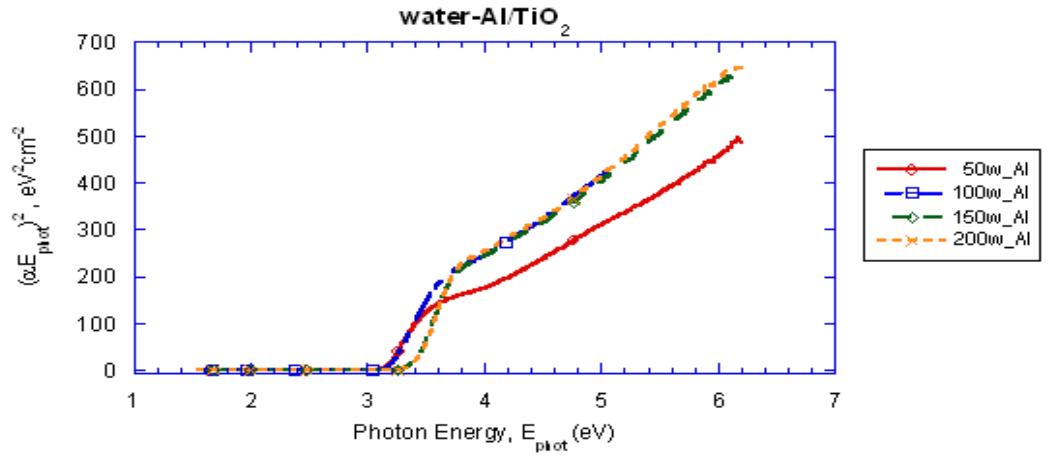


Figure 38 Plot of $(\alpha h\nu)^{1/2}$ versus E_{phot} for an indirect transition of B-doped TiO_2 samples. The band gap (E_g) are obtained by extrapolation to $\alpha = 0$.

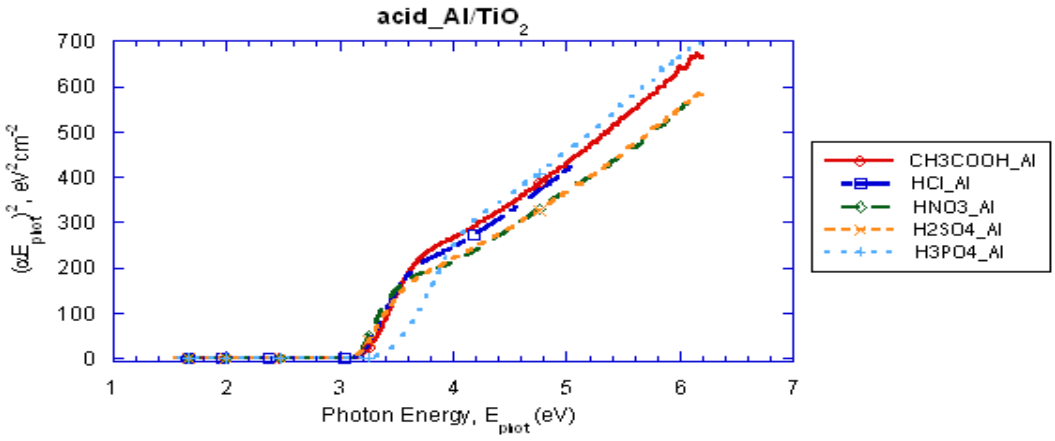
a) amount_ Al/ TiO_2



b) water_ Al/ TiO_2



c) acid_ Al/ TiO_2



d) calcined_ Al/ TiO_2

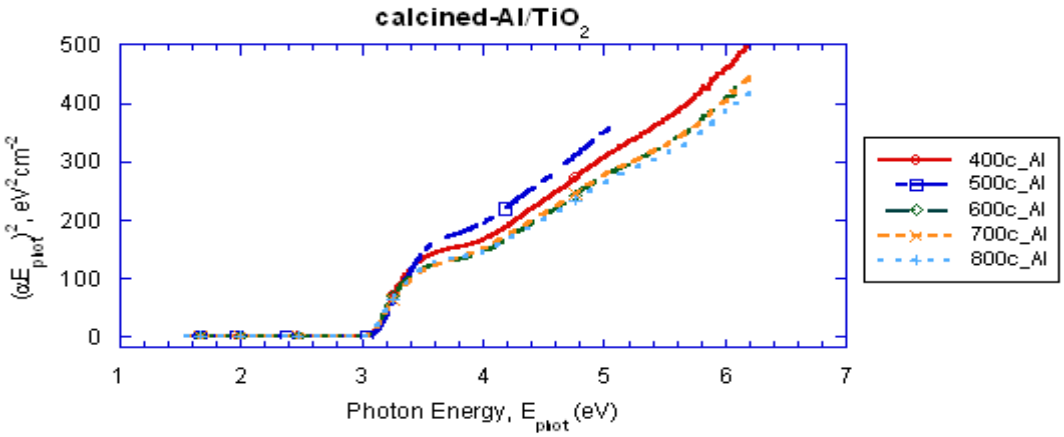
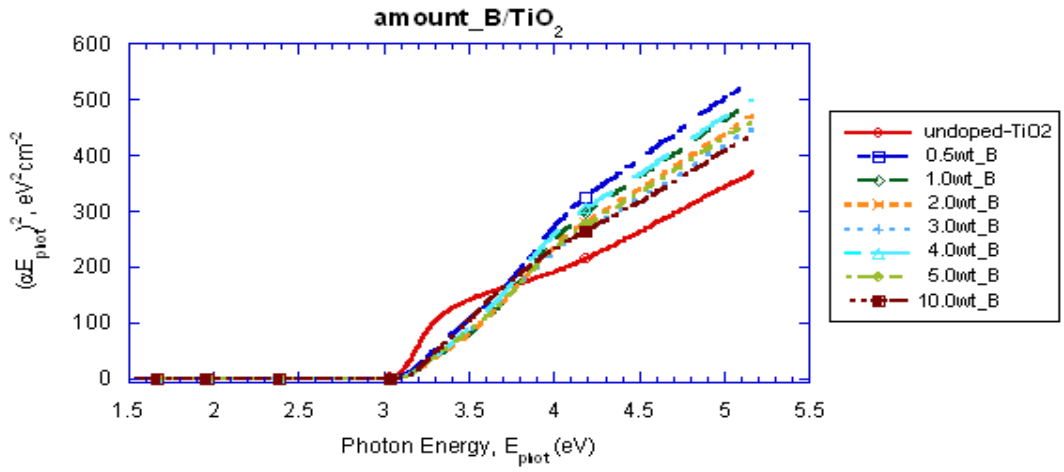
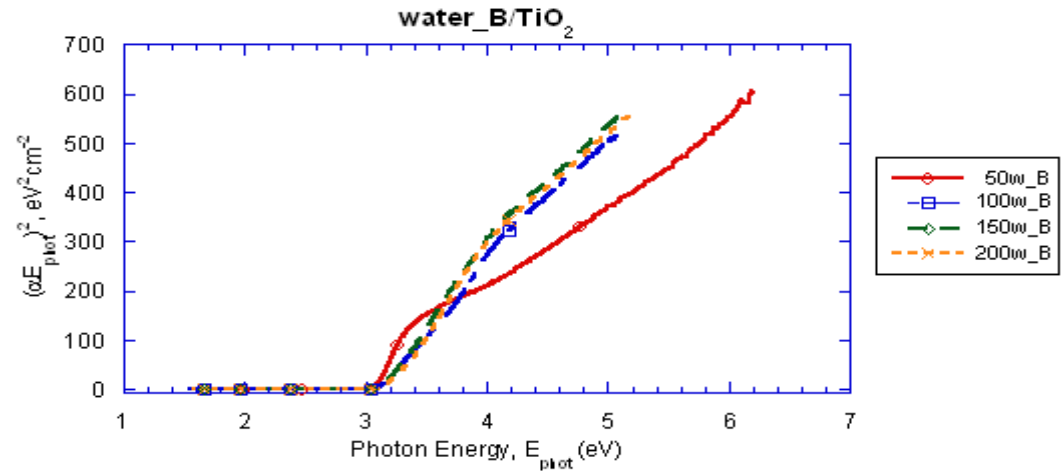


Figure 39 Plot of $(\alpha h\nu)^2$ versus E_{phot} for an direct transition Al-doped TiO_2 samples. The band gap (E_g) are obtained by extrapolation to $\alpha = 0$.

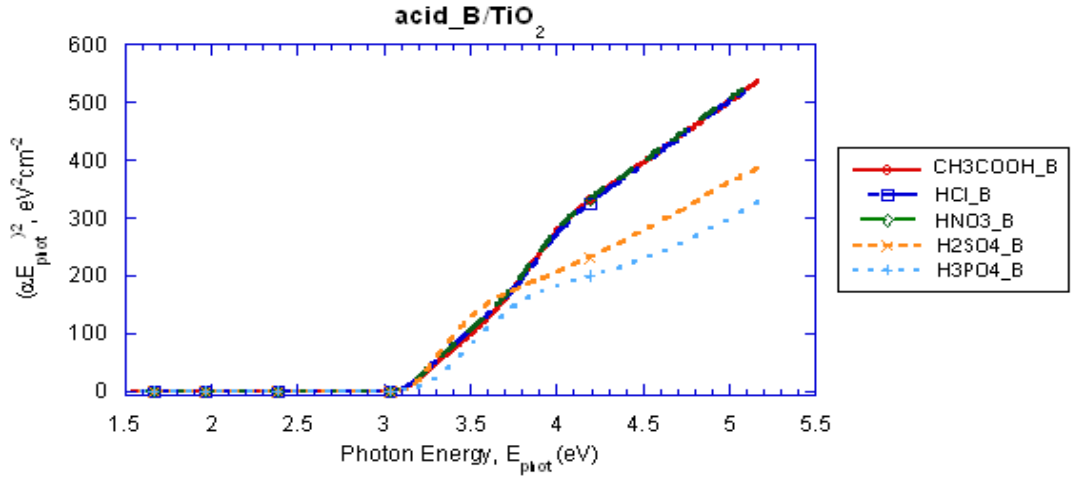
a) amount_ B/ TiO_2



b) water_ B/ TiO_2



c) acid_ B/ TiO_2



d) calcined_ B/ TiO_2

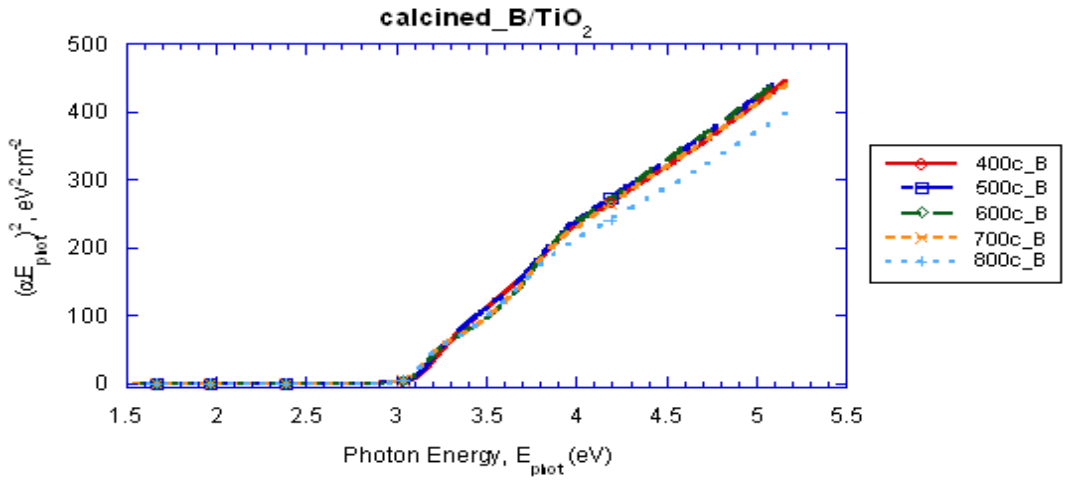


Figure 40 Plot of $(\alpha h\nu)^2$ versus E_{phot} for an direct transition of B-doped TiO_2 samples. The band gap (E_g) are obtained by extrapolation to $\alpha = 0$.

Table 22 Band gap energy from direct and indirect method of Al-doped TiO_2 samples.

Al doped TiO_2 samples	Band gap energy (eV)		
	Equation (8)	Indirect method	Direct method
undoped TiO_2	3.017	2.92	3.07
a)amount_Al/TiO_2			
1_Al/TiO_2	3.100	2.97	3.17
2_Al/TiO_2	3.116	3.01	3.18
3_Al/TiO_2	3.116	3.00	3.19
4_Al/TiO_2	3.123	3.02	3.16
b)water_Al/TiO_2			
50w_Al/TiO_2	3.085	2.99	3.14
100w_Al/TiO_2	3.100	2.97	3.17
150w_Al/TiO_2	3.263	3.08	3.36
200w_Al/TiO_2	3.280	3.07	3.39
c)acid_Al/TiO_2			
CH_3COOH_Al/TiO_2	3.108	2.98	3.20
HCl_Al/TiO_2	3.100	2.97	3.18
HNO_3_Al/TiO_2	3.077	2.95	3.15
H_2SO_4_Al/TiO_2	3.092	2.94	3.14
H_3PO_4_Al/TiO_2	3.238	3.02	3.44
d)calcined_Al/TiO_2			
400c_Al/TiO_2	3.017	2.90	3.06
500c_Al/TiO_2	3.050	2.94	3.09
600c_Al/TiO_2	3.010	2.92	3.06
700c_Al/TiO_2	3.010	2.91	3.05
800c_Al/TiO_2	3.017	2.90	3.04

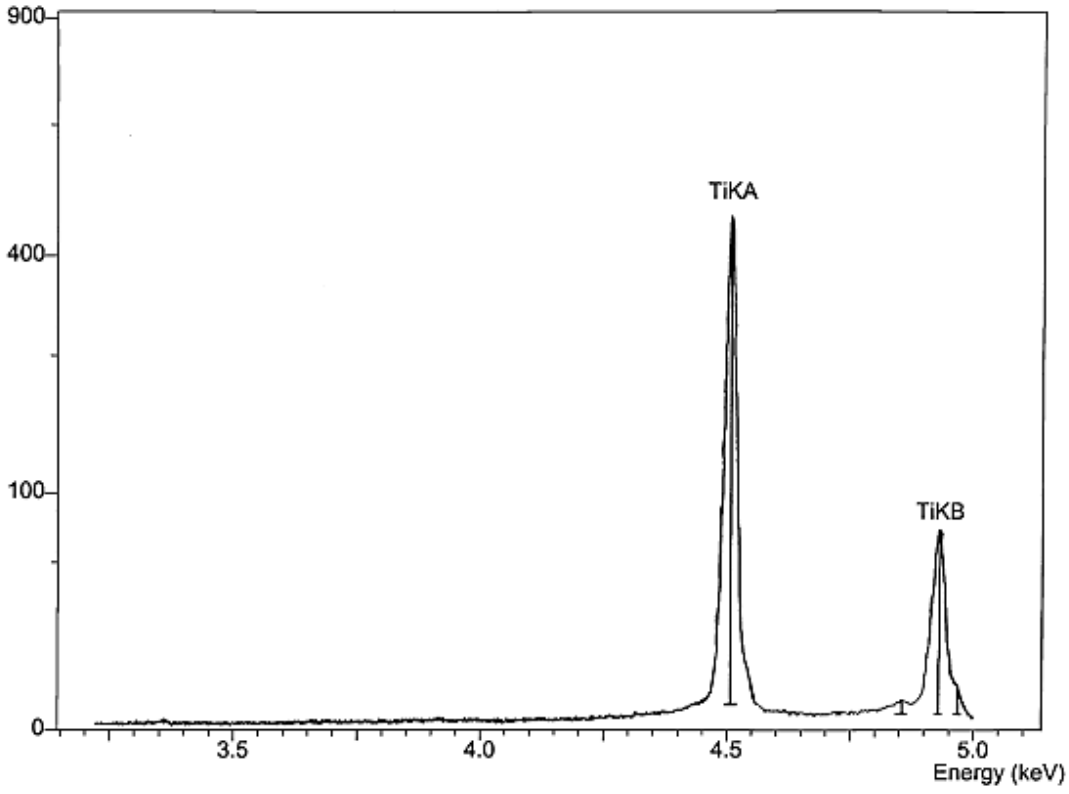
Table 23 Band gap energy from direct and indirect method of B-doped TiO_2 samples.

B doped TiO_2 samples	Band gap energy (eV)		
	Equation (8)	Indirect method	Direct method
undoped TiO_2	3.017	2.92	3.07
a)amount_B/TiO_2			
0.5wt_B/TiO_2	3.024	2.92	3.10
1.0wt_B/TiO_2	3.039	2.92	3.11
2.0wt_B/TiO_2	3.039	2.93	3.13
3.0wt_B/TiO_2	3.054	2.94	3.12
4.0wt_B/TiO_2	3.047	2.93	3.14
5.0wt_B/TiO_2	3.047	2.94	3.12
10.0wt_B/TiO_2	3.069	2.95	3.12
b)water_B/TiO_2			
50w_B/TiO_2	3.002	2.91	3.06
100w_B/TiO_2	3.024	2.92	3.10
150w_B/TiO_2	3.009	2.92	3.09
200w_B/TiO_2	3.017	2.93	3.17
c)acid_B/TiO_2			
CH_3COOH_B/TiO_2	3.047	2.91	3.07
HCl_B/TiO_2	3.024	2.92	3.10
HNO_3_B/TiO_2	3.024	2.90	3.08
H_2SO_4_B/TiO_2	3.062	2.96	3.14
H_3PO_4_B/TiO_2	3.062	2.87	3.19
d)calcined_B/TiO_2			
400c_B/TiO_2	3.002	2.88	3.04
500c_B/TiO_2	2.981	2.87	3.04
600c_B/TiO_2	2.988	2.86	3.00
700c_B/TiO_2	2.981	2.86	2.99
800c_B/TiO_2	2.959	2.84	2.99

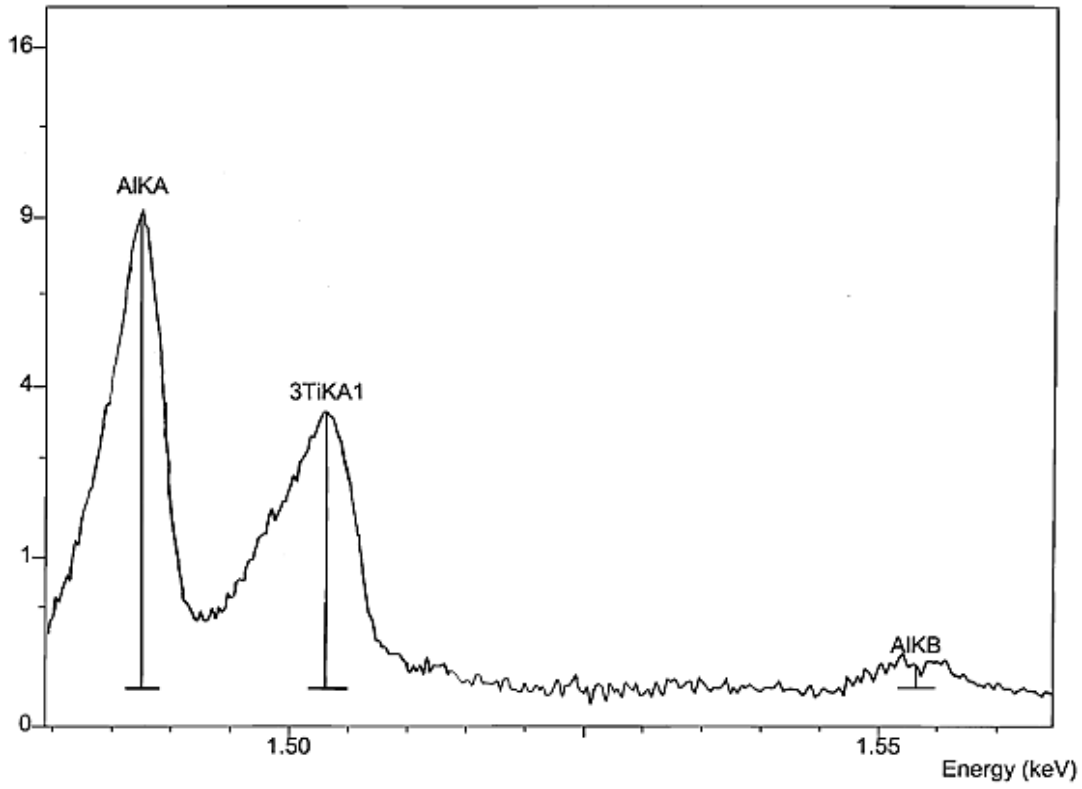
3.1.2.9 Wavelength dispersive x-ray fluorescence spectrometry (WDXRF)

X-ray fluorescence analysis is a rapid, non destructive, qualitative and quantitative method of determining element in solids. This technique is based on the measurement of wavelengths and intensities of x-rays emitted by a sample, when excited by the rays from a primary x-ray tube. It is essentially a surface technique, since the primary beam does not penetrate very far into the specimen. The XRF spectrum of Al-doped TiO_2 samples and B-doped TiO_2 samples are shown in Figures 41 and 42, respectively.

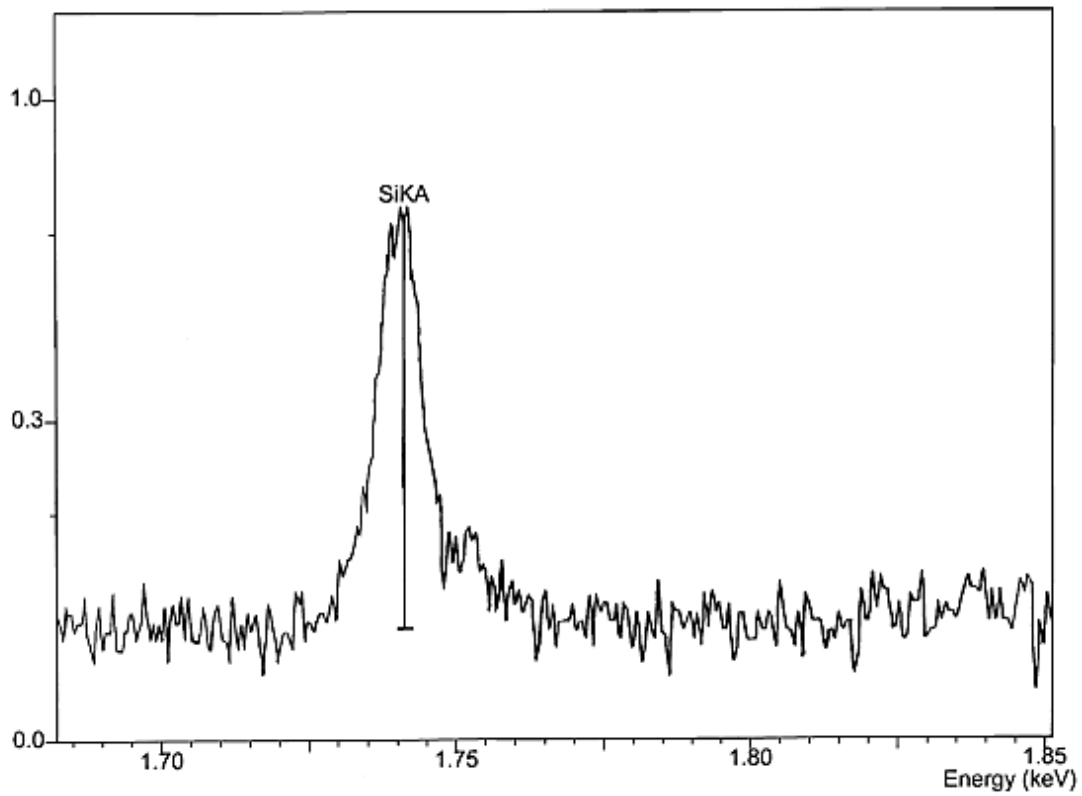
a) Ti peak of Al/ TiO_2



b) Al peak of Al/ TiO_2



c) Si peak of Al/ TiO_2



d) S, Cl peak of Al/ TiO_2

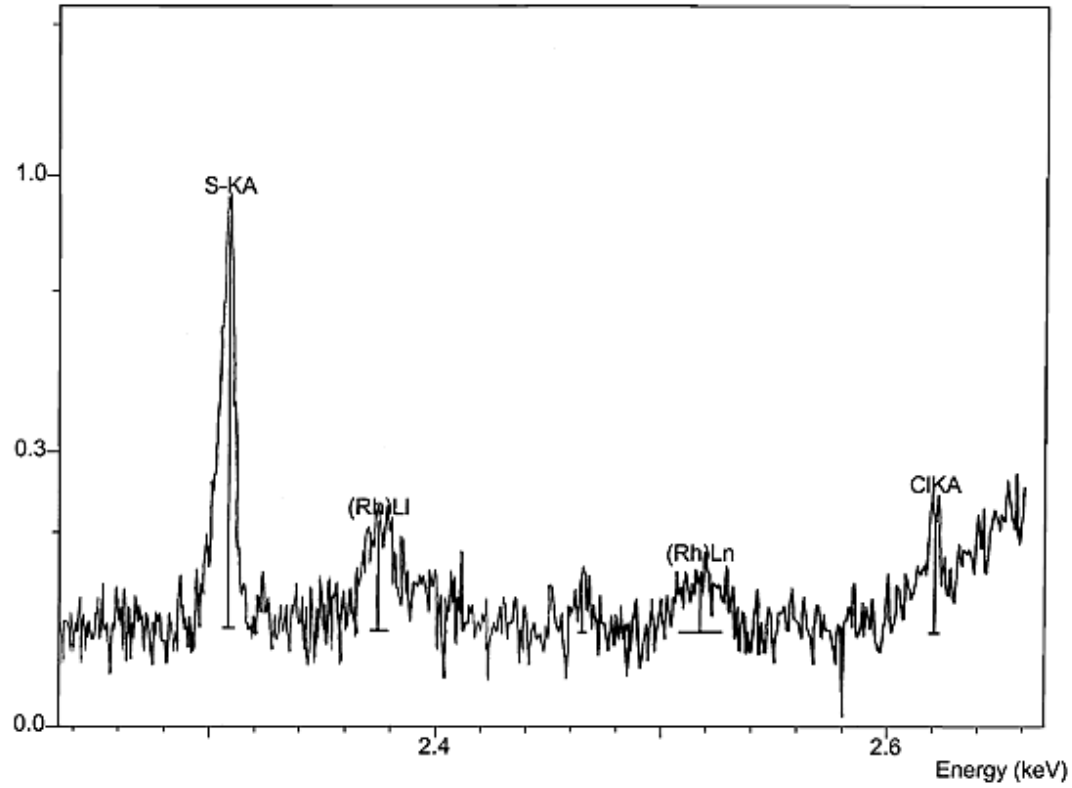
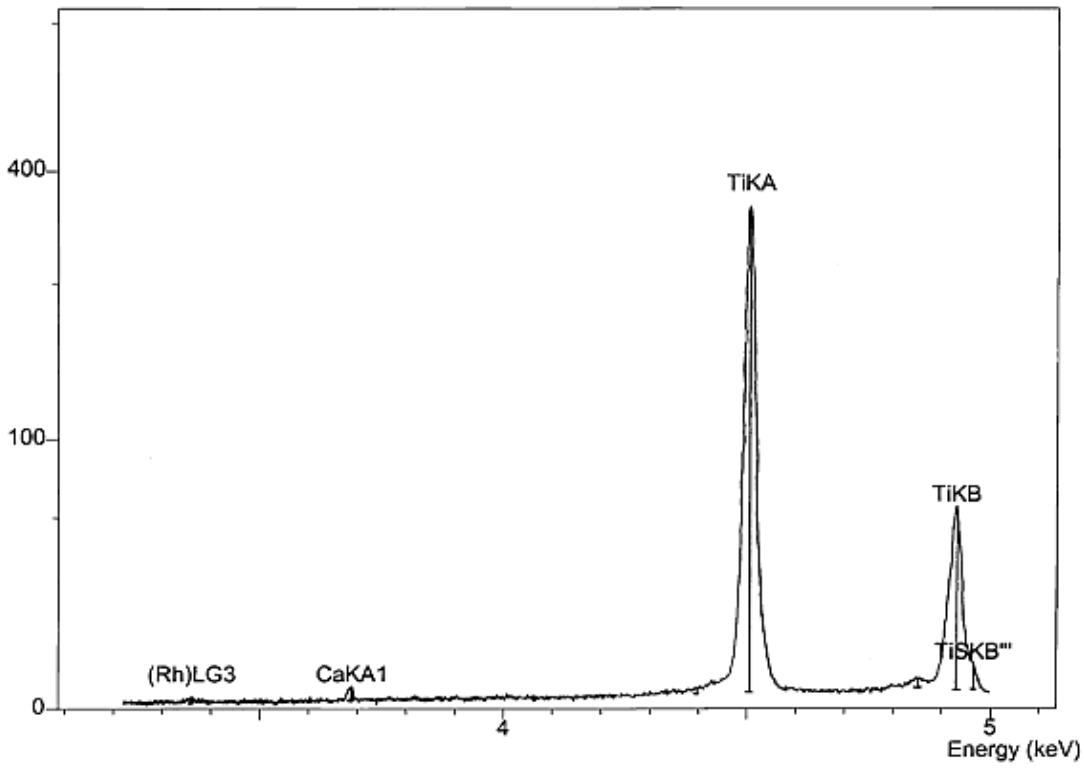


Figure 41 XRF spectrum of Al-doped TiO_2 sample

a) Ti peak of B/ TiO_2



b) Si peak of B/ TiO_2

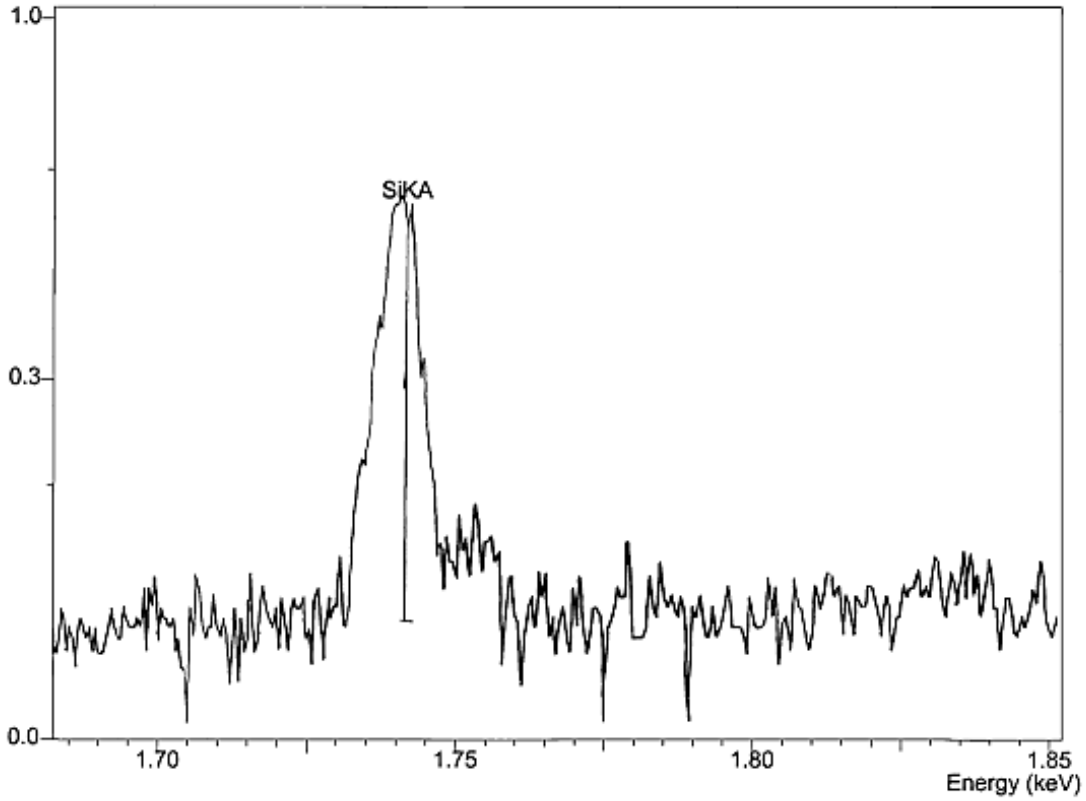


Figure 42 XRF spectrum of B-doped TiO_2 sample

From Figure 41 it appeared that Al-doped TiO_2 sample contained trace amount of Si, S, and Cl (besides the two main elements: Ti and Al). From Figure 42, it was found that the B-doped TiO_2 sample contained trace amount of Ca, Si, and S element (besides the main element: Ti). In this study, the XRF technique could not determine the B element of B-doped TiO_2 sample because of the limitation of the element.

3.2 Photocatalytic activities of methylene blue (MB) by undoped TiO_2, comercial P25-TiO_2 and trivalent (Al,B)-doped TiO_2

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 1.0×10^{-4} M to 1.0×10^{-7} M. in order to construct reliable standard calibration curve of methylene blue, the concentration devided into three ranges: 1.0×10^{-4} M to 1.0×10^{-5} M, 1.0×10^{-5} M to 1.0×10^{-6} M and 1.0×10^{-6} M to 1.0×10^{-7} M. The absorbance of methylene blue solution was measured with SPECORD S100 spectrophotometer. The spectra of methylene blue in these ranges are shown in Figures 43 – 45.

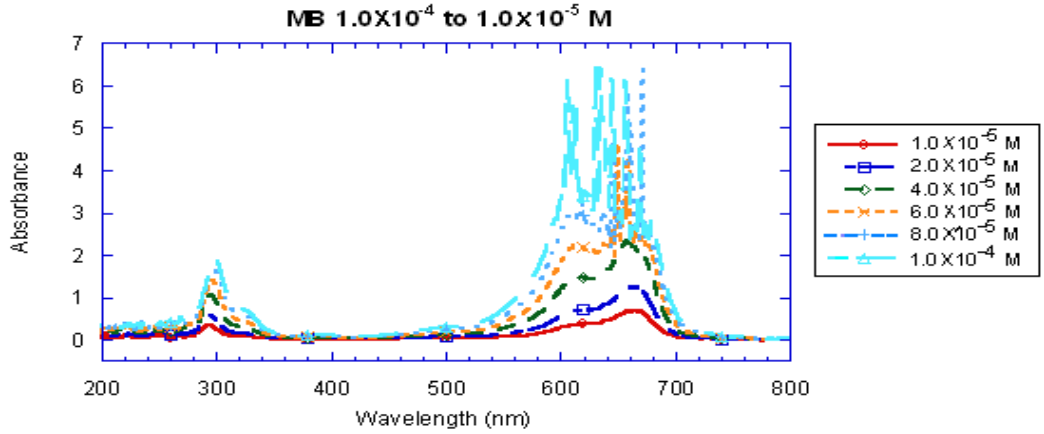


Figure 43 The absorbance of methylene blue in the concentration range of 1.0×10^{-4} M to 1.0×10^{-5} M.

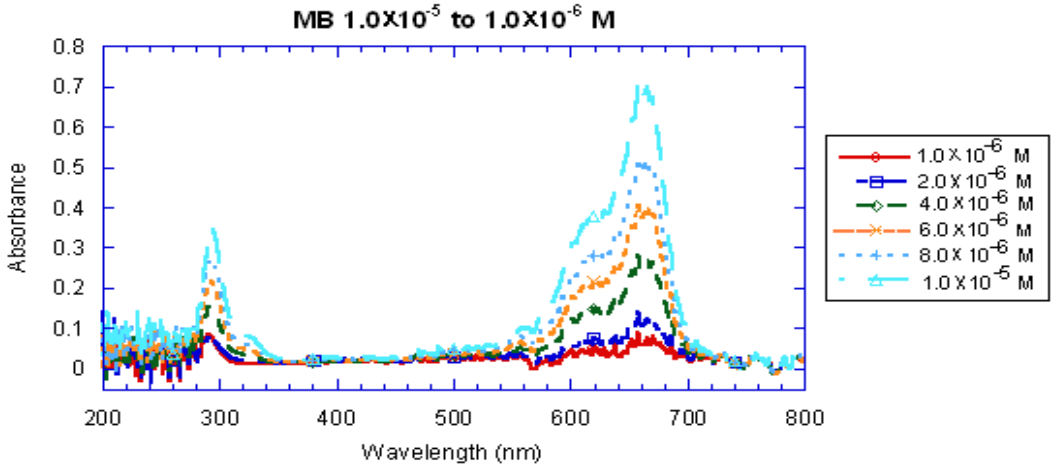


Figure 44 The absorbance of methylene blue in the concentration range of 1.0×10^{-5} M to 1.0×10^{-6} M.

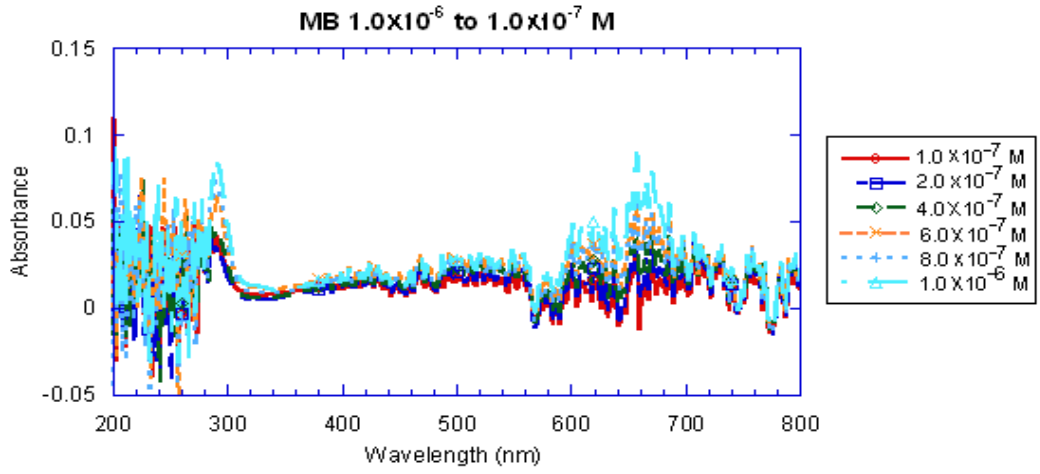


Figure 45 The absorbance of methylene blue in the concentration range of 1.0×10^{-6} M to 1.0×10^{-7} M.

The standard calibration curves of methylene blue solution in the range of 1.0×10^{-4} M to 1.0×10^{-5} M and 1.0×10^{-5} M to 1.0×10^{-7} M are shown in Figures 46-47.

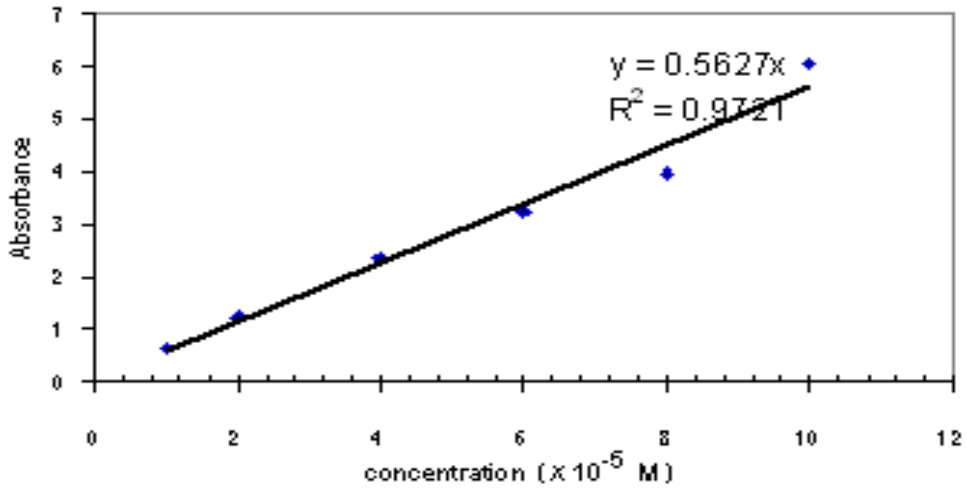


Figure 46 The standard calibration curve of methylene blue in the concentration range of 1.0×10^{-4} M to 1.0×10^{-5} M.

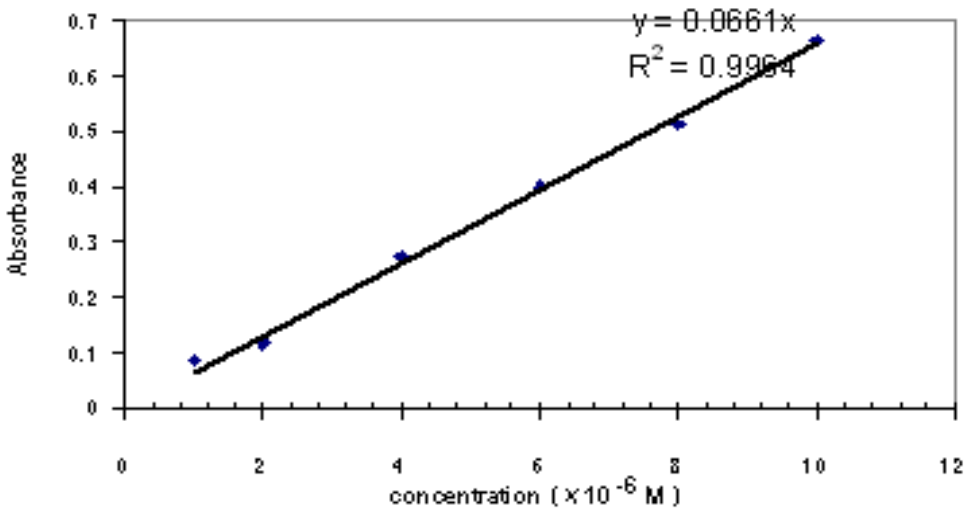


Figure 47 The standard calibration curve of methylene blue in the concentration range of 1.0×10^{-5} M to 1.0×10^{-7} M.

The standard calibration curve of methylene blue solution in the range of 1.0×10^{-6} M to 1.0×10^{-7} M does not conform to a good straight line due to large fluctuation in the measurement of concentration of methylene blue in 1.0×10^{-6} M to 1.0×10^{-7} M range which are almost colorless as shown in Figures 46-48.

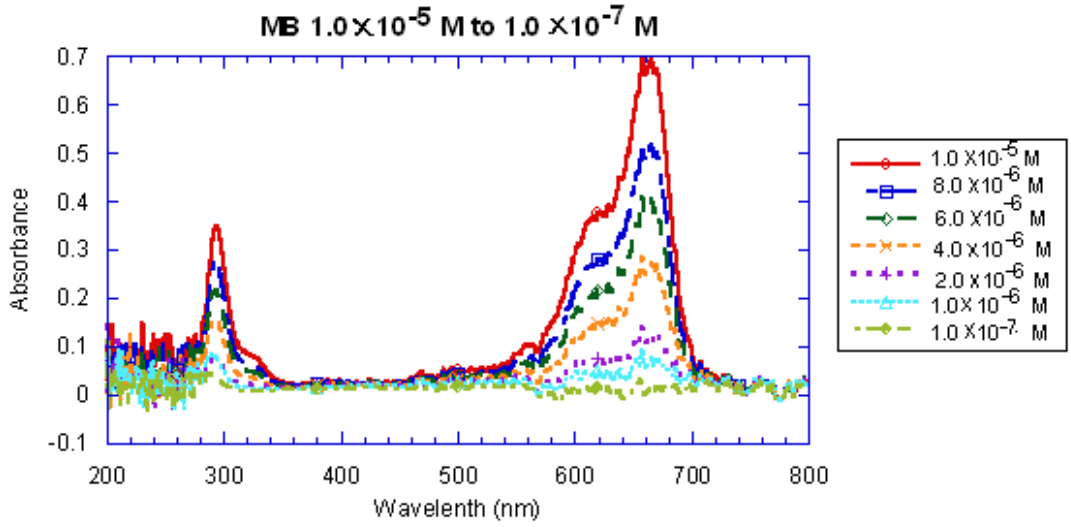
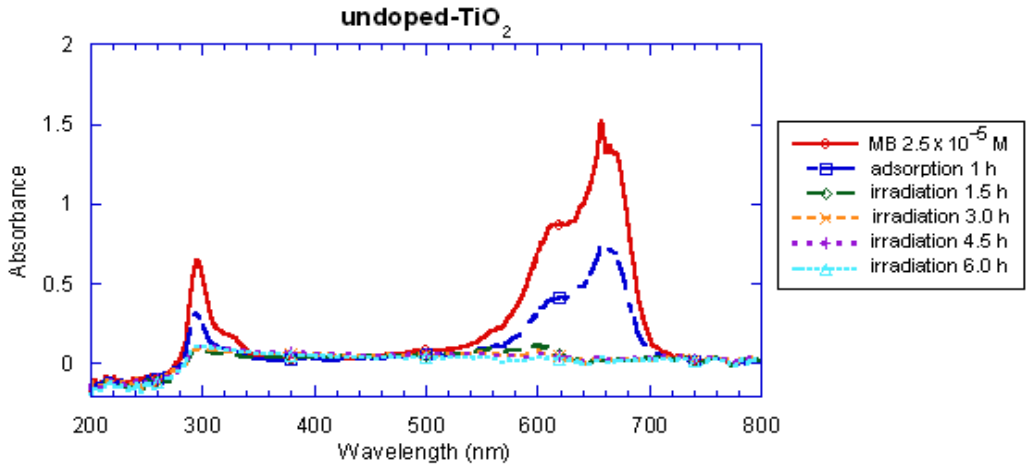


Figure 48 The absorbance of methylene blue in the concentration range of 1.0×10^{-5} M to 1.0×10^{-7} M.

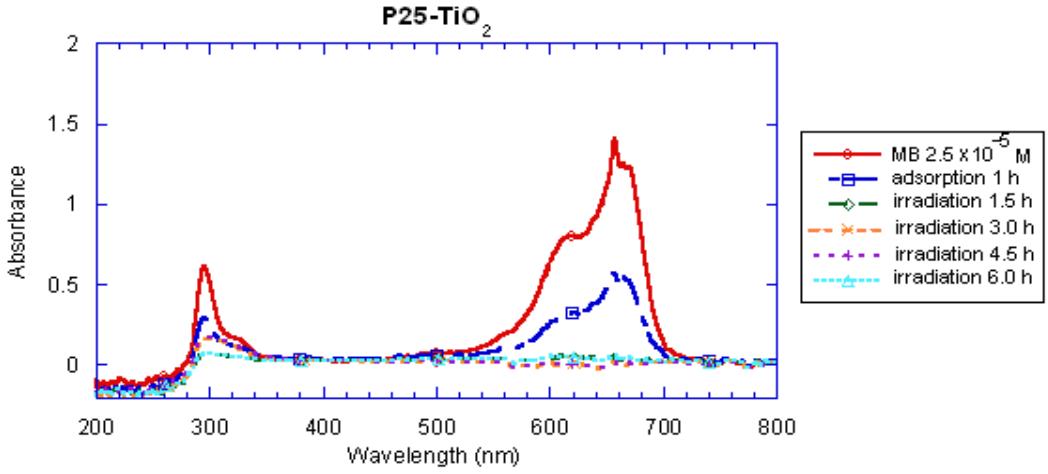
3.2.2 The experiment for photocatalytic degration of methylene blue by undoped TiO_2, comercial P25-TiO_2 and trivalent (Al, B)-doped TiO_2

In the photocatalysis studies, the mixed synthesized TiO_2 with methylene blue solution (MB 2.5×10^{-5} M) it was found that the adsorption of methylene blue on the catalyst surface takes place instantly prior to the photocatalytic measurements. Since the purpose was to test and compare the photocatalytic activity alone, so the first adsorption stage must be excluded by allowing the TiO_2 samples (undoped TiO_2, comercial P25-TiO_2 and trivalent (Al, B)-doped TiO_2) to adsorbed MB until reaching their adsorption equilibrium prior to irradiation with UV light in tightly closed wooden compartment (0.5 m×0.5 m×0.5 m).The results from this photocatalytic experiment of Al-doped TiO_2 samples and B-doped TiO_2 samples are shown in Figures 49 and 50, respectively.

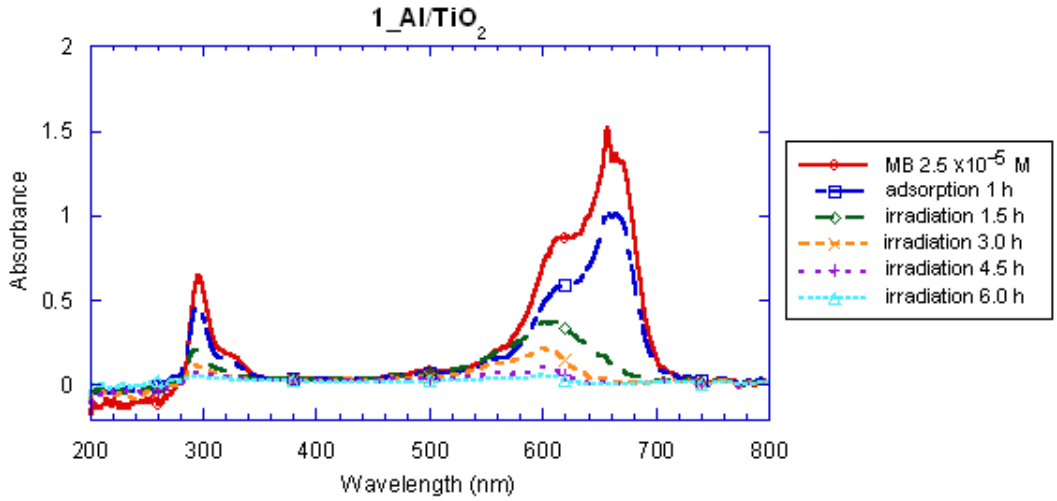
a) undoped TiO_2



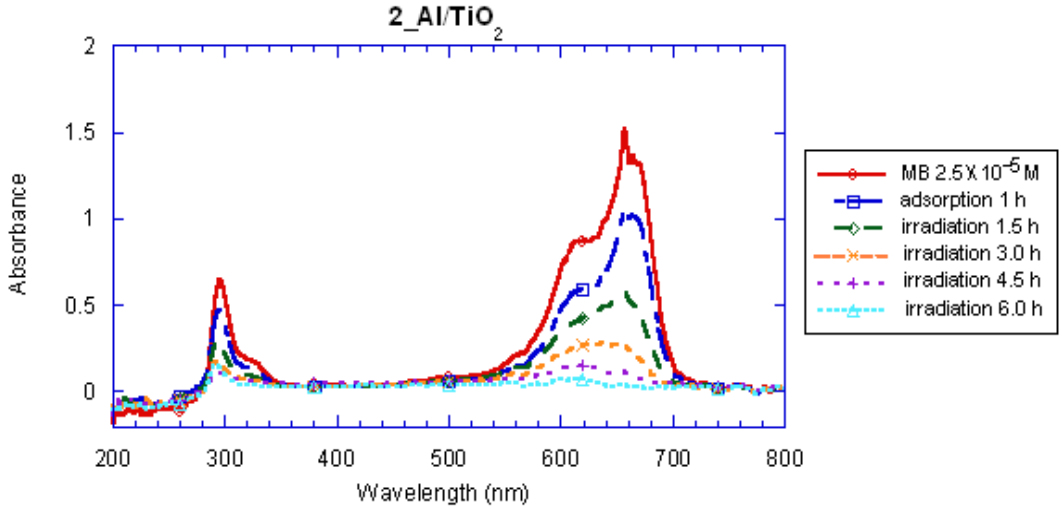
b) P25-TiO_2



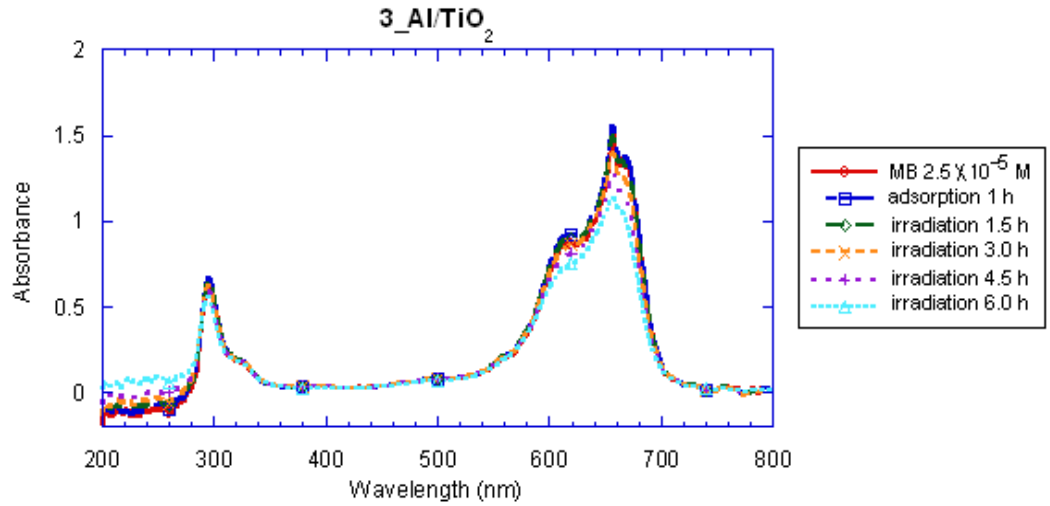
c) 1_Al/TiO_2



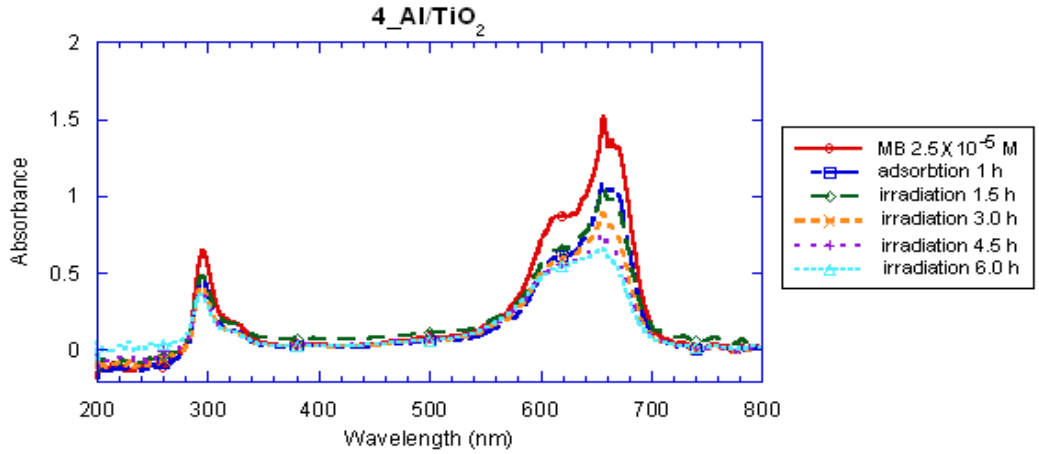
d) 2_Al/TiO_2



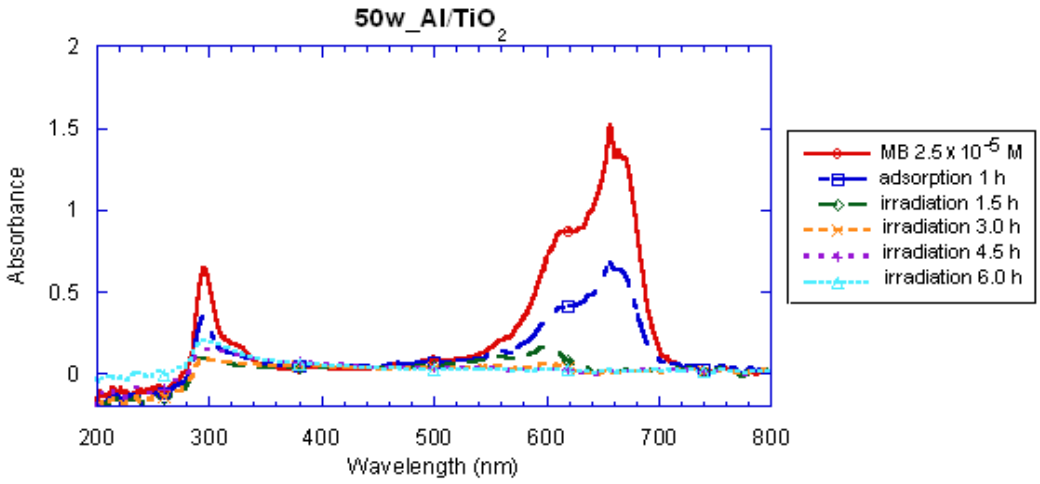
e) 3_Al/TiO_2



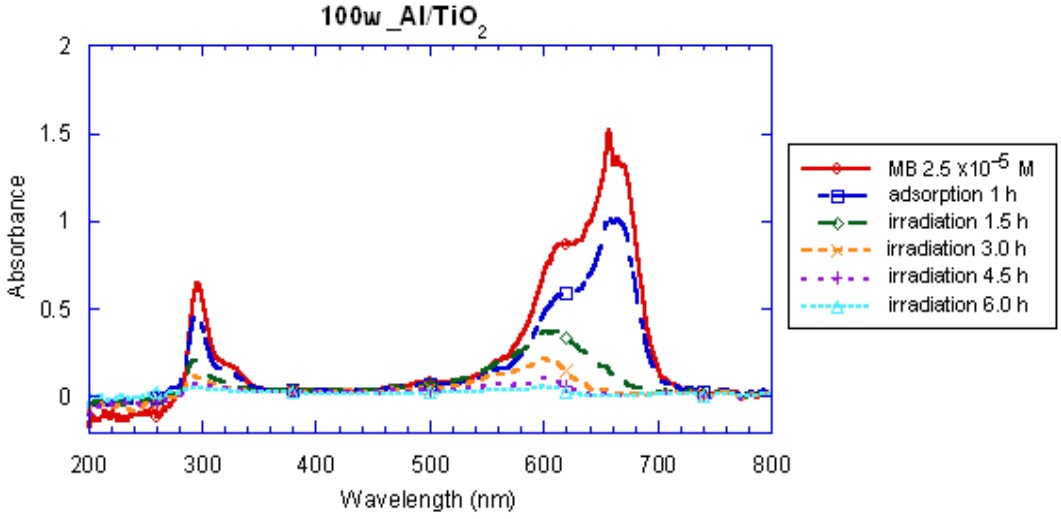
f) 4_Al/TiO_2



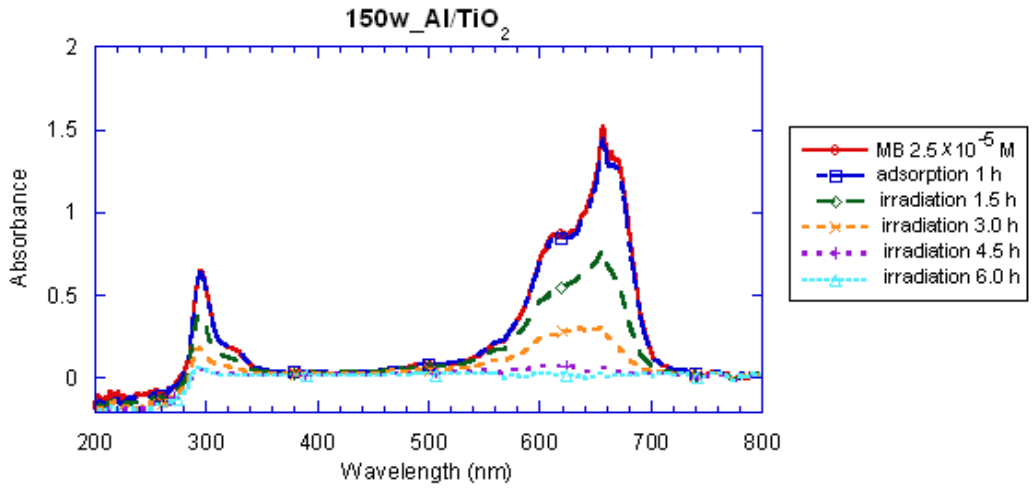
g) 50w_Al/TiO_2



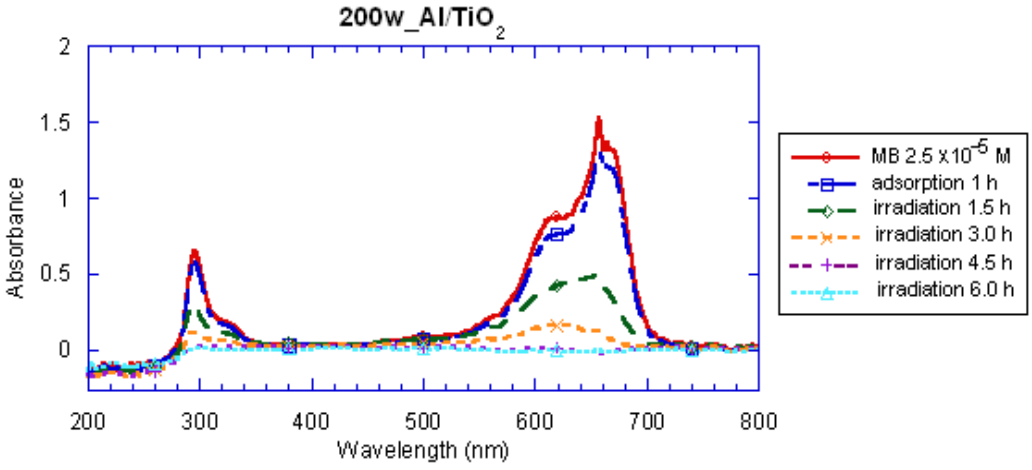
h) 100w_Al/TiO_2



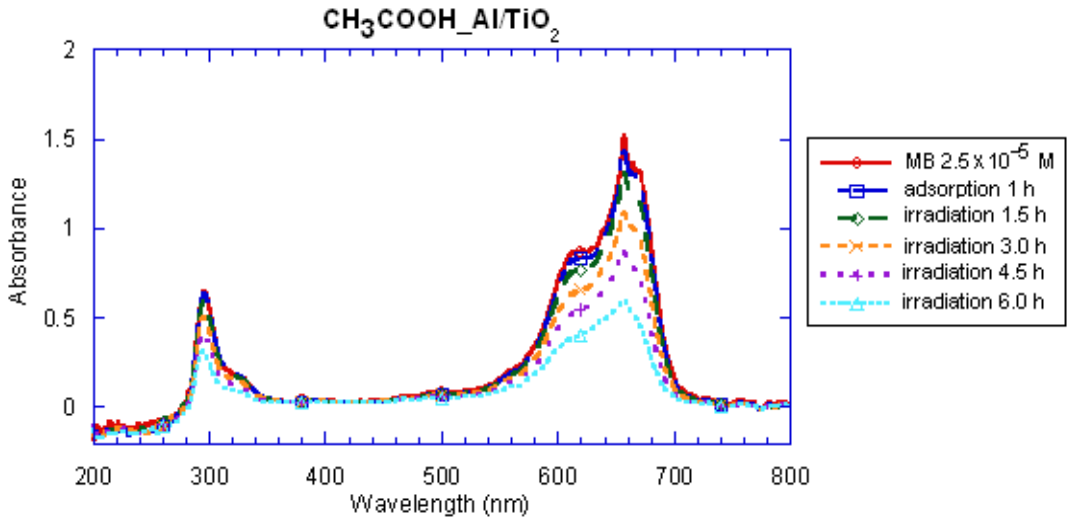
i) 150w_Al/TiO_2



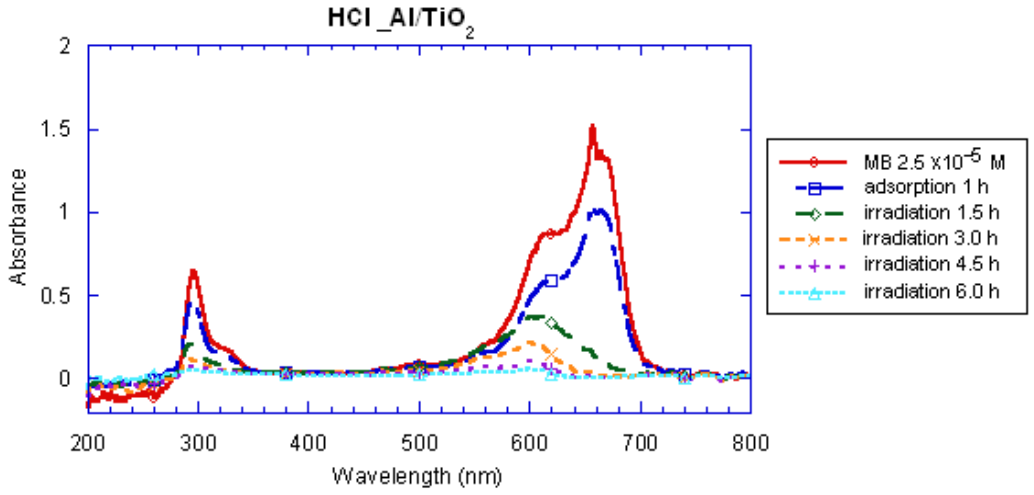
j) 200w_Al/TiO_2



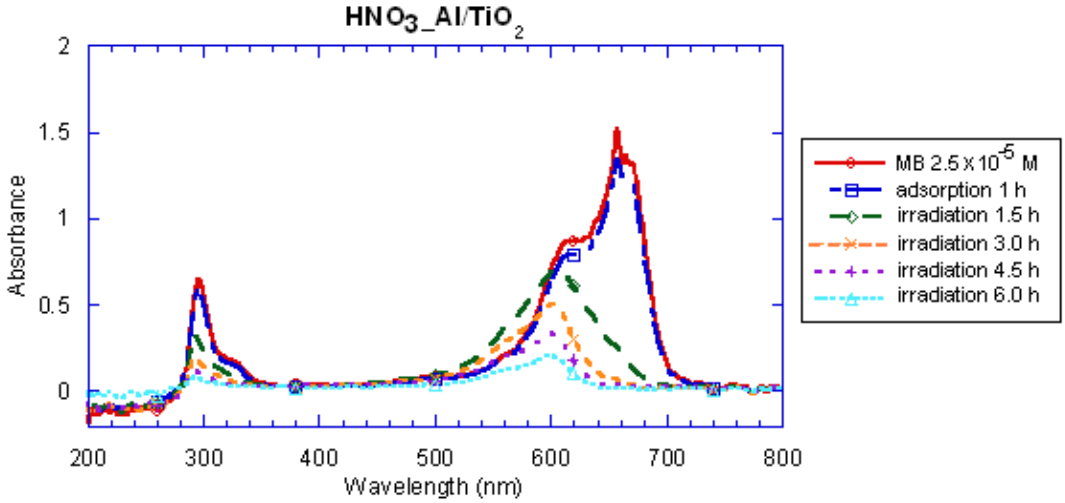
k) CH_3COOH_ Al/TiO_2



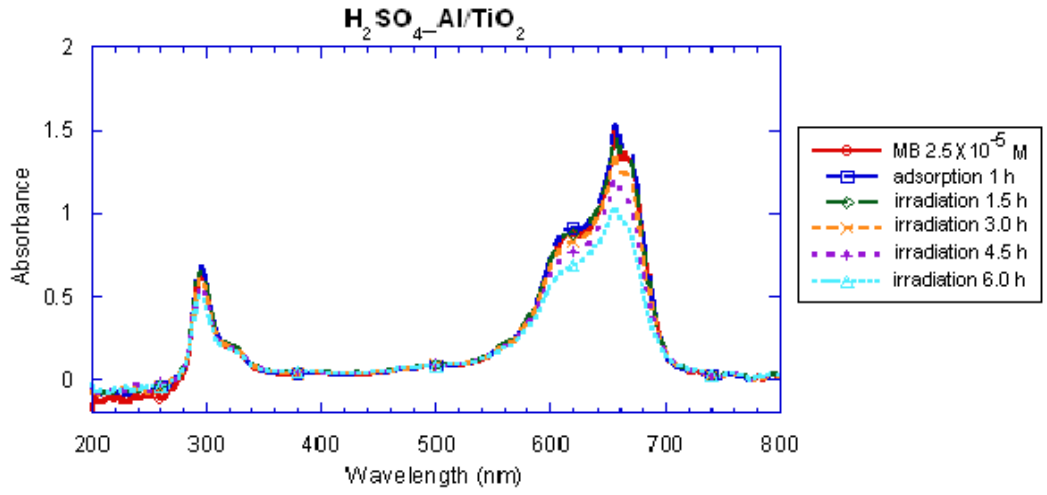
l) HCl_ Al/TiO_2



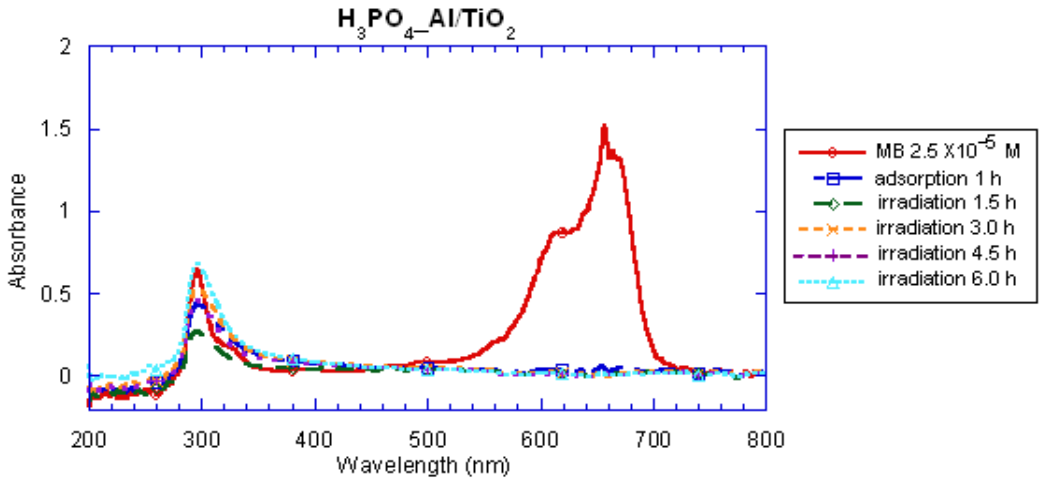
m) HNO_3_ Al/TiO_2



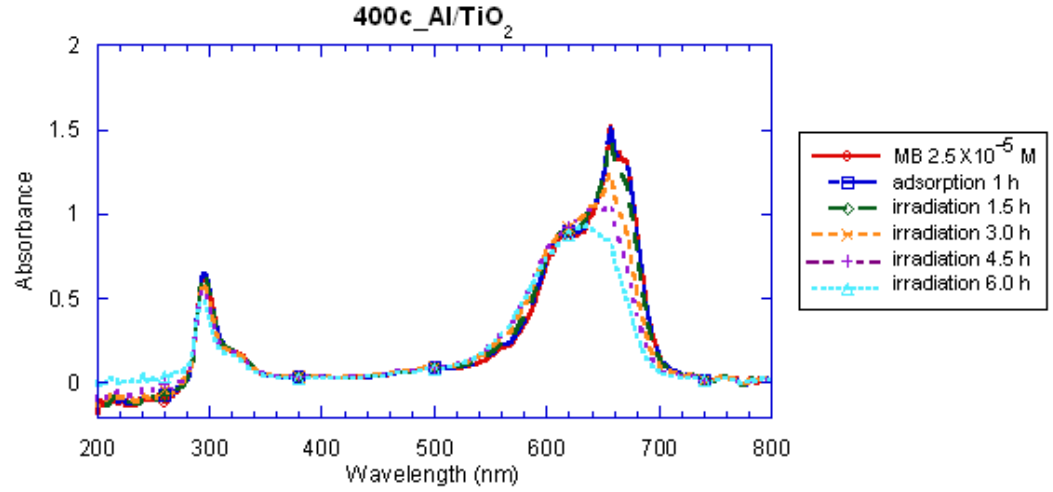
n) H_2SO_4_ Al/TiO_2



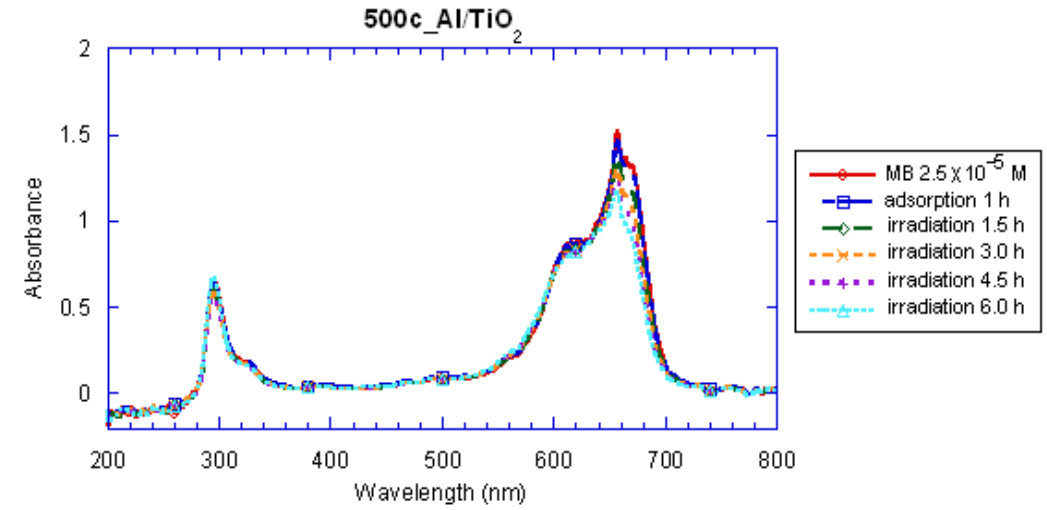
o) H_3PO_4_ Al/TiO_2



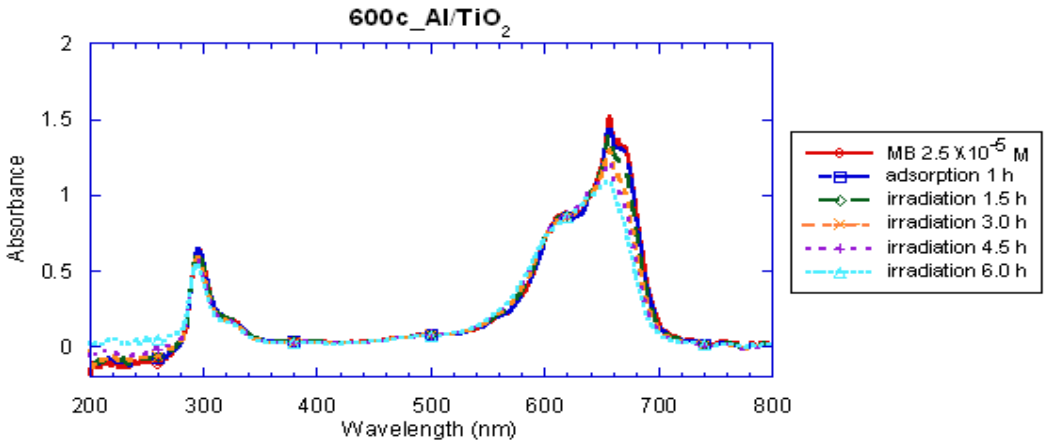
p) 400c_ Al/TiO_2



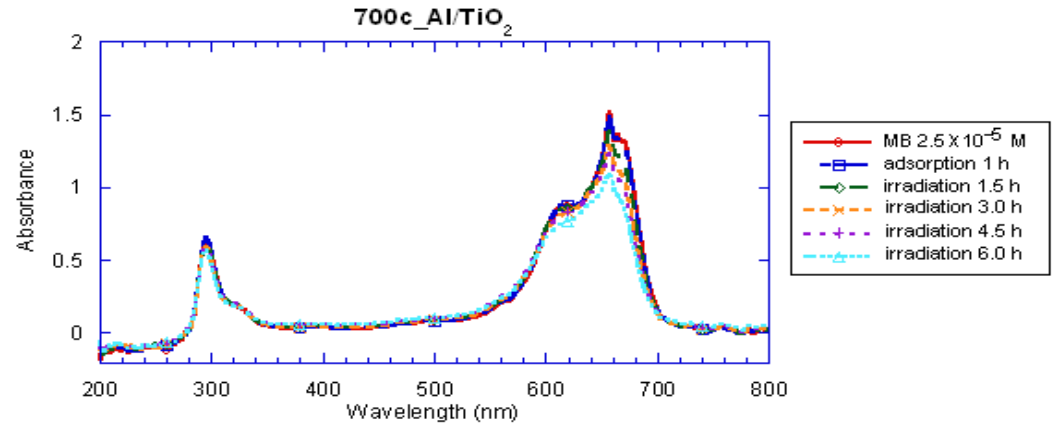
q) 500c_ Al/TiO_2



r) 600c_ Al/TiO_2



s) 700c_ Al/TiO_2



t) 800c_ Al/TiO_2

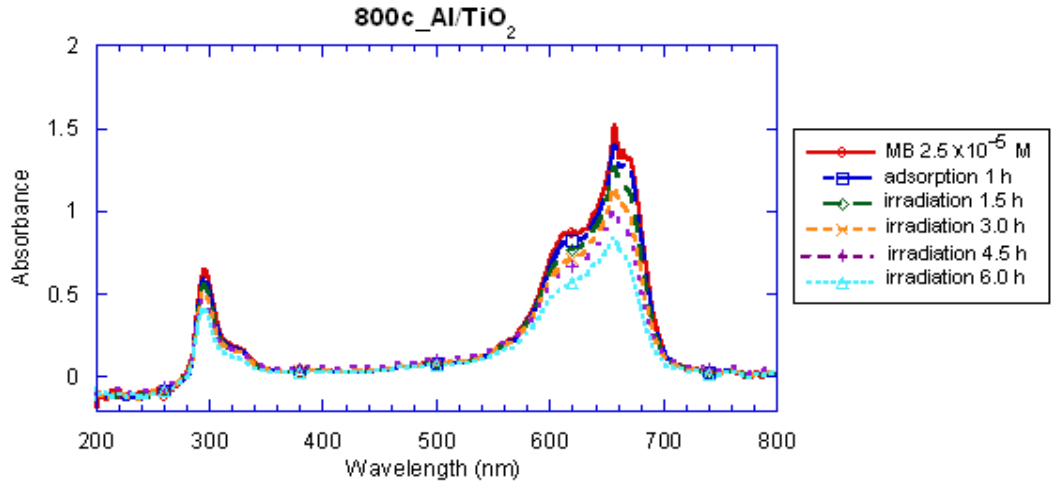
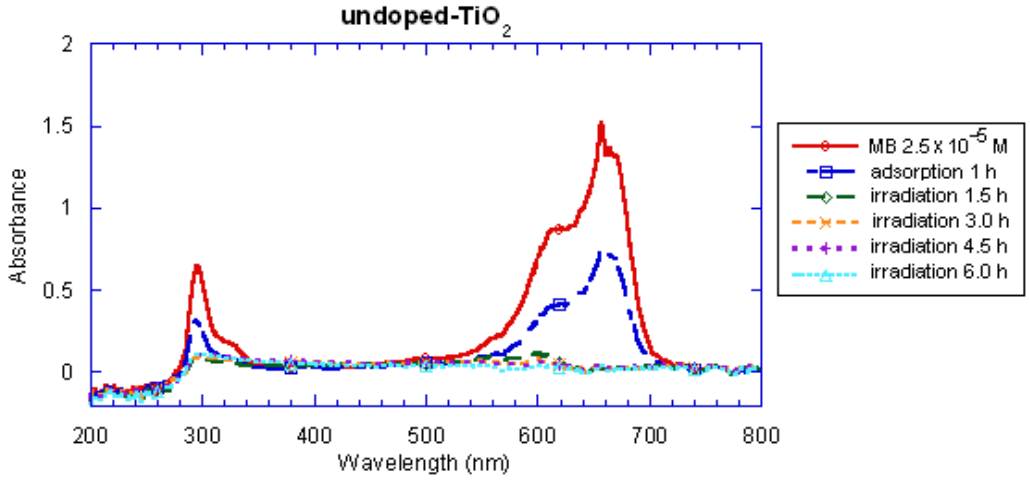
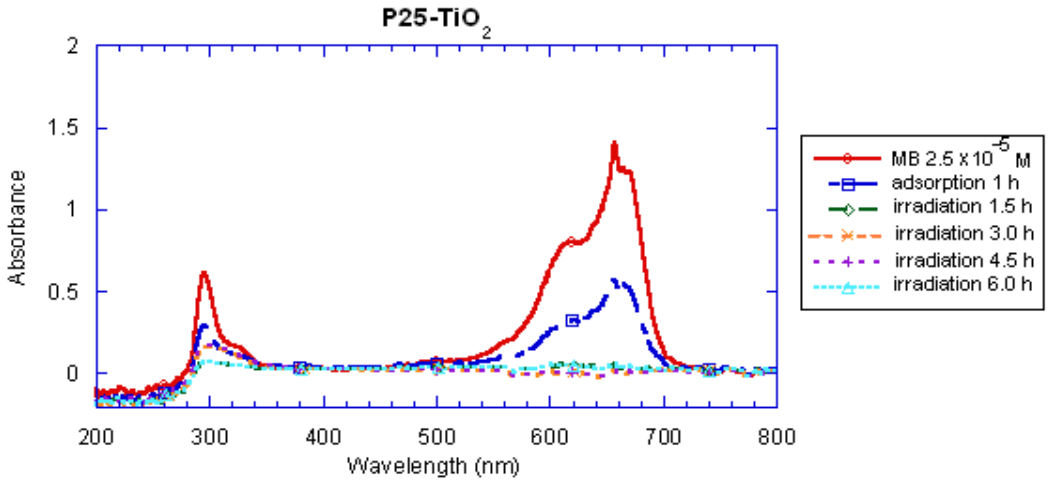


Figure 49 The UV-Vis spectral change of methylene blue in synthesized Al-doped TiO_2 samples suspension as a function of time of irradiation.

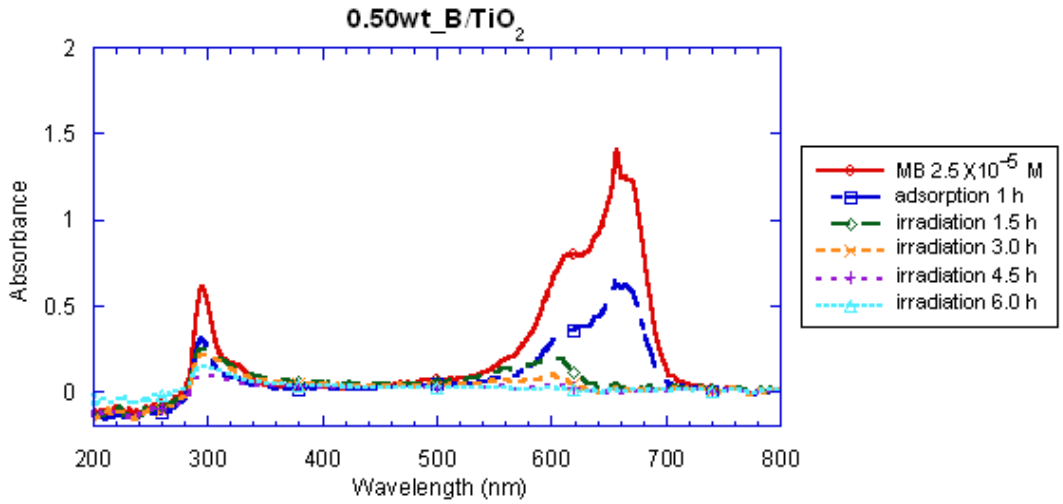
a) undoped TiO_2



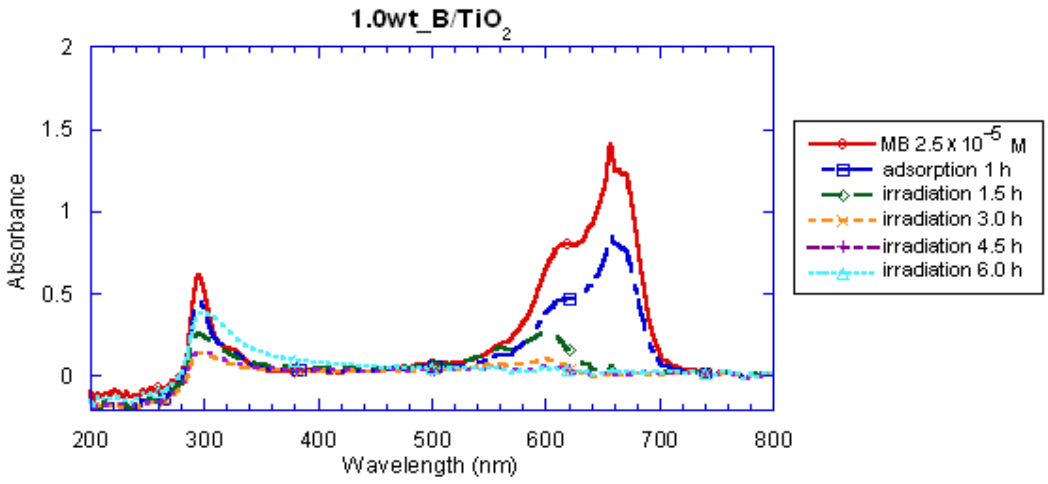
b) P25- TiO_2



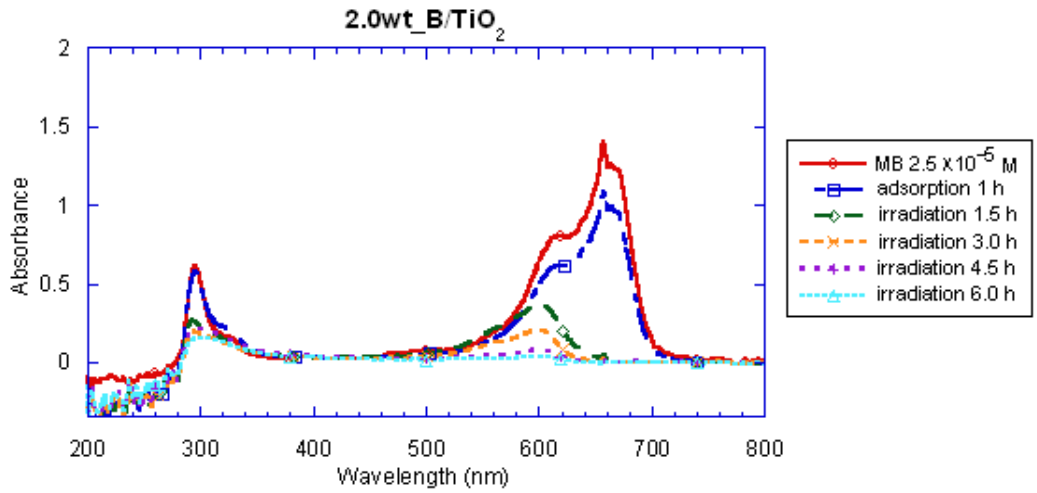
c) 0.5wt_B/ TiO_2



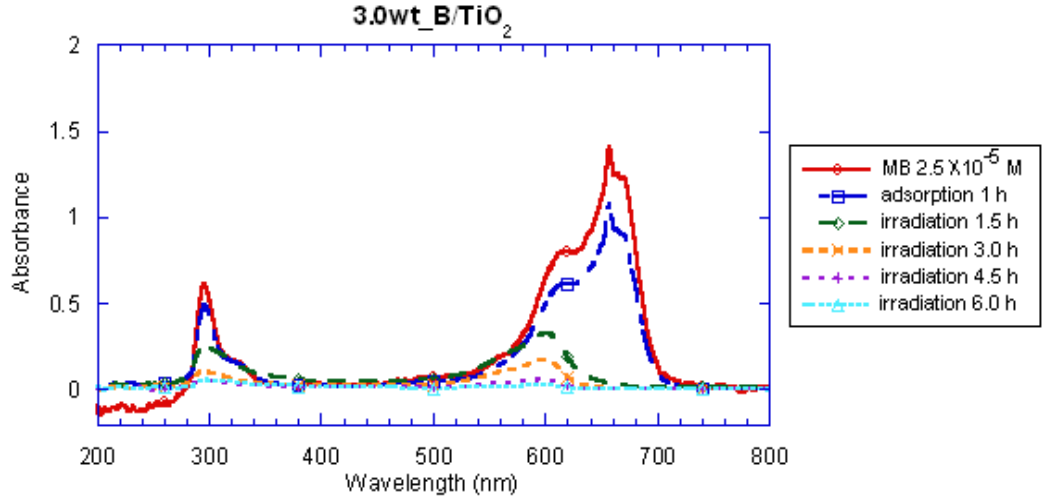
d) 1.0wt_ B/ TiO_2



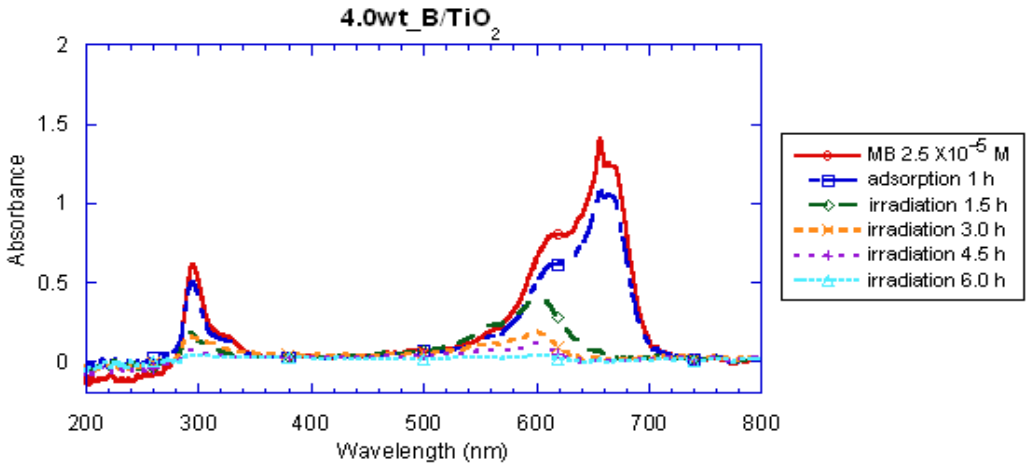
e) 2.0wt_ B/ TiO_2



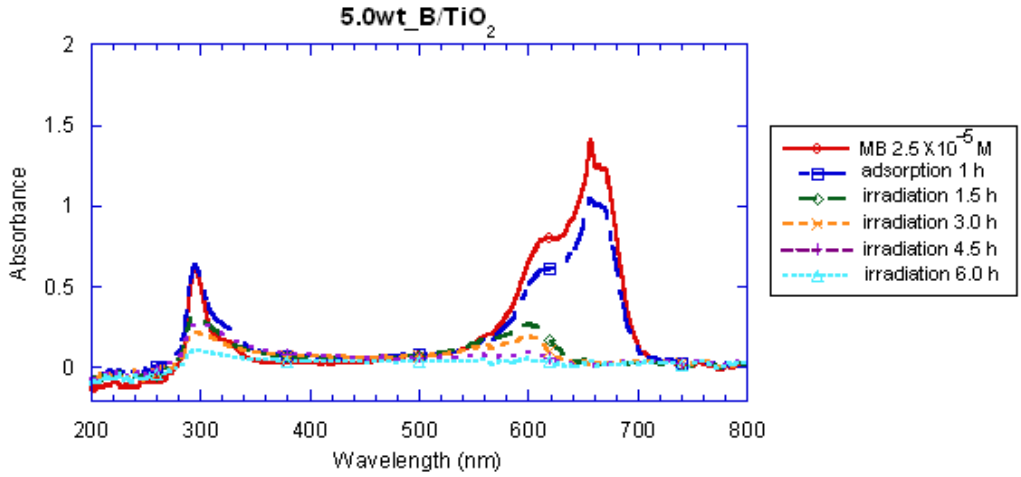
f) 3.0wt_ B/ TiO_2



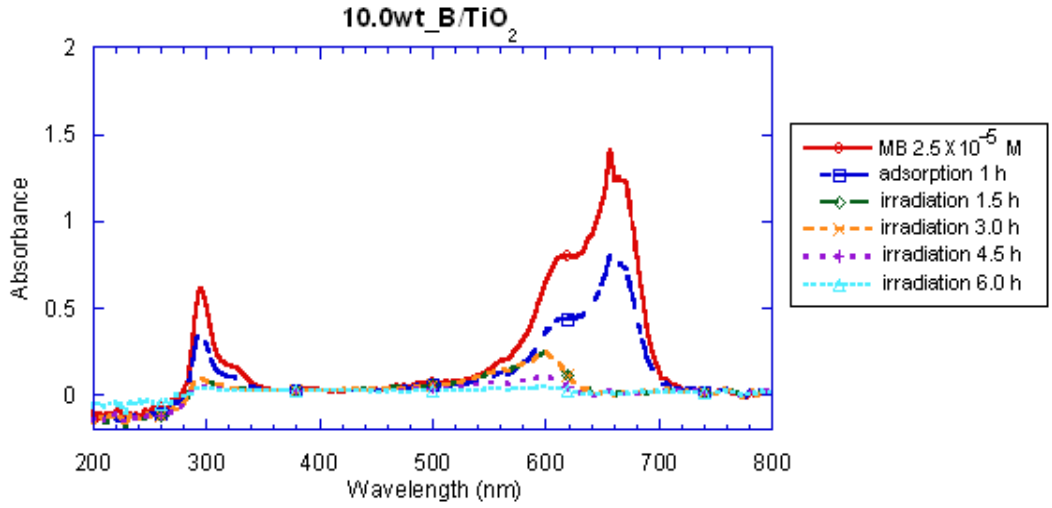
g) 4.0wt_ B/ TiO_2



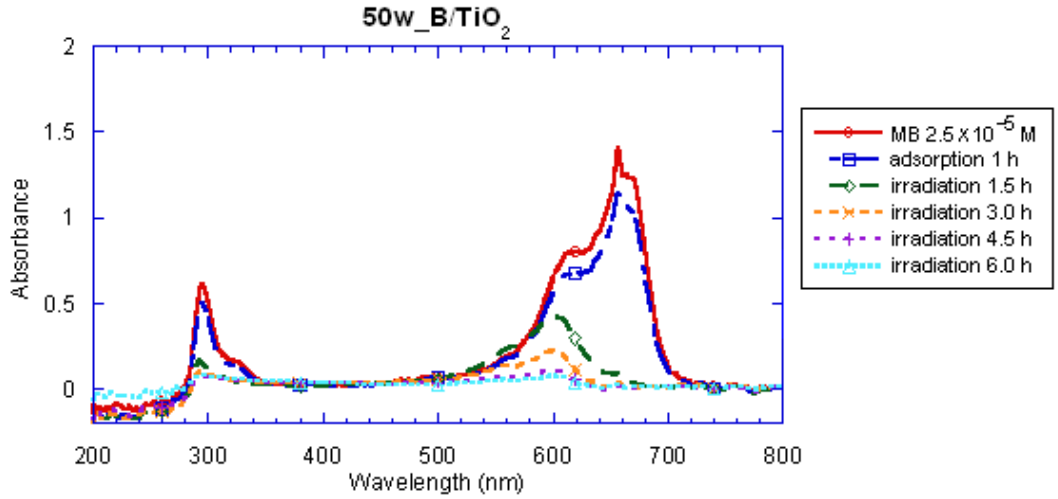
h) 5.0wt_ B/ TiO_2



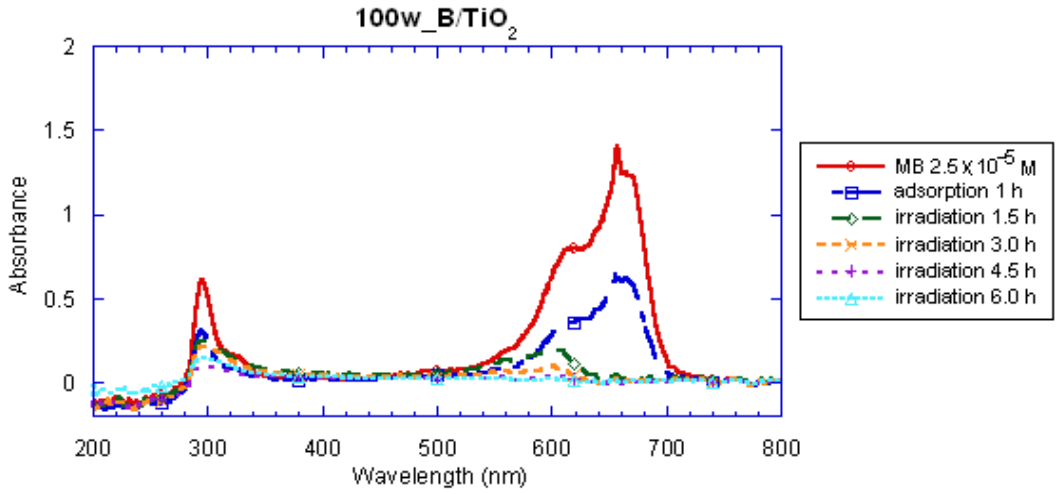
i) 10.0wt_ B/ TiO_2



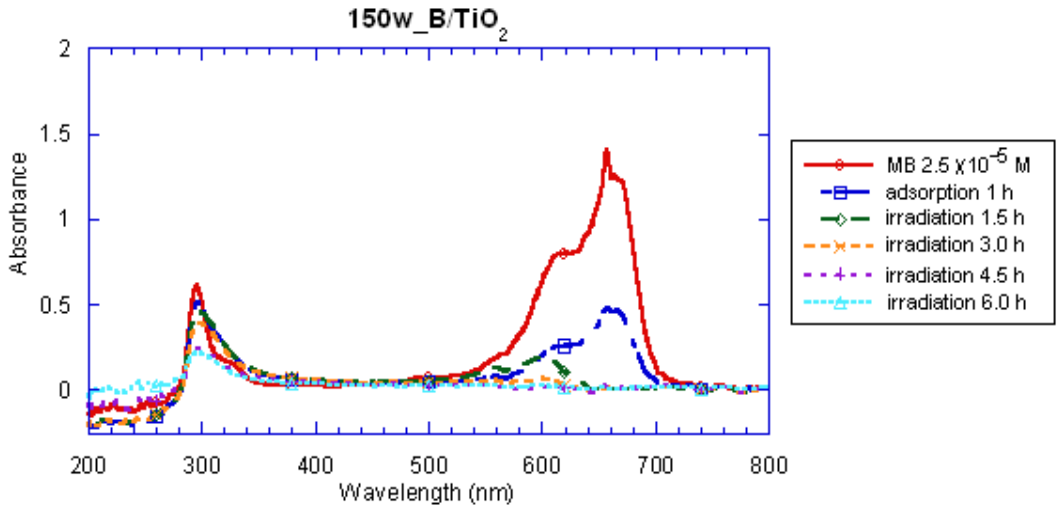
j) 50w_ B/ TiO_2



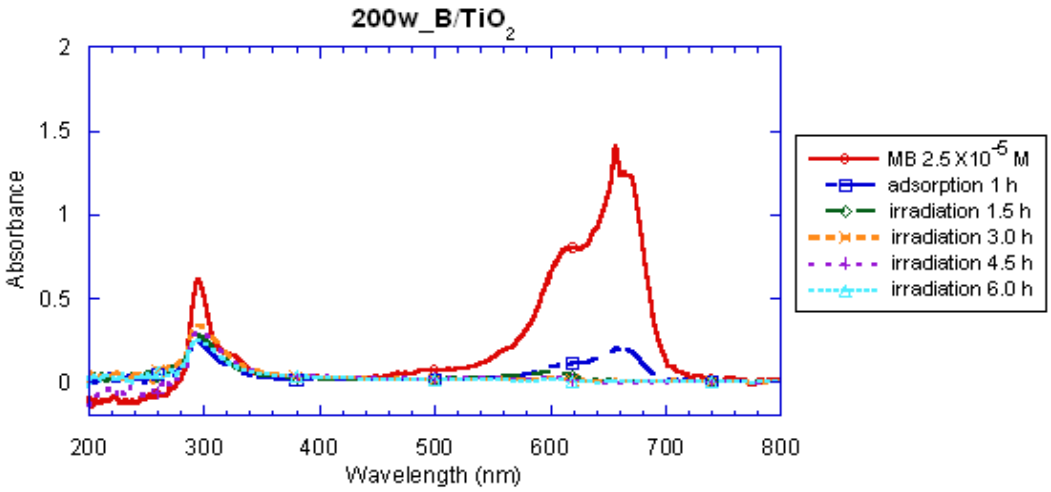
k) 100w_ B/ TiO_2



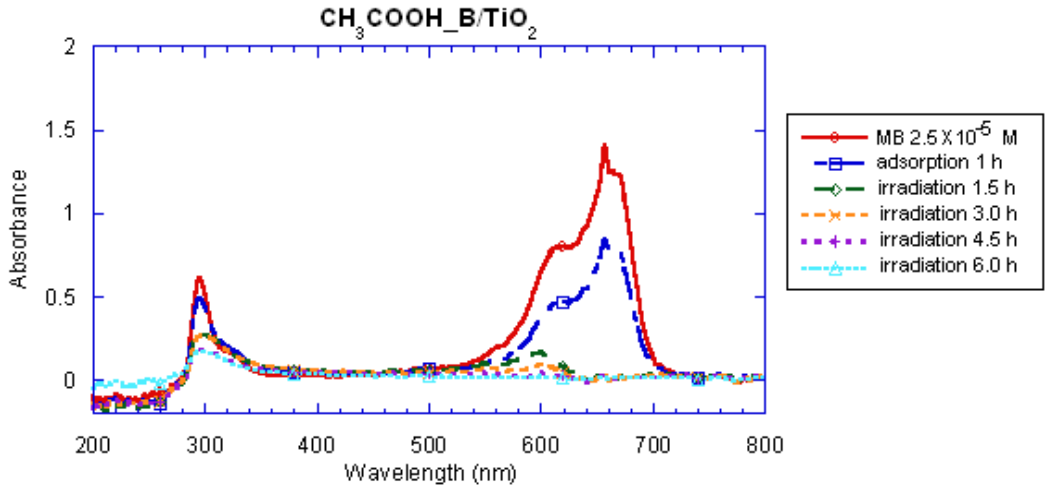
l) 150w_ B/ TiO_2



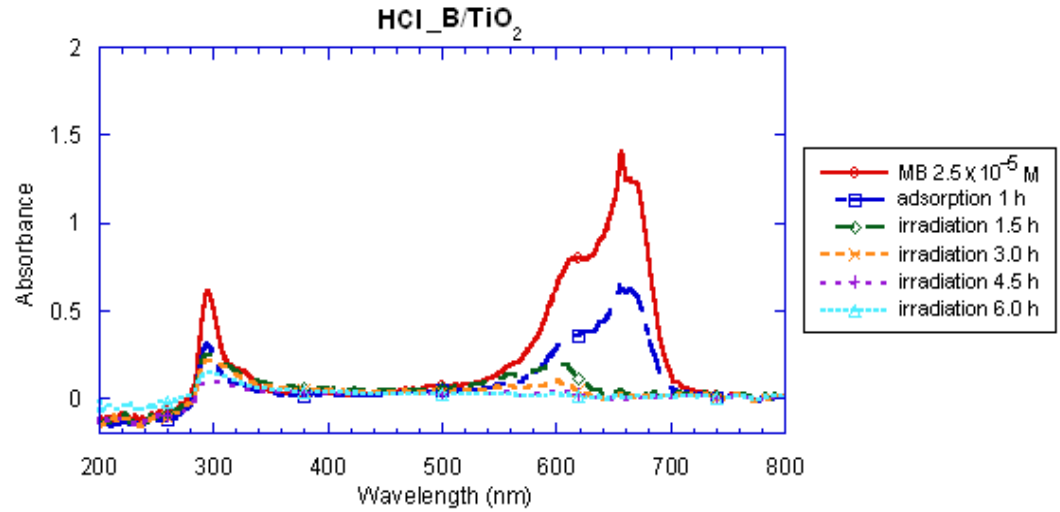
m) 200w_ B/ TiO_2



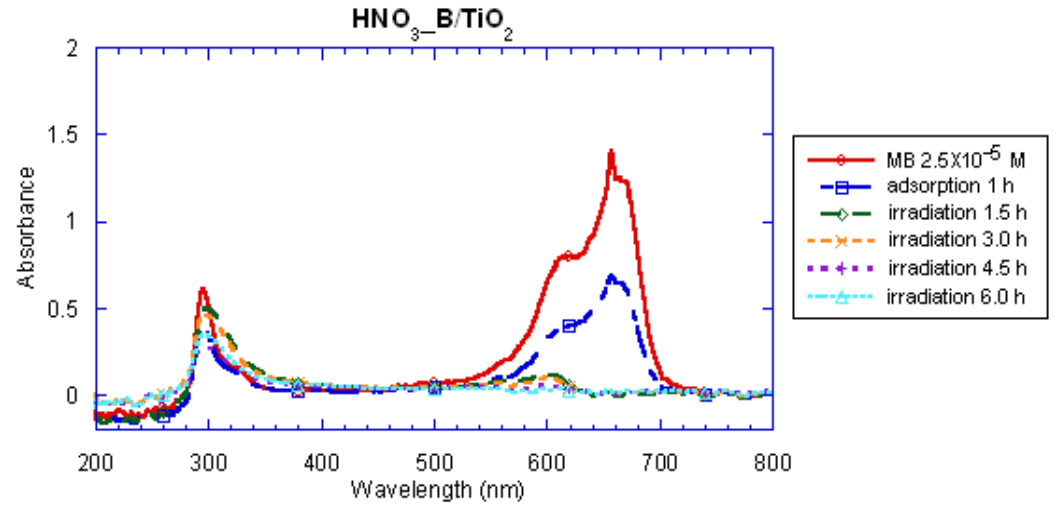
n) CH_3COOH_ B/ TiO_2



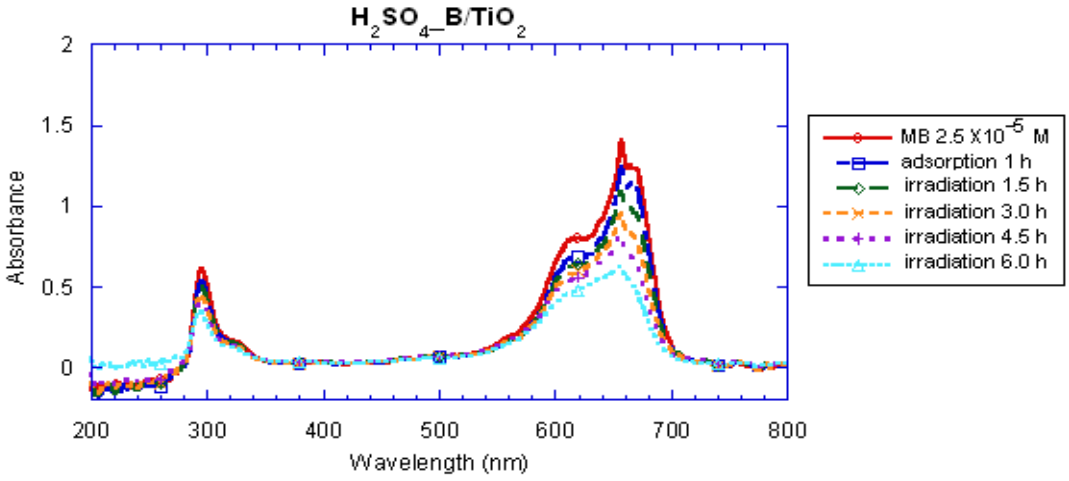
o) HCl_ B/ TiO_2



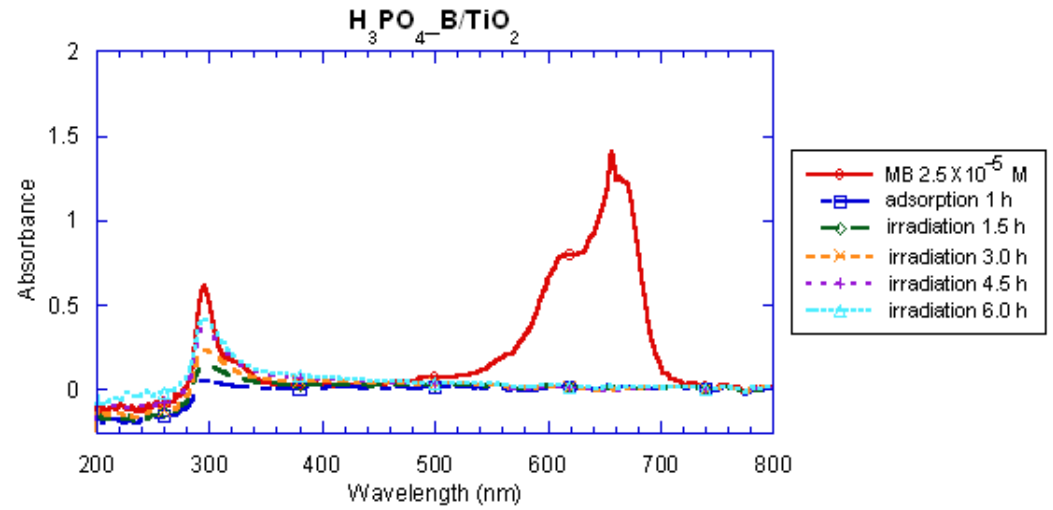
p) HNO_3_ B/ TiO_2



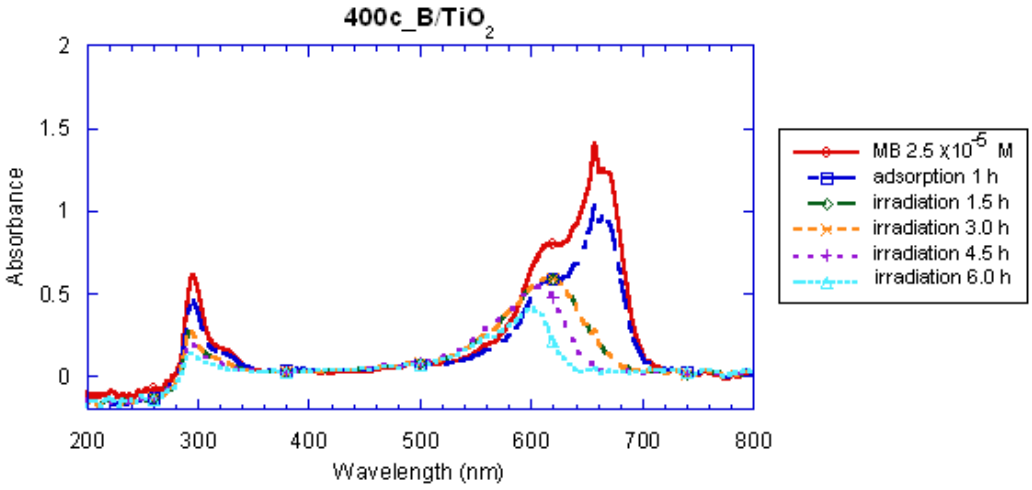
q) H_2SO_4_ B/ TiO_2



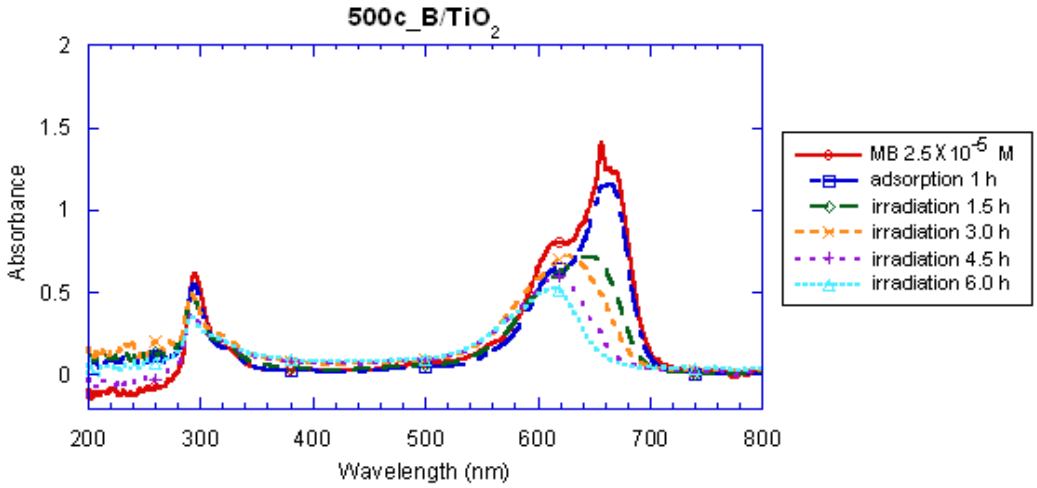
r) H_3PO_4_ B/ TiO_2



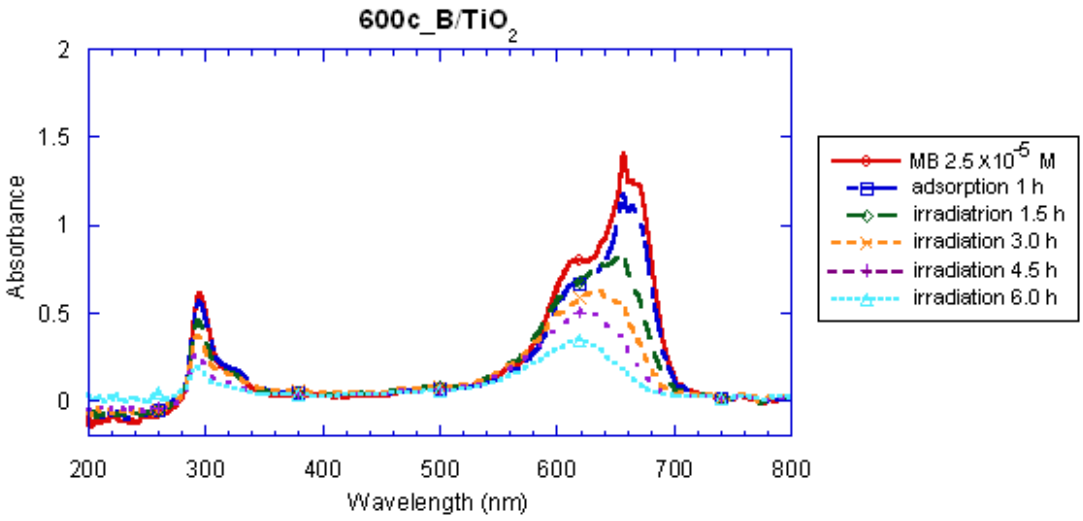
s) 400c_ B/ TiO_2



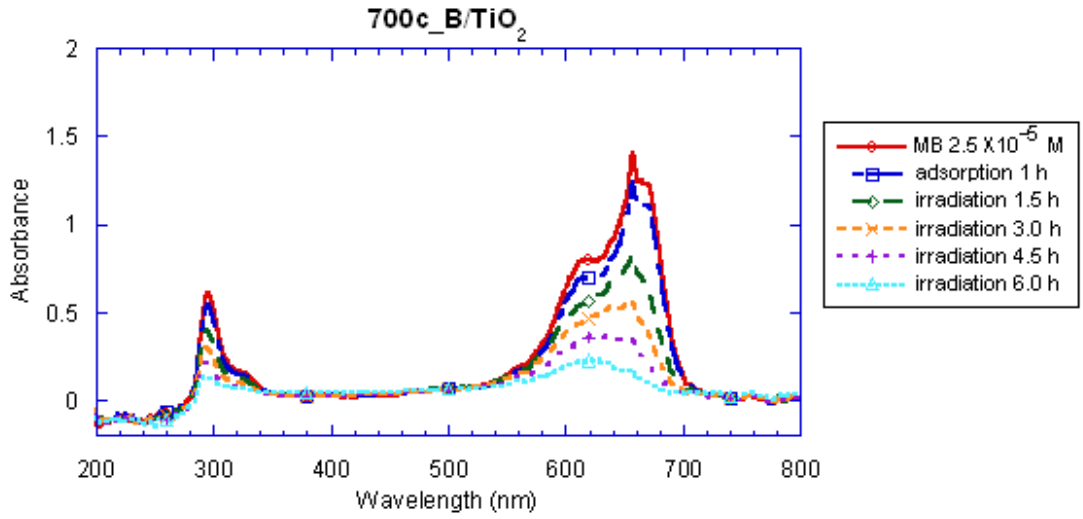
t) 500c_ B/ TiO_2



u) 600c_ B/ TiO_2



v) 700c_ B/ TiO_2



w) 800c_ B/ TiO_2

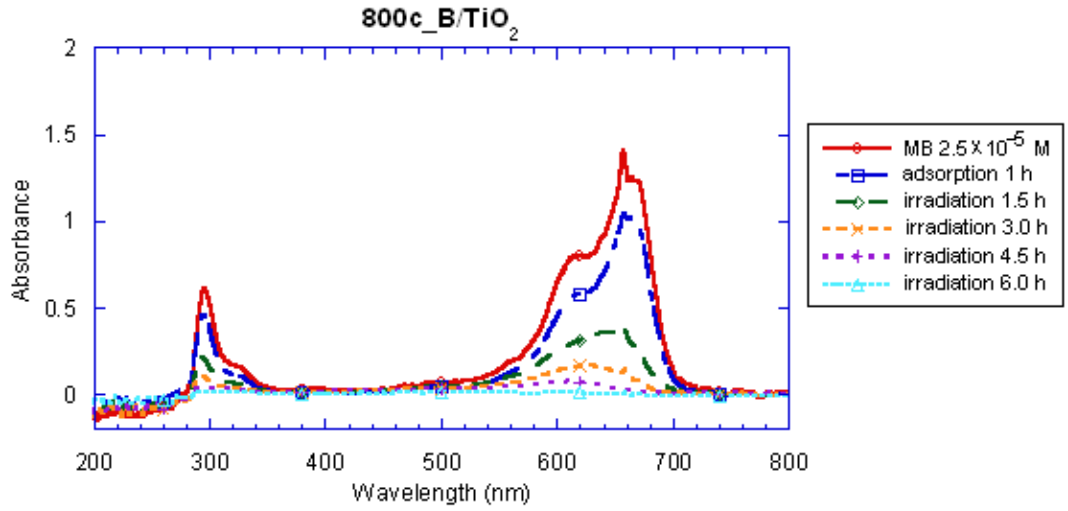
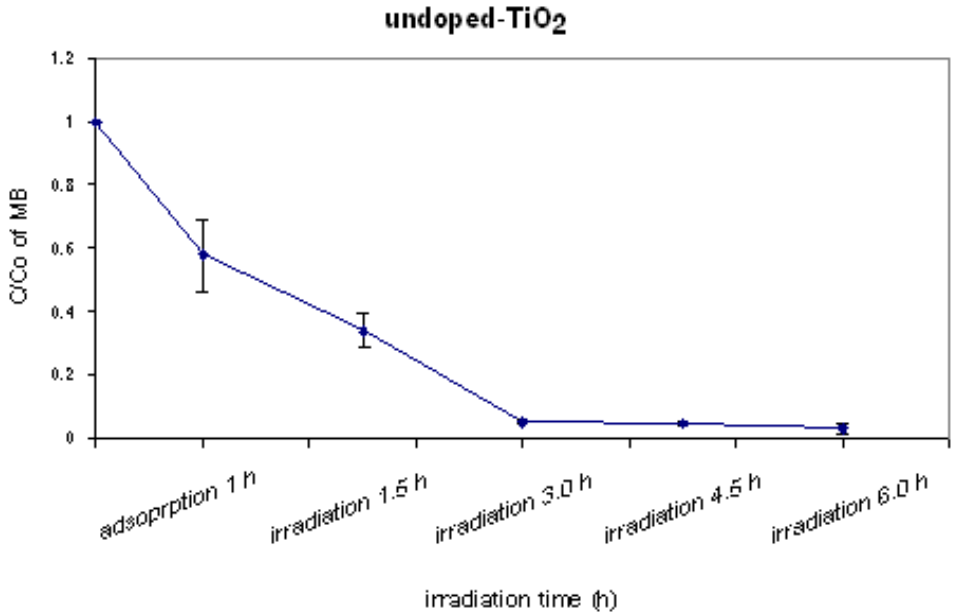


Figure 50 The UV-Vis spectral change of methylene blue in synthesized B-doped TiO_2 samples suspension as a function of time of irradiation.

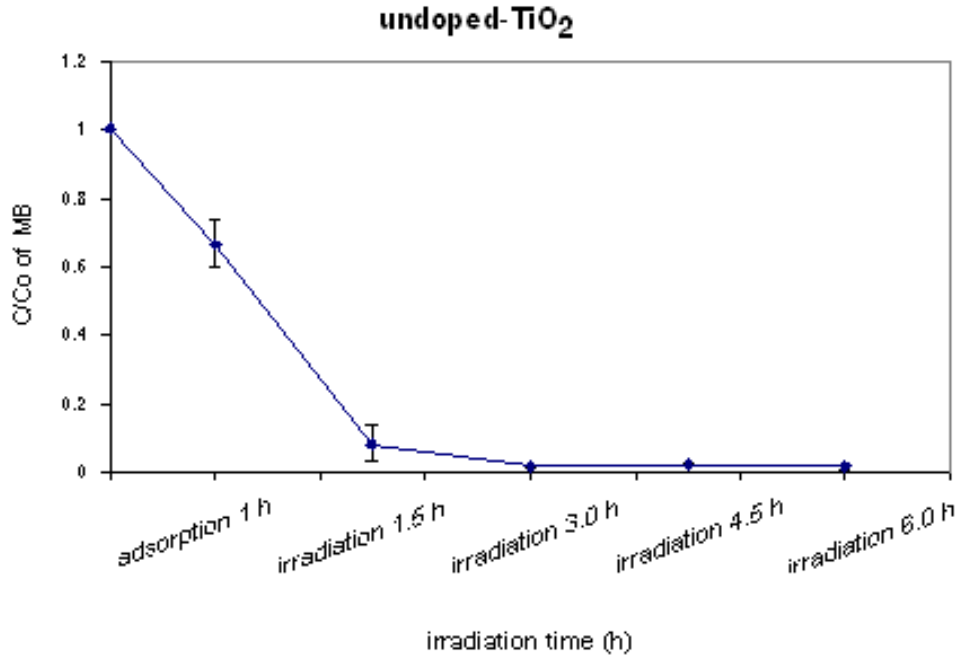
The relative MB remained C/C_o of Al-doped TiO_2 samples and B-doped TiO_2 samples as a function of time of irradiation are shown in Figure 51 and Figure 52, respectively.

a) undoped TiO_2

1) C/C_o at 614 nm

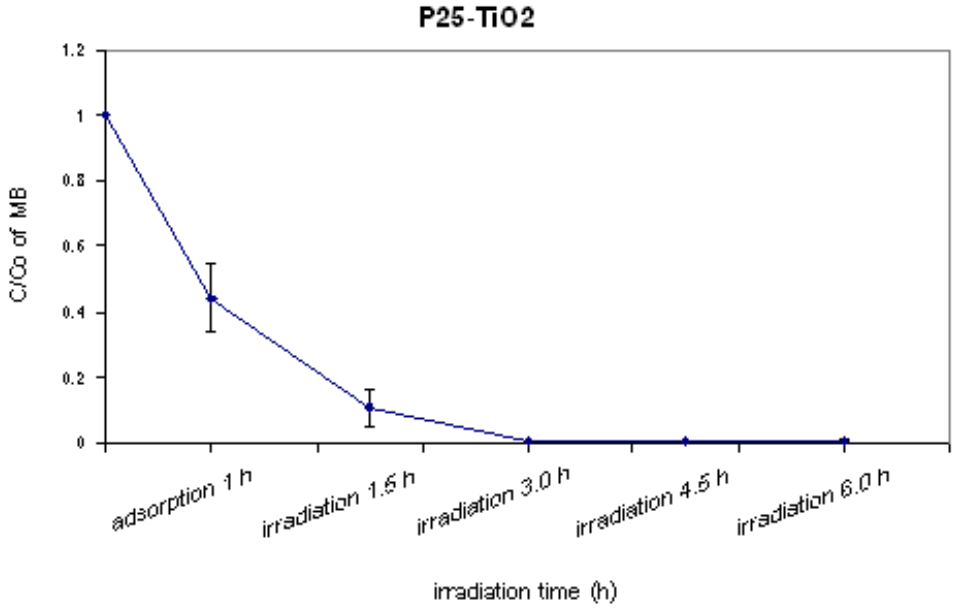


2) C/C_o at 656 nm

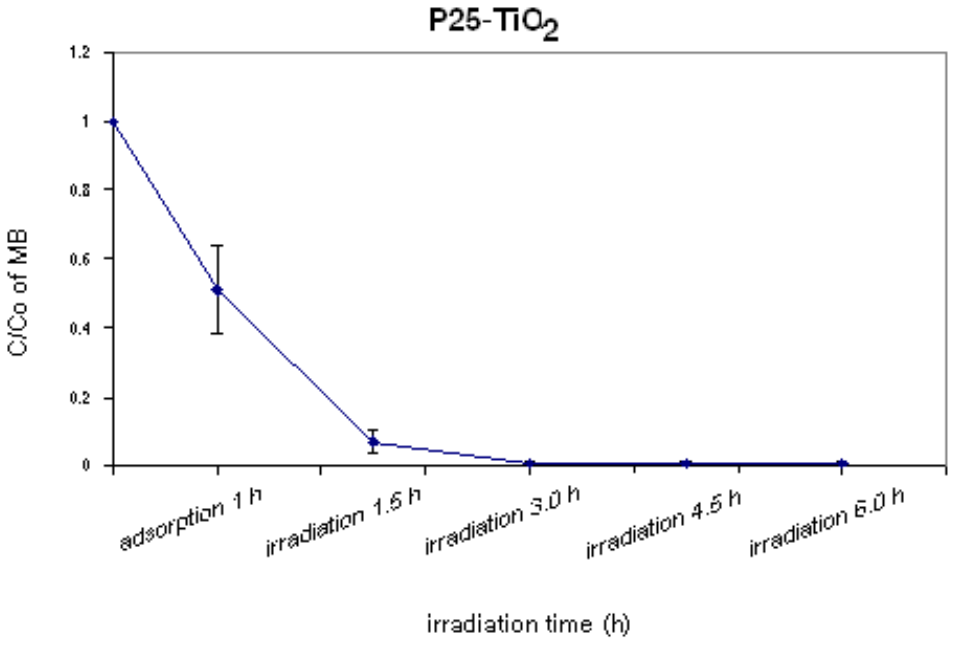


b) P25- TiO_2

1) C/C_o at 614 nm

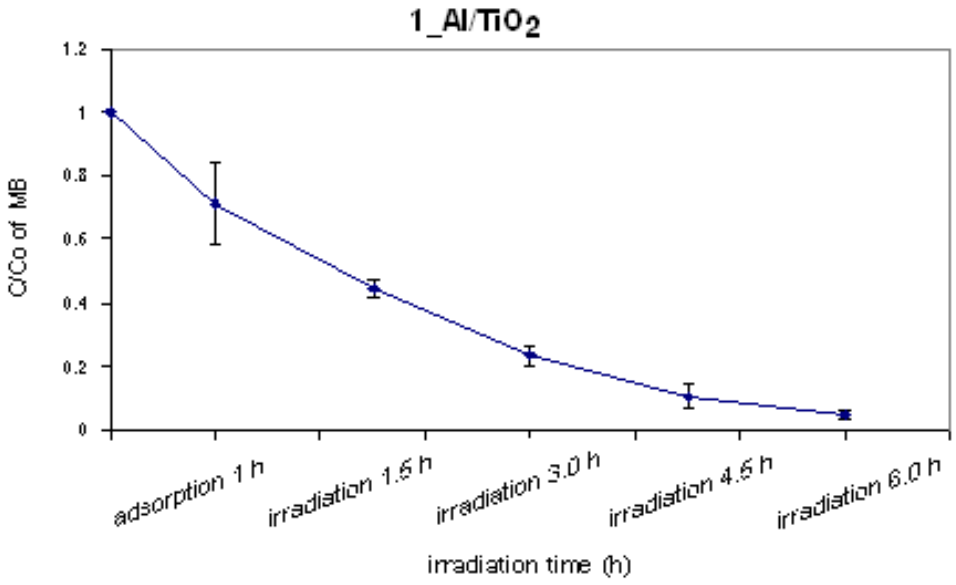


2) C/C_o at 656 nm

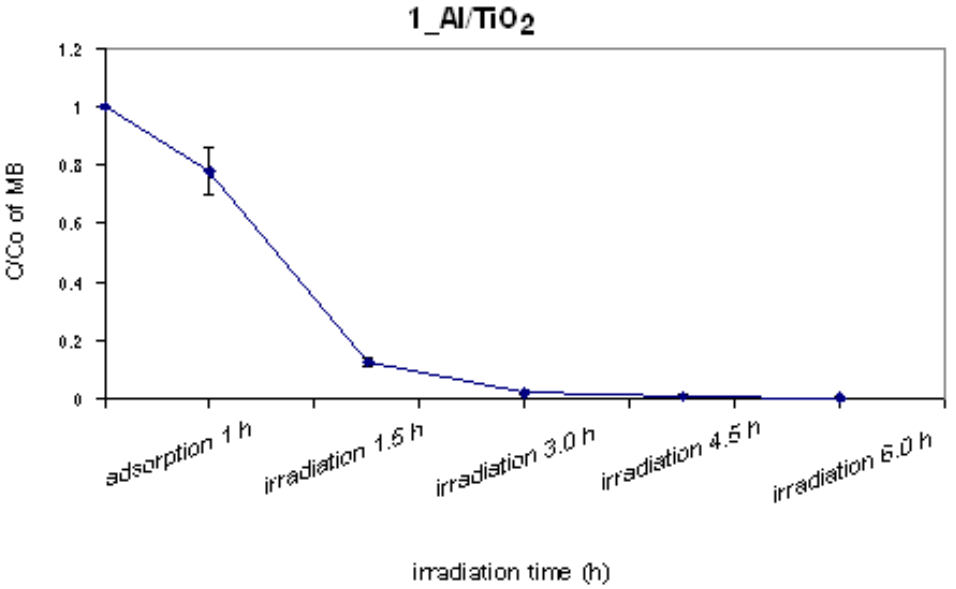


c) 1_Al/ TiO_2

1) C/C_o at 614 nm

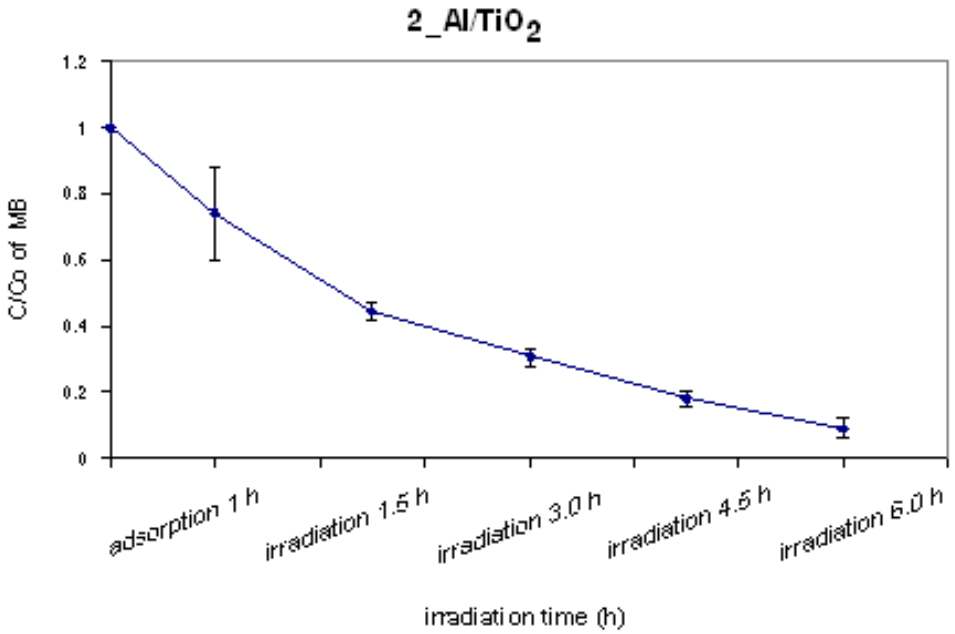


2) C/C_o at 656 nm

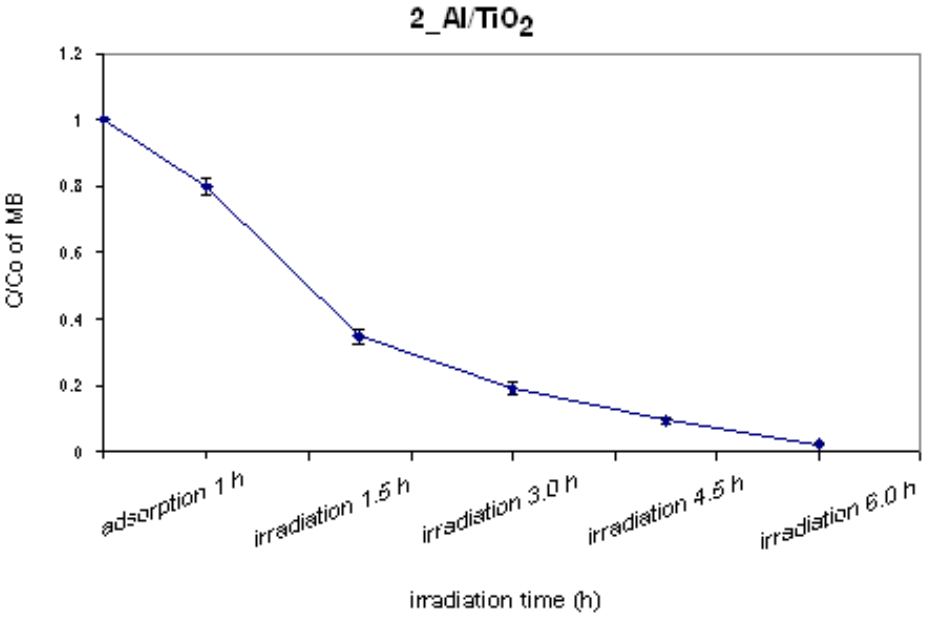


d) 2_Al/ TiO_2

1) C/C_o at 614 nm

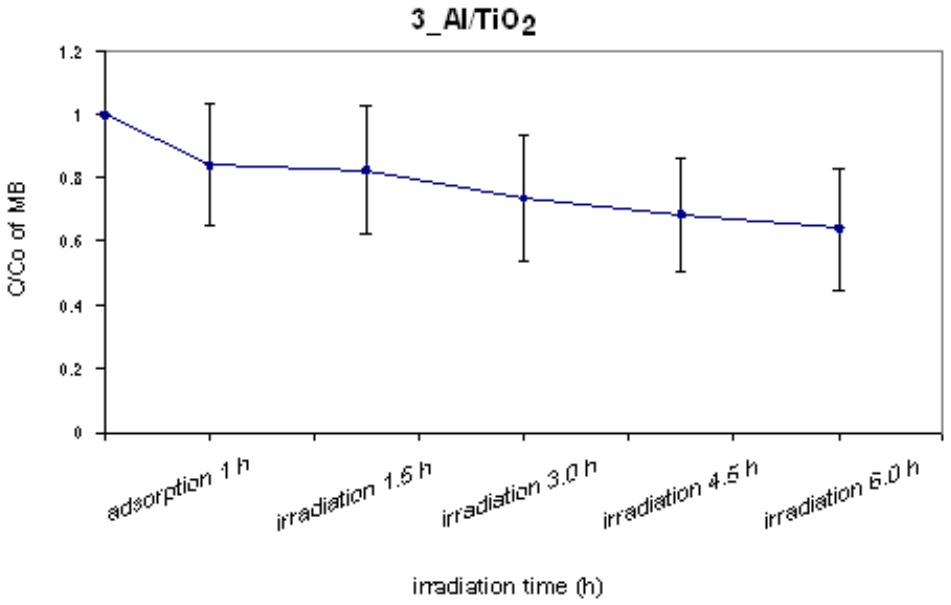


2) C/C_o at 656 nm

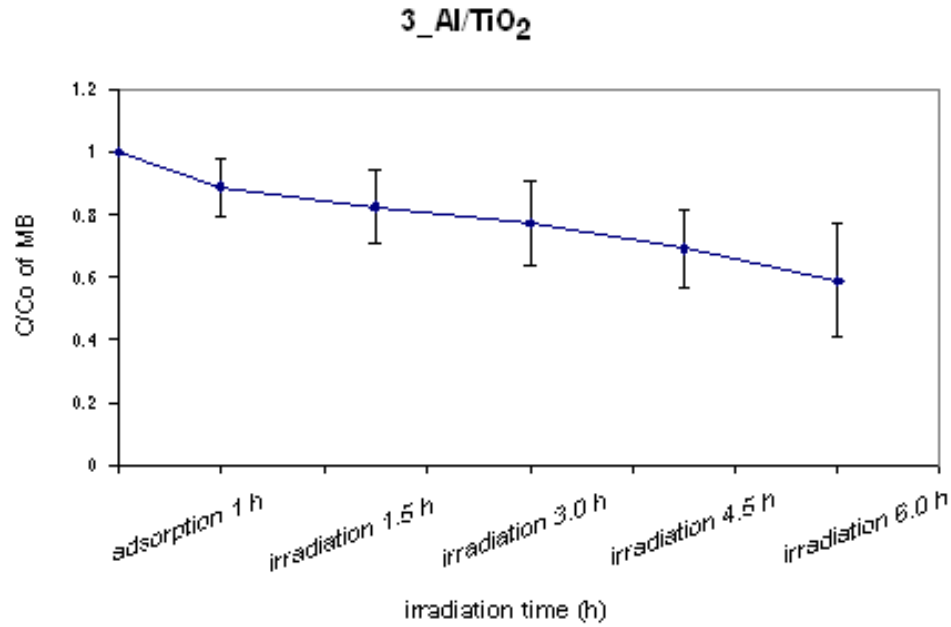


e) 3_Al/ TiO_2

1) C/C_o at 614 nm

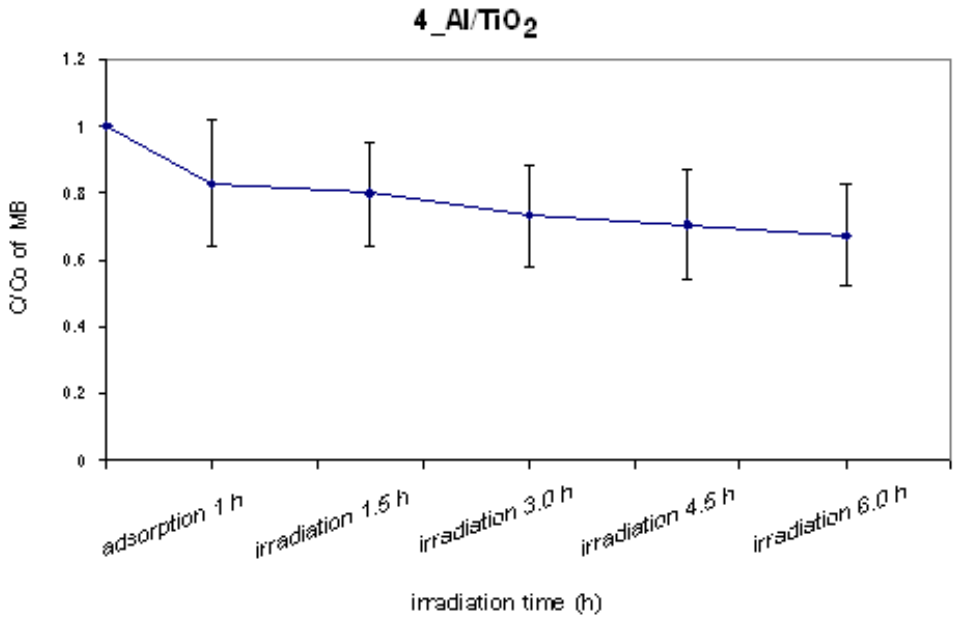


2) C/C_o at 656 nm

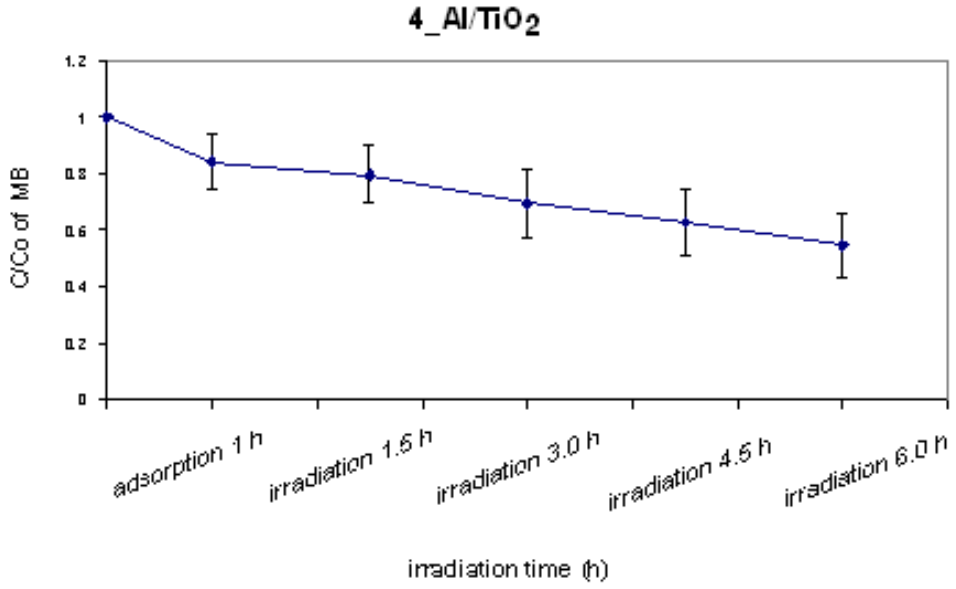


f) 4_Al/ TiO_2

1) C/C_o at 614 nm

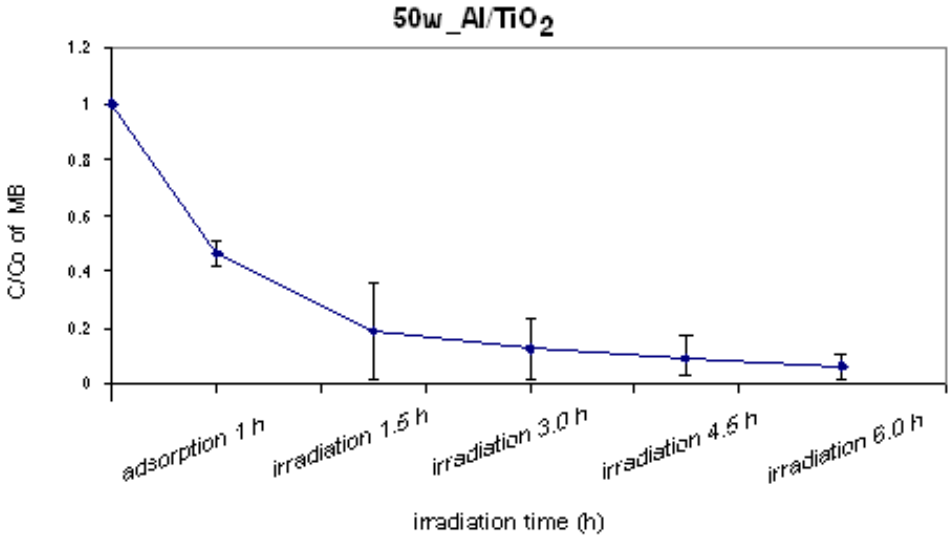


2) C/C_o at 656 nm

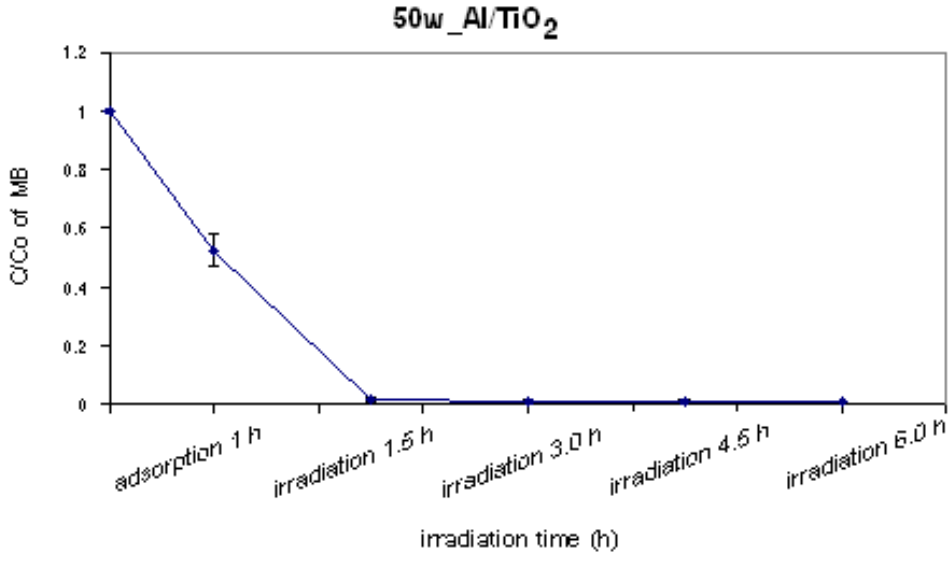


g) 50w_Al/ TiO_2

1) C/C_o at 614 nm

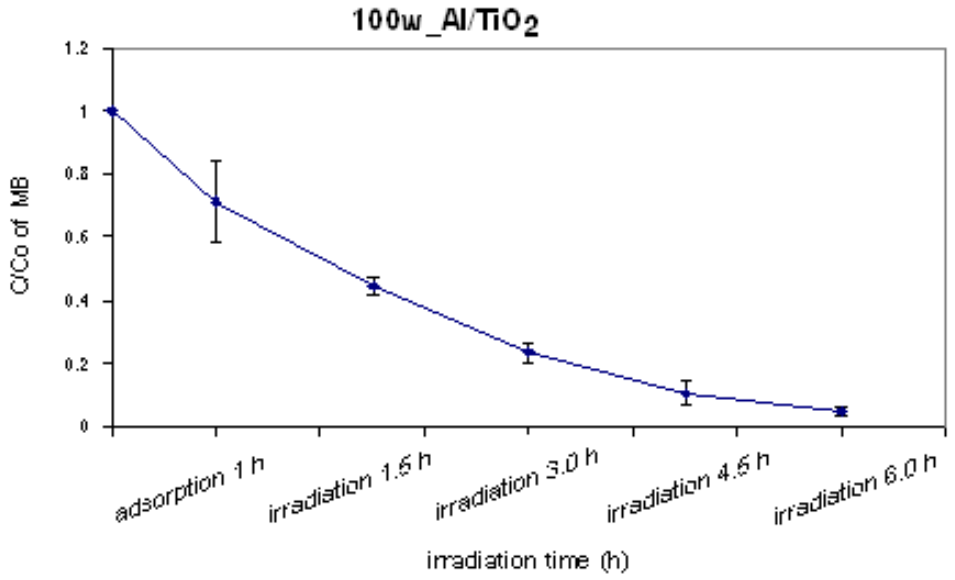


2) C/C_o at 656 nm

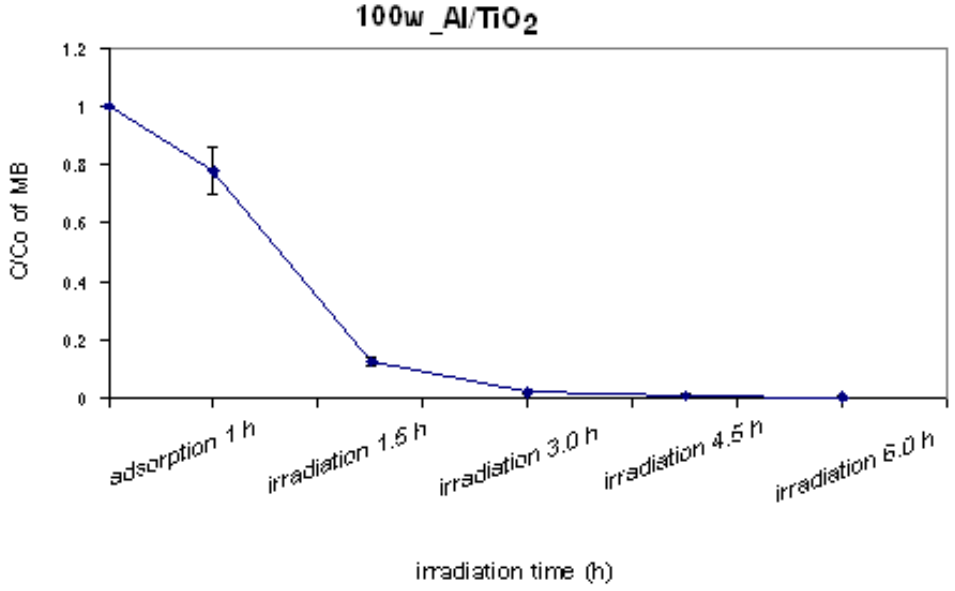


h) 100w_Al/ TiO_2

1) C/C_o at 614 nm

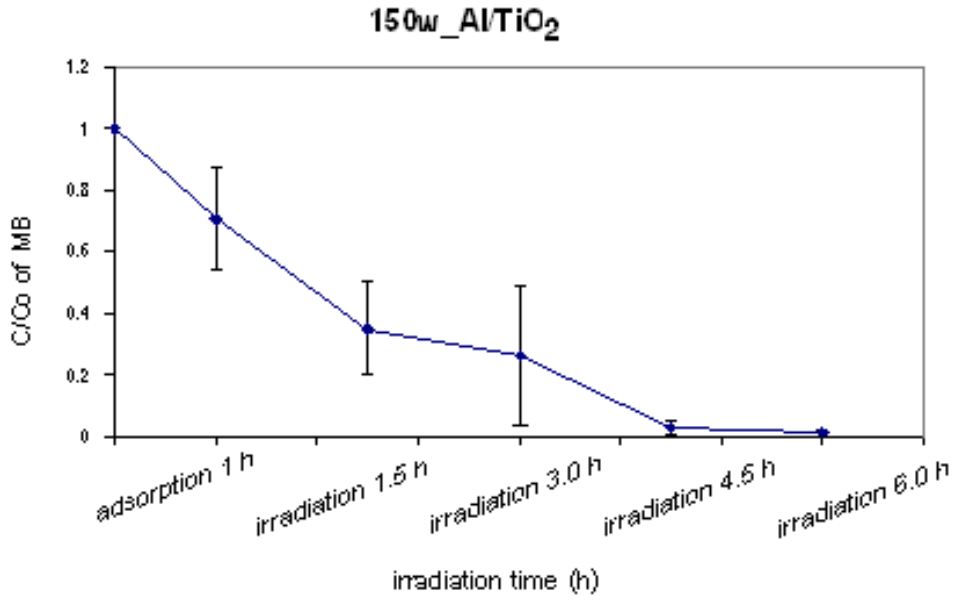


2) C/C_o at 656 nm

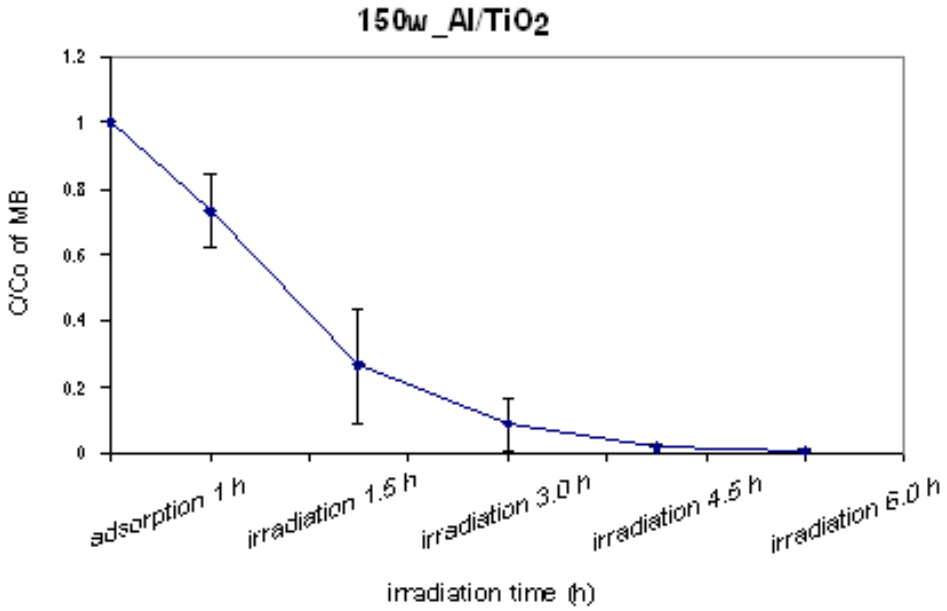


i) 150w_Al/ TiO_2

1) C/C_o at 614 nm

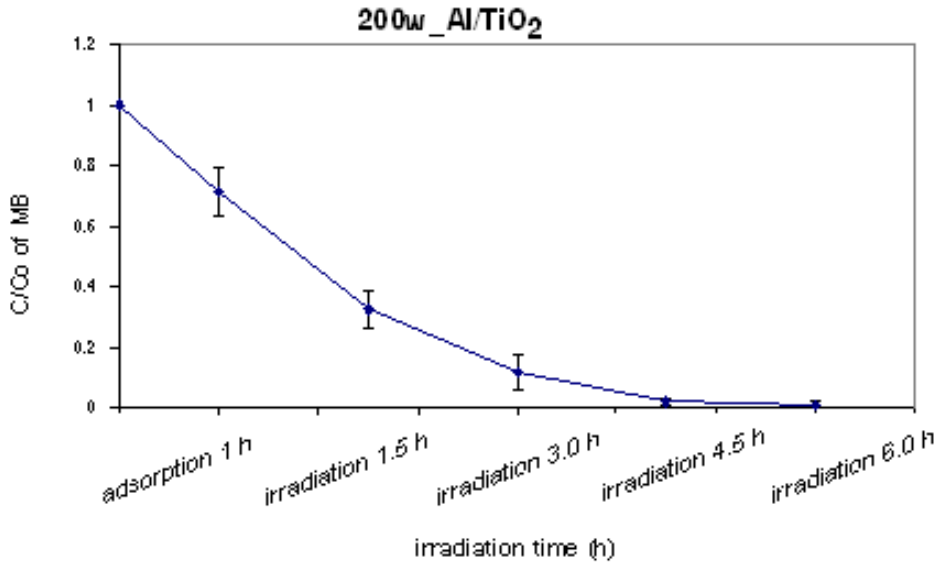


2) C/C_o at 656 nm

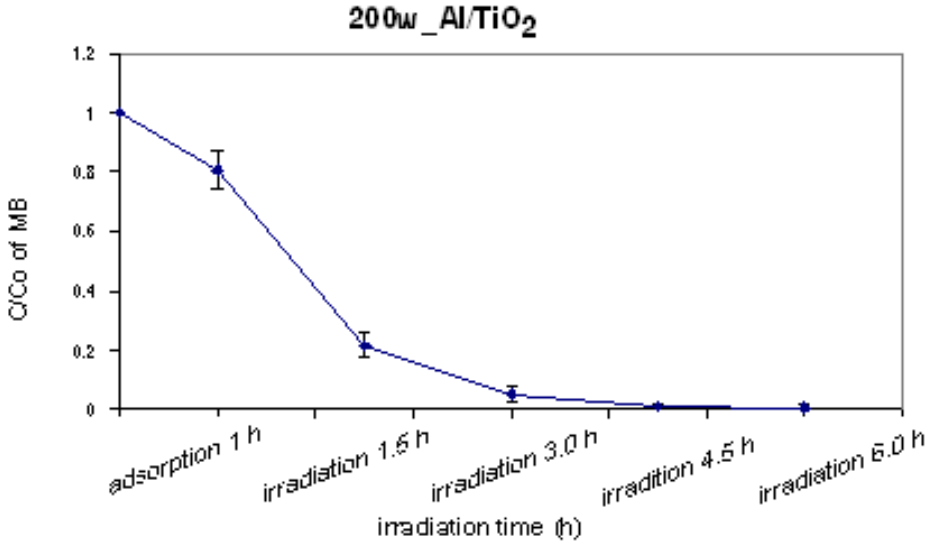


j) 200w_Al/ TiO_2

1) C/C_o at 614 nm

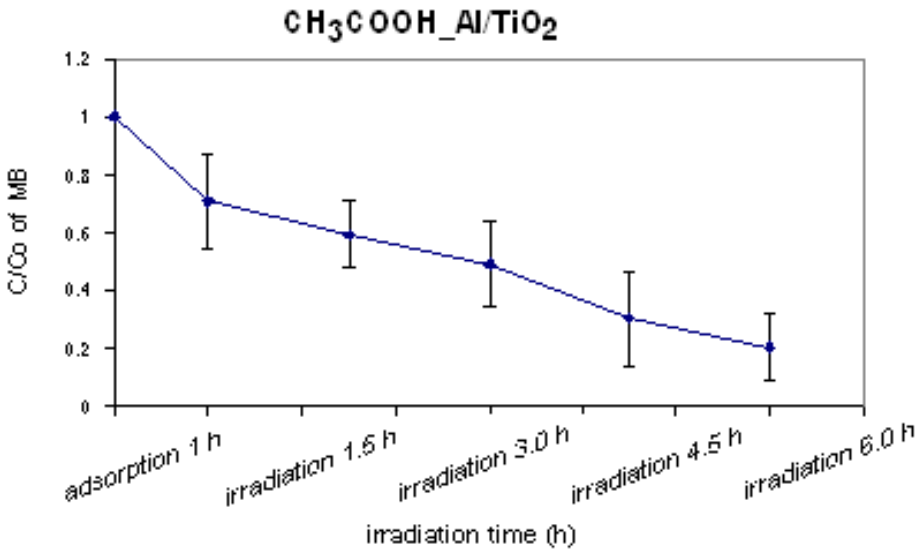


2) C/C_o at 656 nm

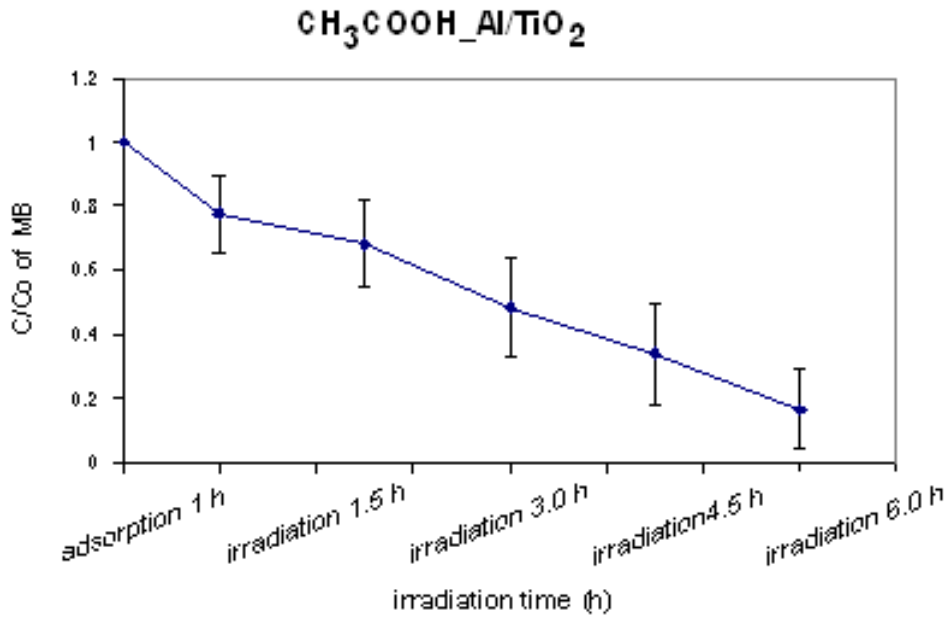


k) $CH_3COOH\_Al/\ TiO_2$

1) C/C_o at 614 nm

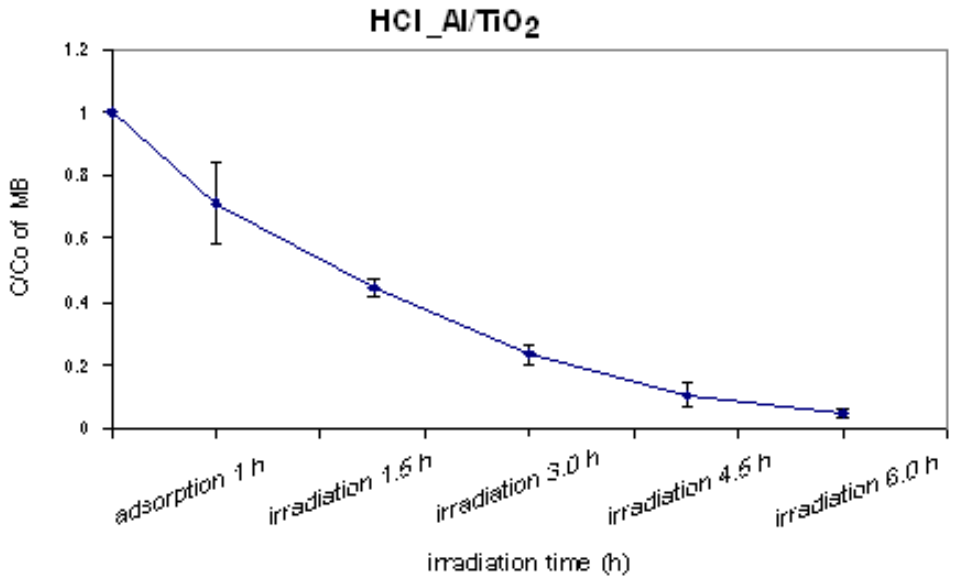


2) C/C_o at 656 nm

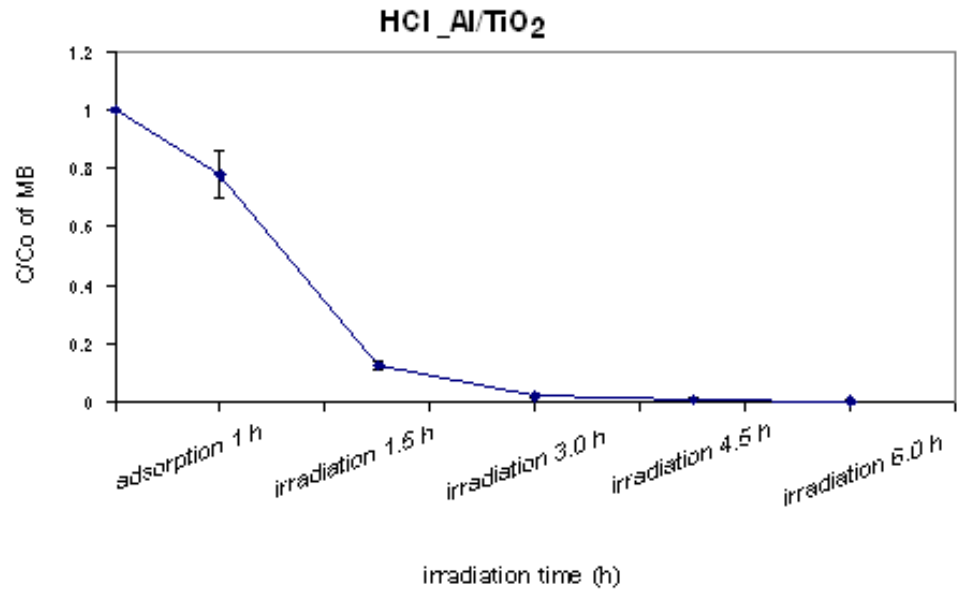


l) HCl_Al/ TiO_2

1) C/C_o at 614 nm

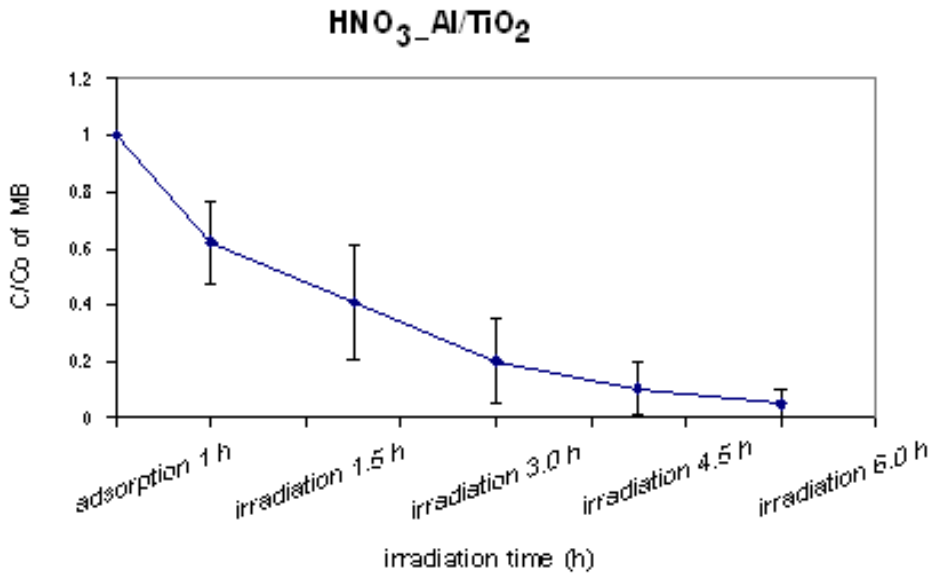


2) C/C_o at 656 nm

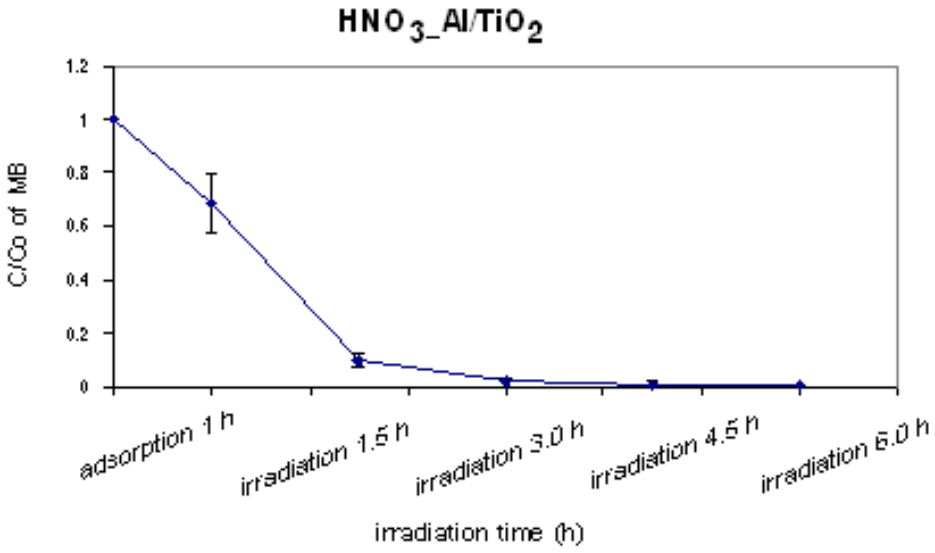


m) HNO_3_Al/ TiO_2

1) C/C_o at 614 nm

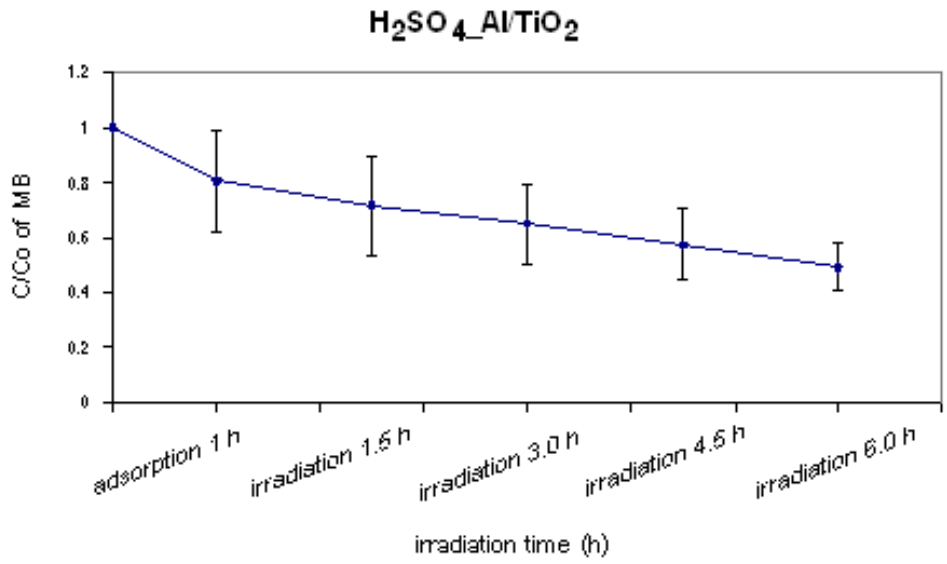


2) C/C_o at 656 nm

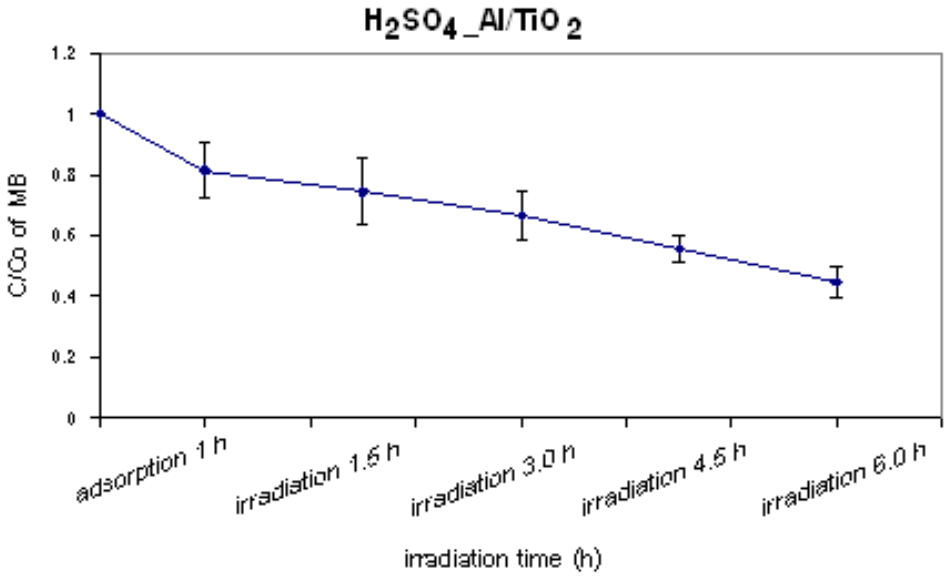


n) H_2SO_4_Al/ TiO_2

1) C/C_o at 614 nm

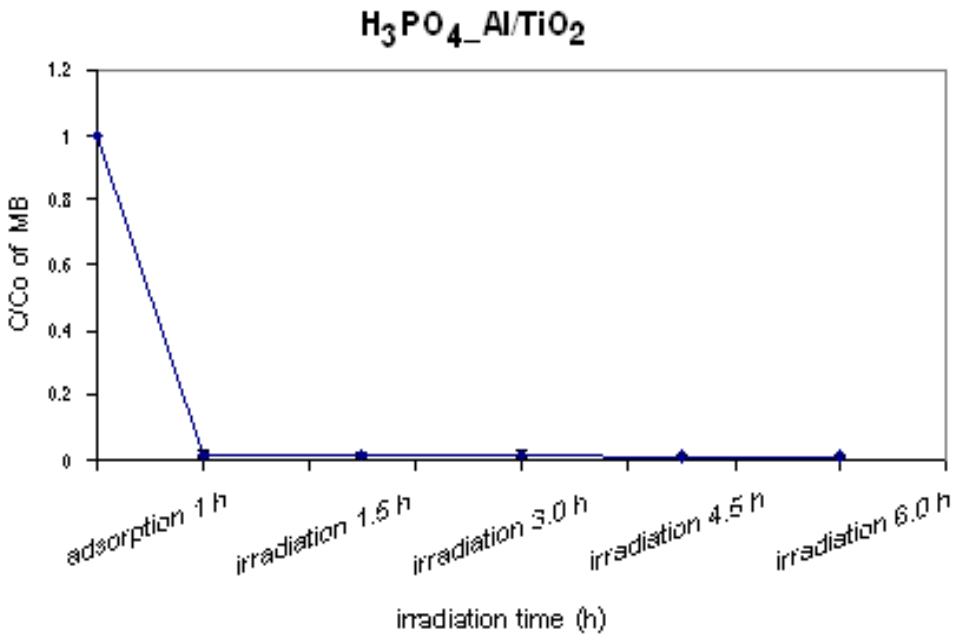


2) C/C_o at 656 nm

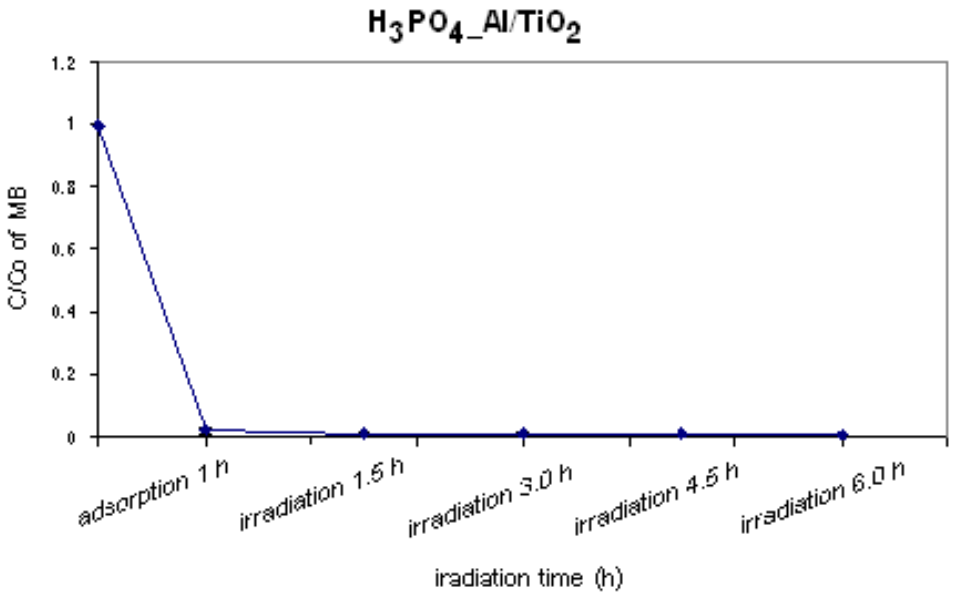


o) H_3PO_4_Al/ TiO_2

1) C/C_o at 614 nm

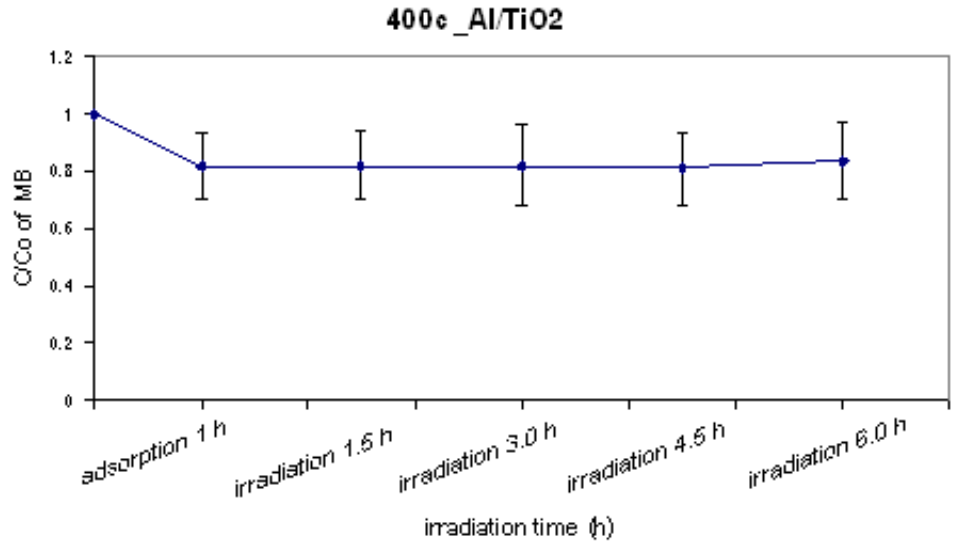


2) C/C_o at 656 nm

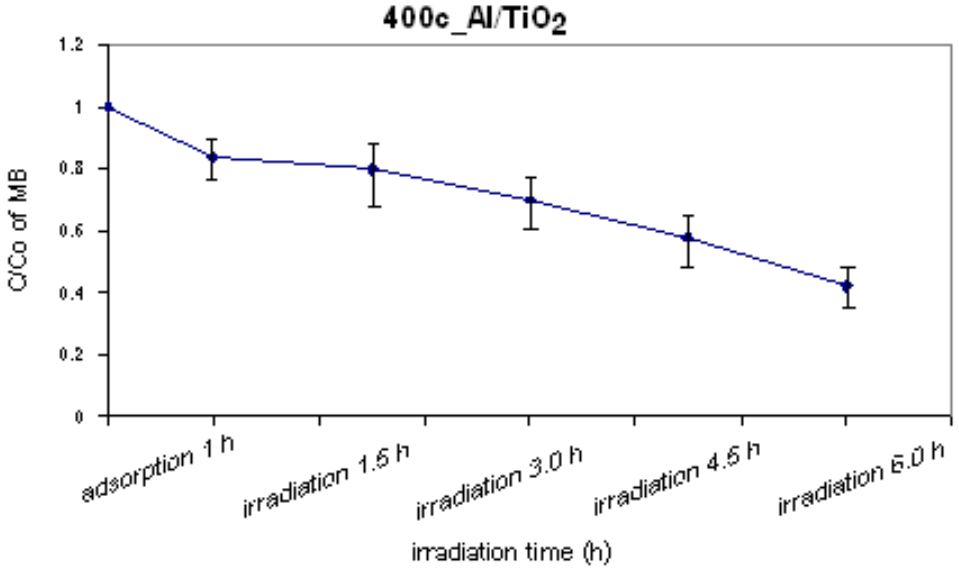


p) 400c_Al/ TiO_2

1) C/C_o at 614 nm

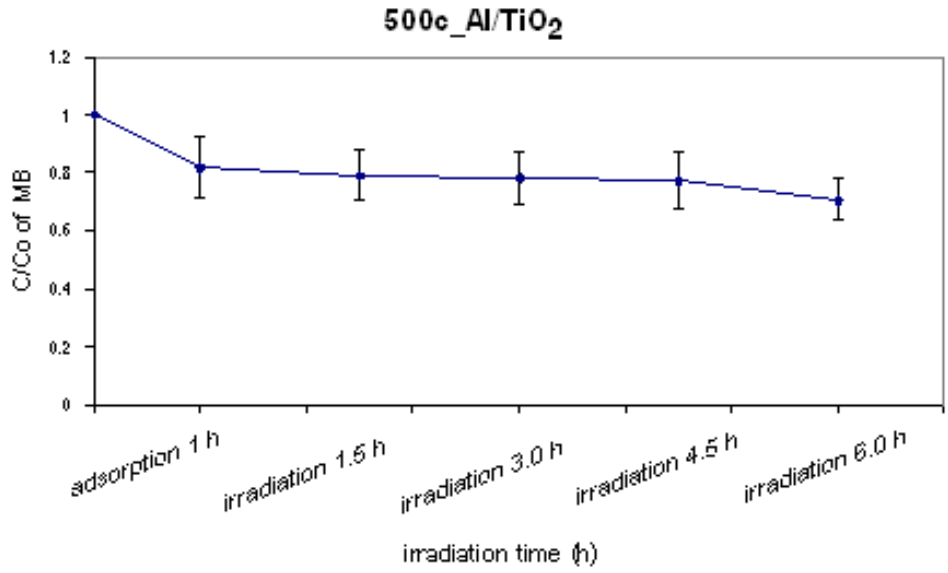


2) C/C_o at 656 nm

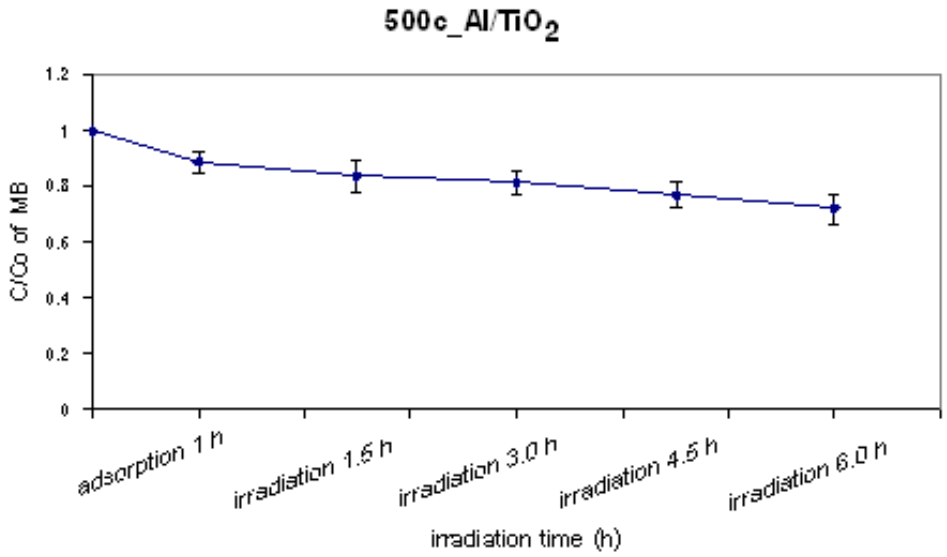


q) 500c_Al/ TiO_2

1) C/C_o at 614 nm

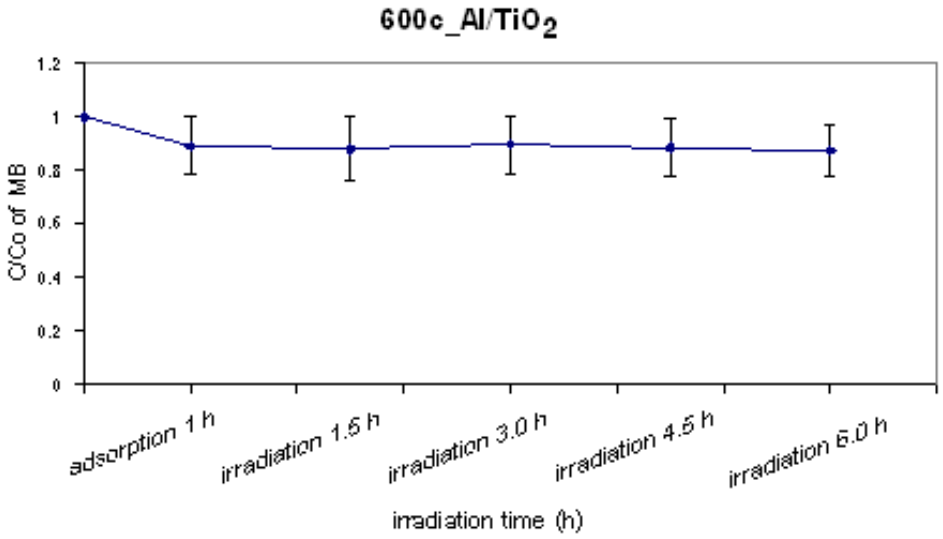


2) C/C_o at 656 nm

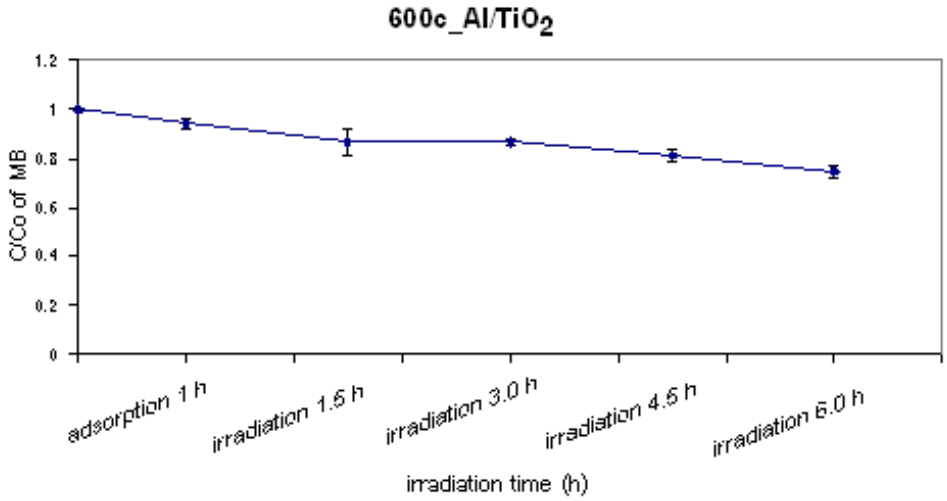


r) 600c_Al/ TiO_2

1) C/C_o at 614 nm

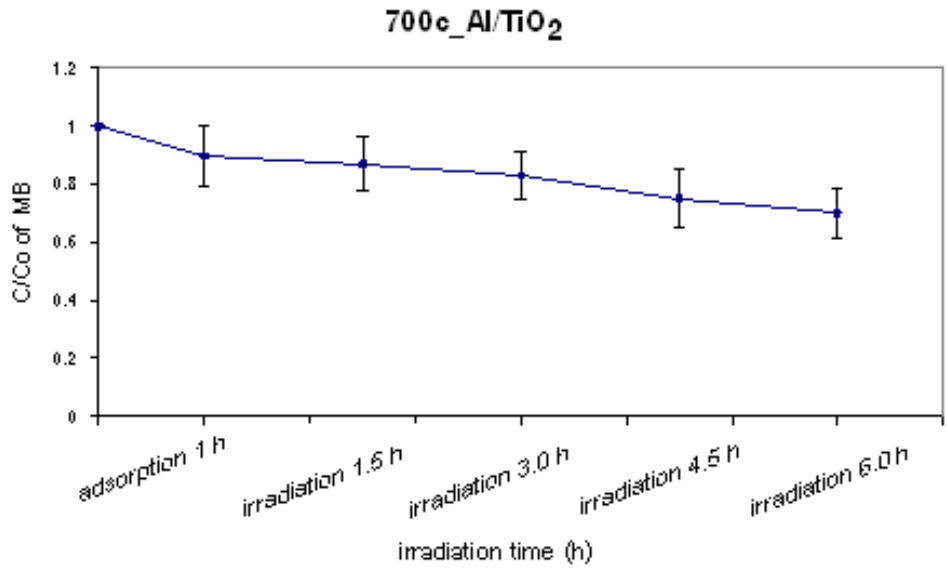


2) C/C_o at 656 nm

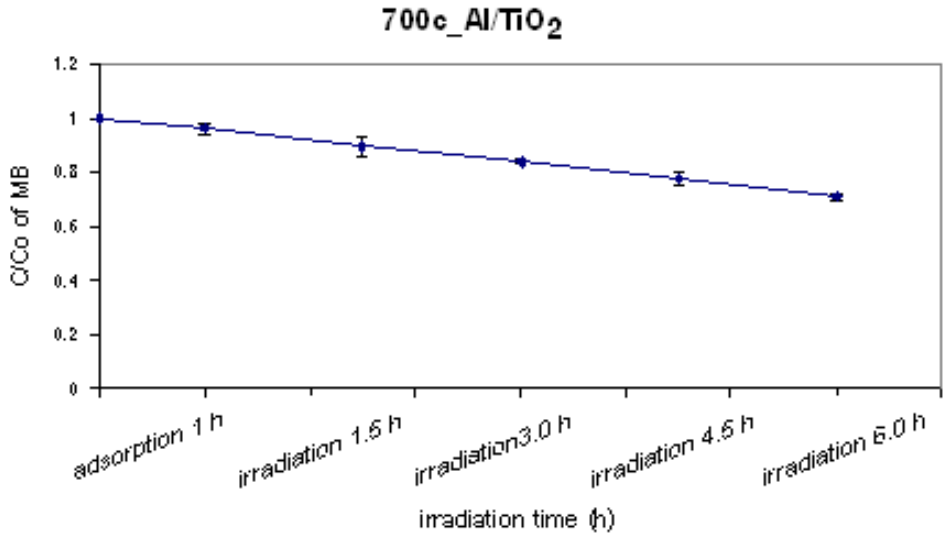


s) 700c_Al/ TiO_2

1) C/C_o at 614 nm

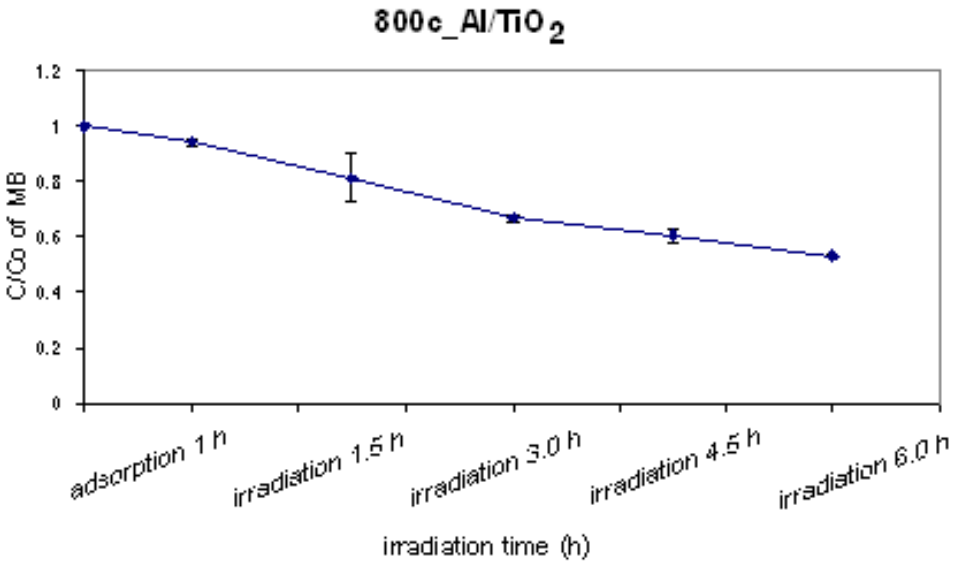


2) C/C_o at 656 nm



t) 800c_Al/ TiO_2

1) C/C_o at 614 nm



2) C/C_o at 656 nm

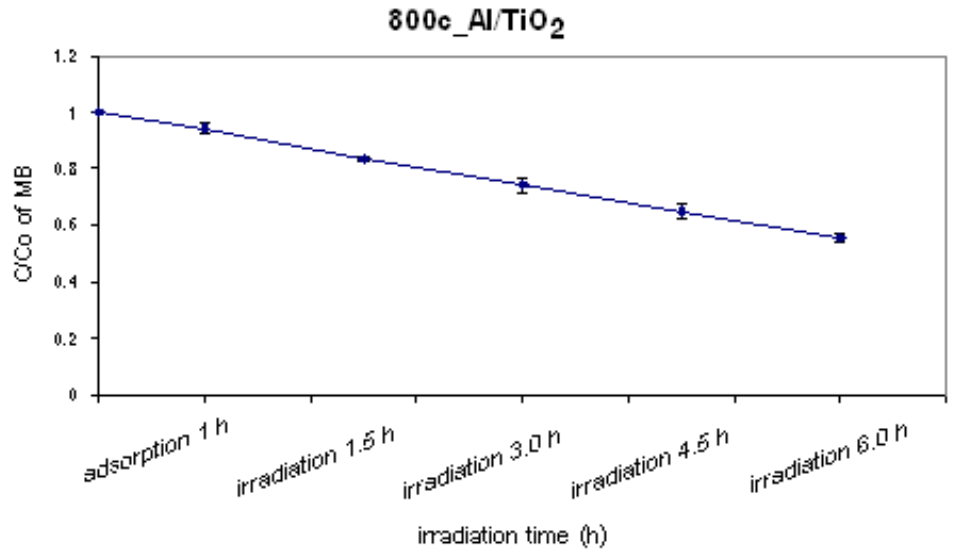
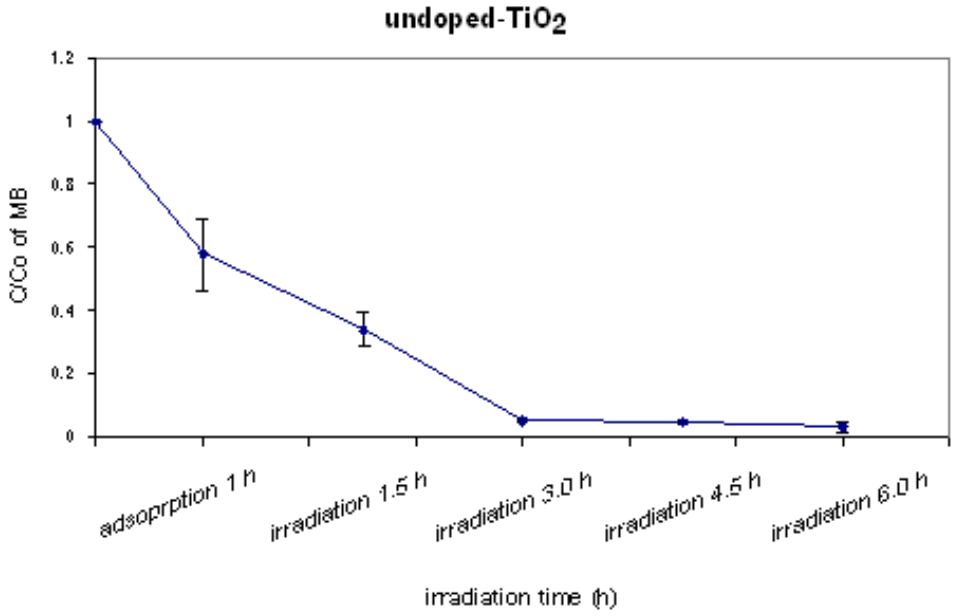


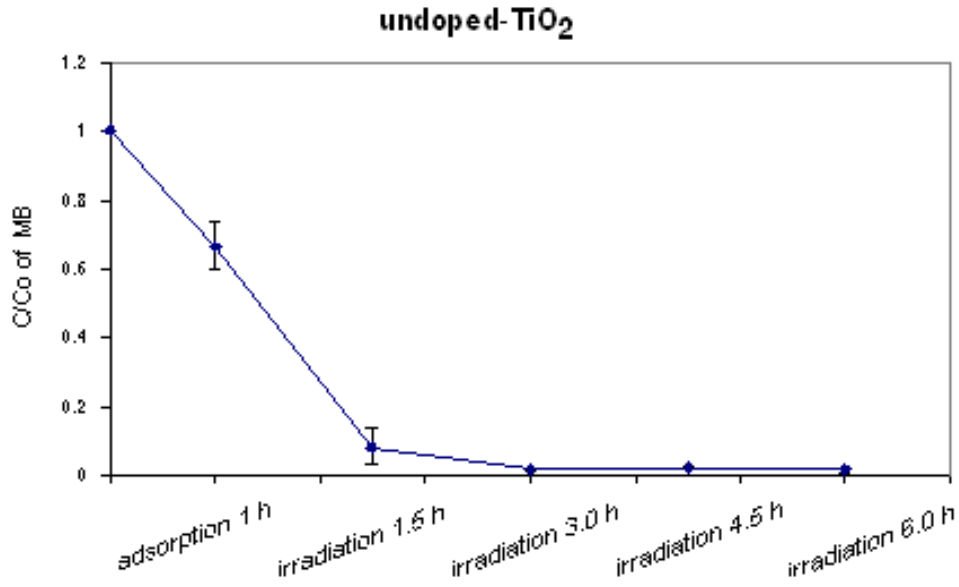
Figure 51 The reletive remained C/C_o of methylene blue in synthesized Al-doped TiO_2 samples suspension as a function of time of irradiation.

a) undoped TiO_2

1) C/C_o at 614 nm

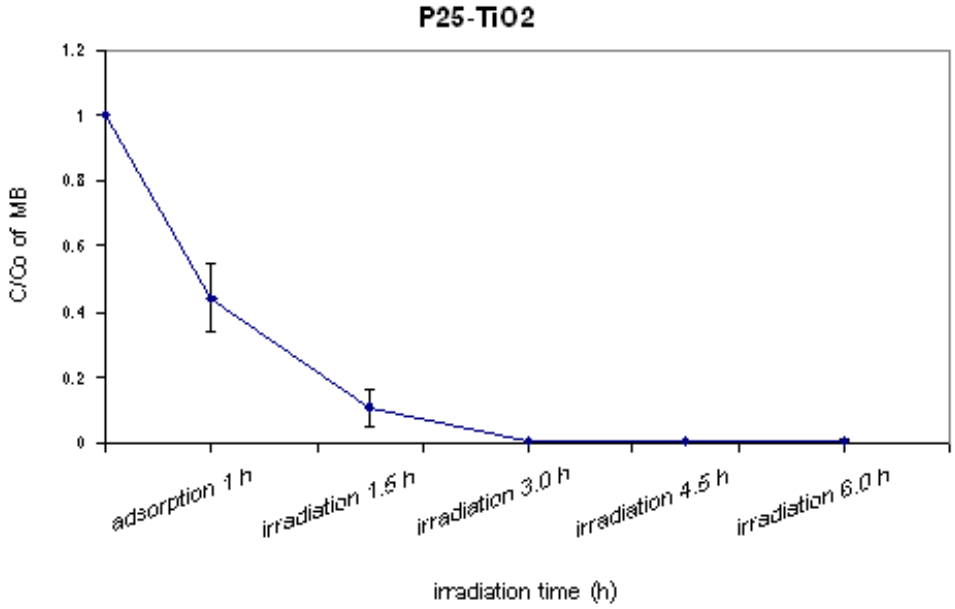


2) C/C_o at 656 nm

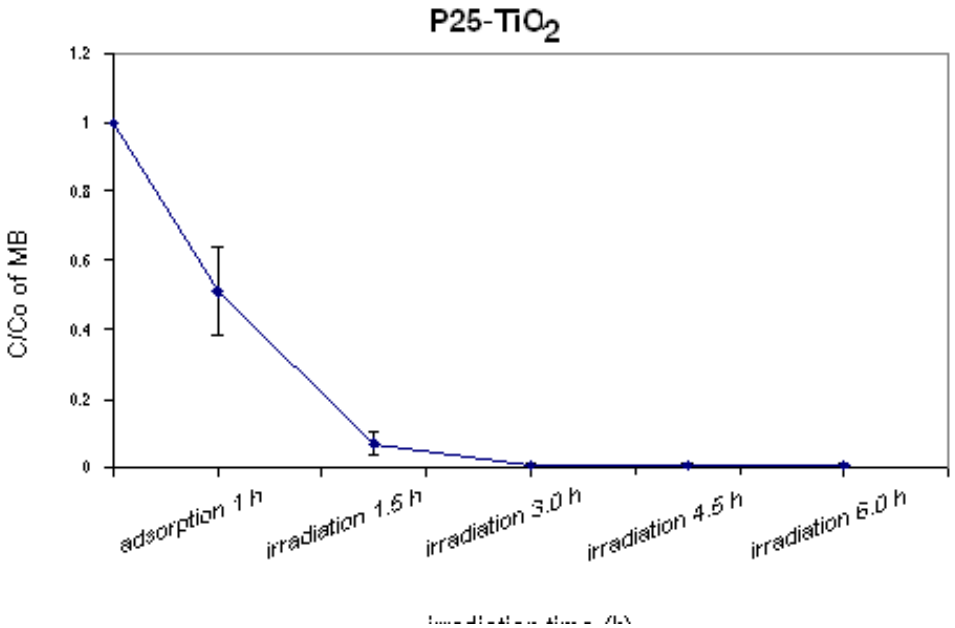


b) P25-TiO_2

1) C/C_o at 614 nm

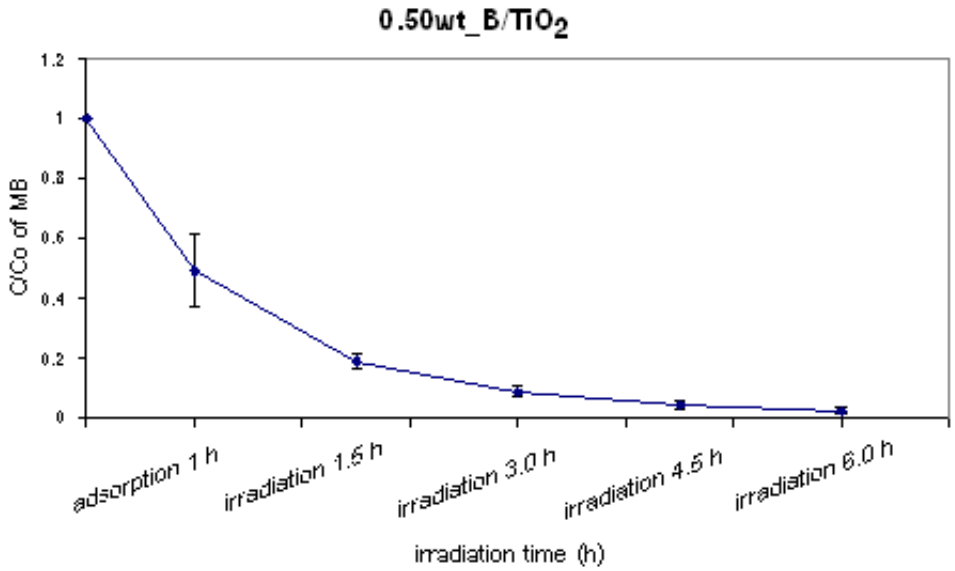


2) C/C_o at 656 nm

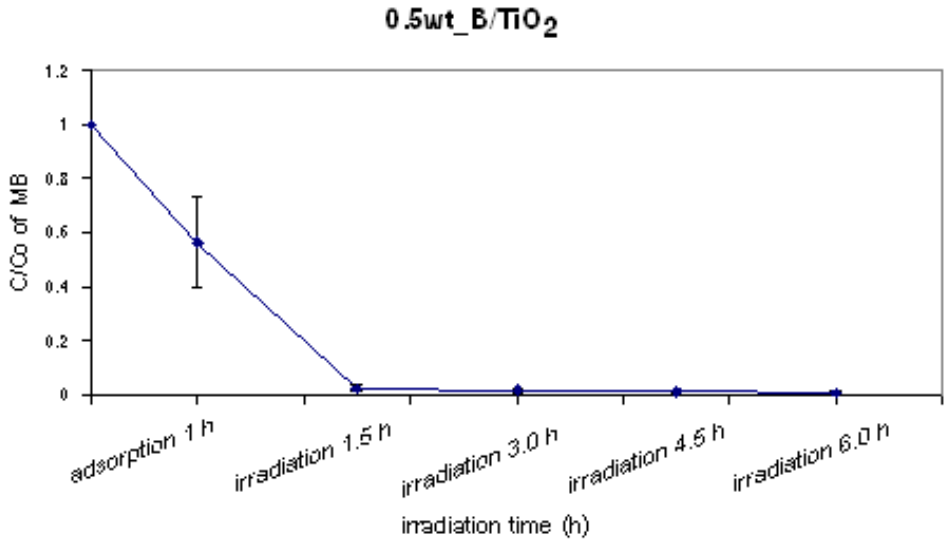


c) 0.5wt_B/TiO_2

1) C/C_o at 614 nm

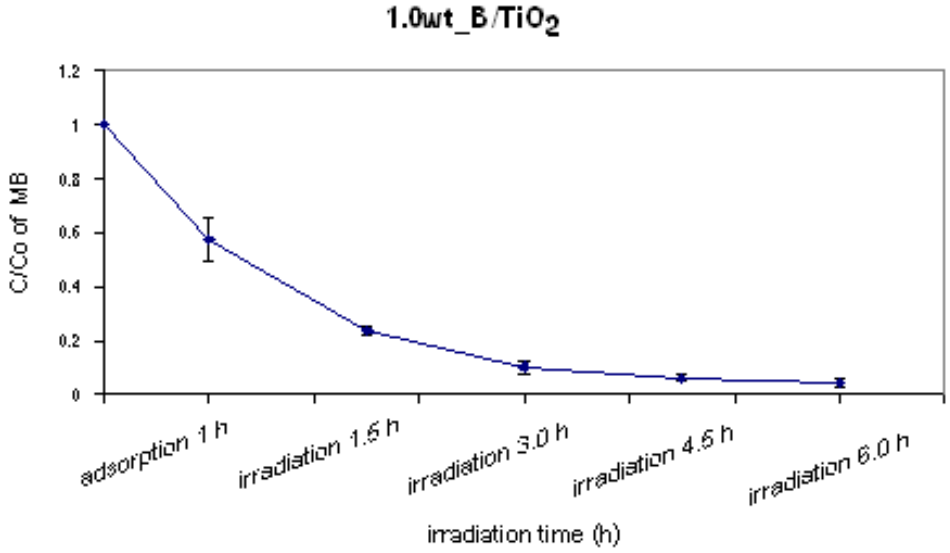


2) C/C_o at 656 nm

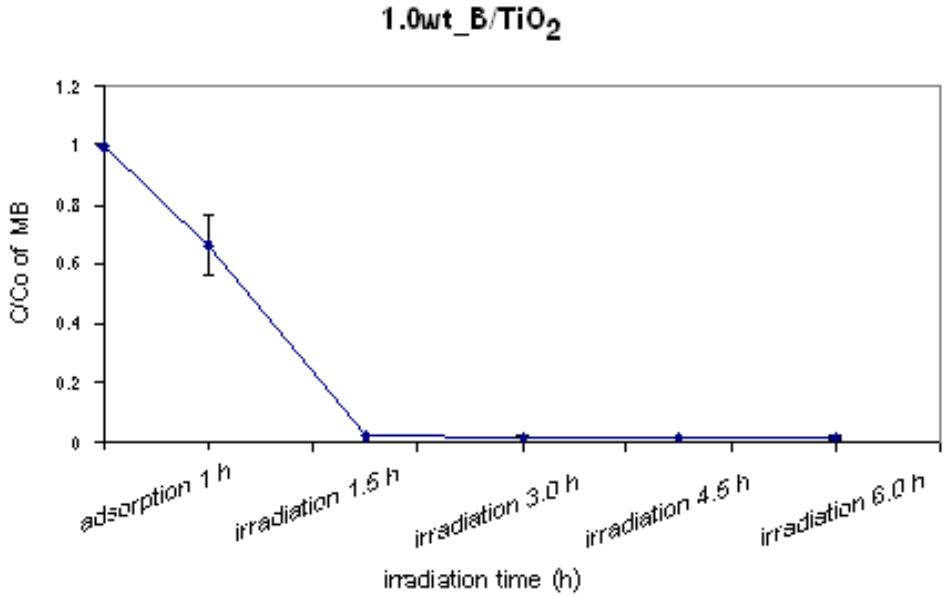


d) 1.0wt_B/TiO_2

1) C/C_o at 614 nm

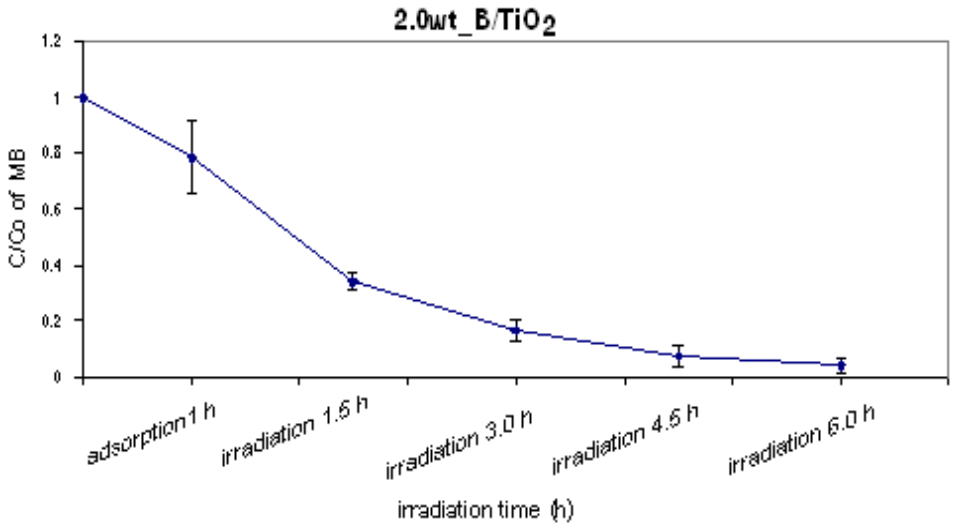


2) C/C_o at 656 nm

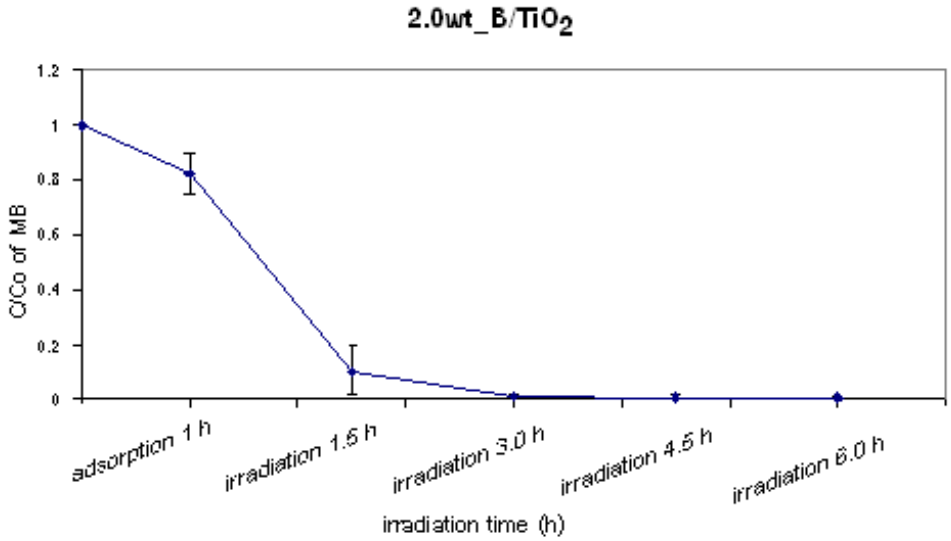


e) 2.0wt_B/TiO_2

1) C/C_o at 614 nm

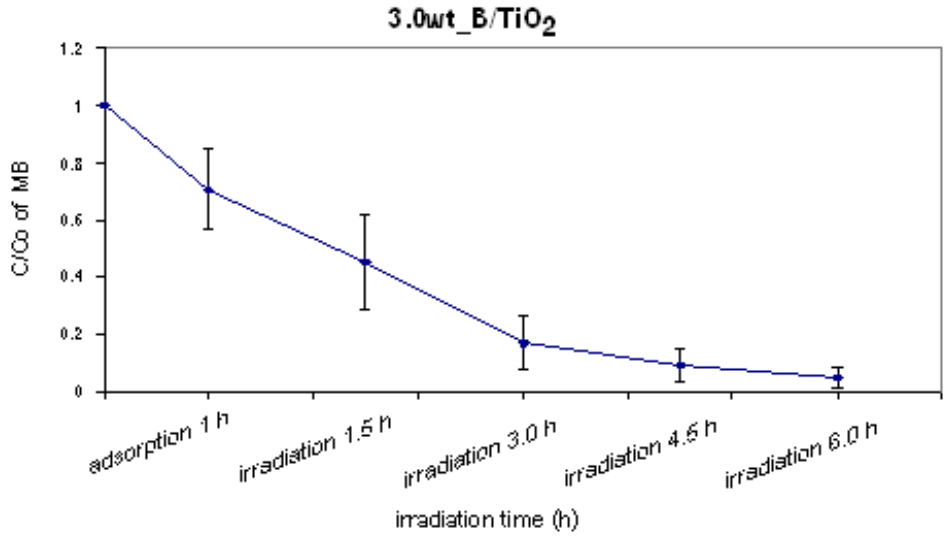


2) C/C_o at 656 nm

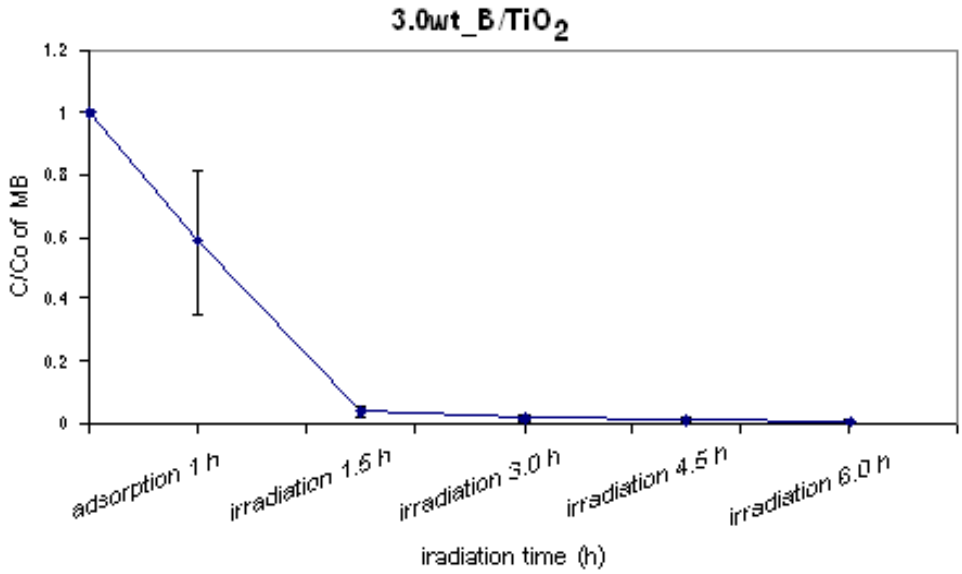


f) 3.0wt_B/TiO_2

1) C/C_o at 614 nm

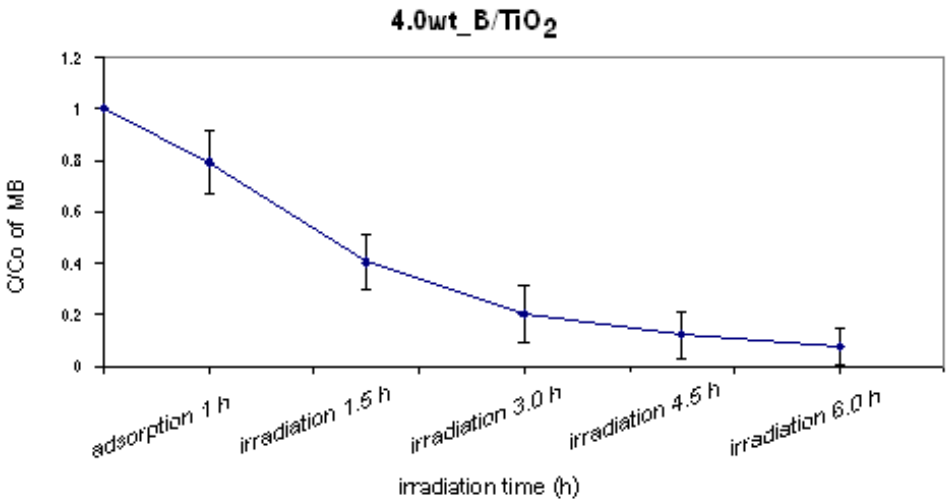


2) C/C_o at 656 nm

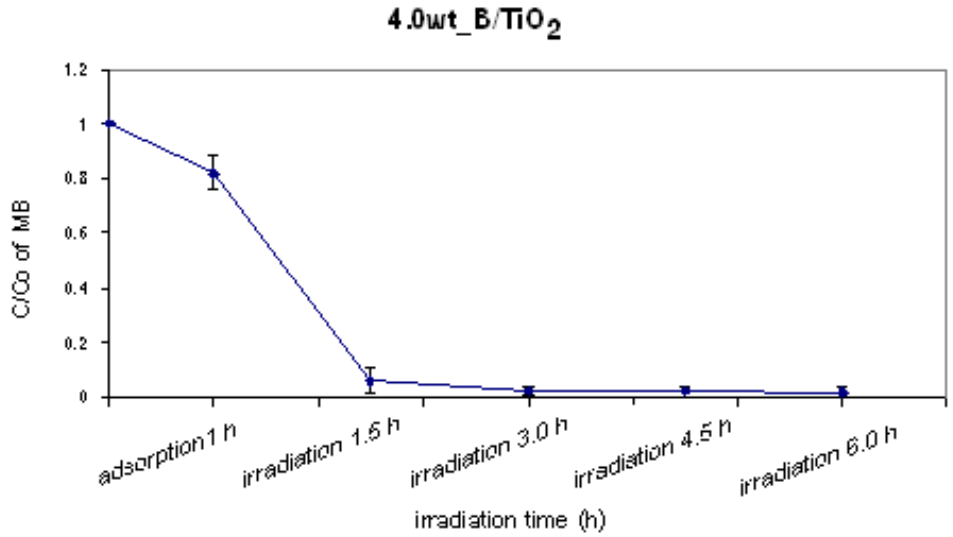


g) 4.0wt_B/TiO_2

1) C/C_o at 614 nm

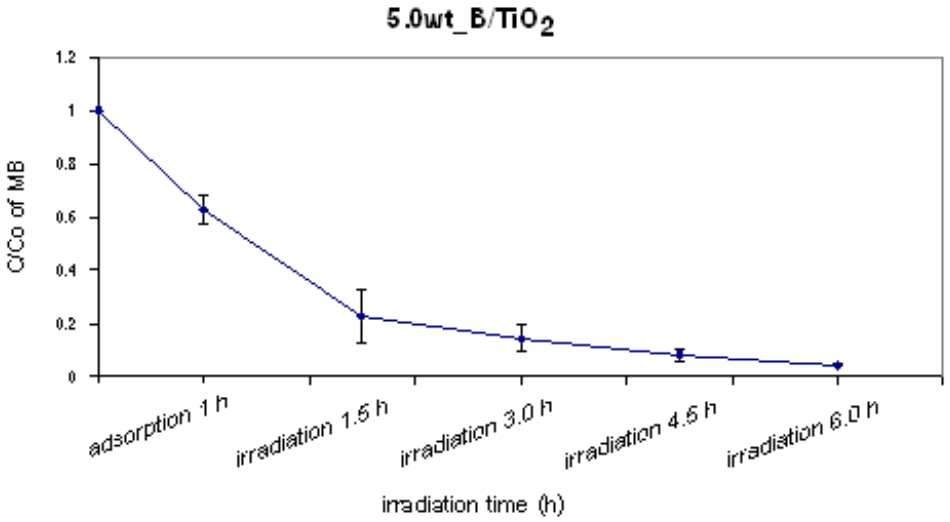


2) C/C_o at 656 nm

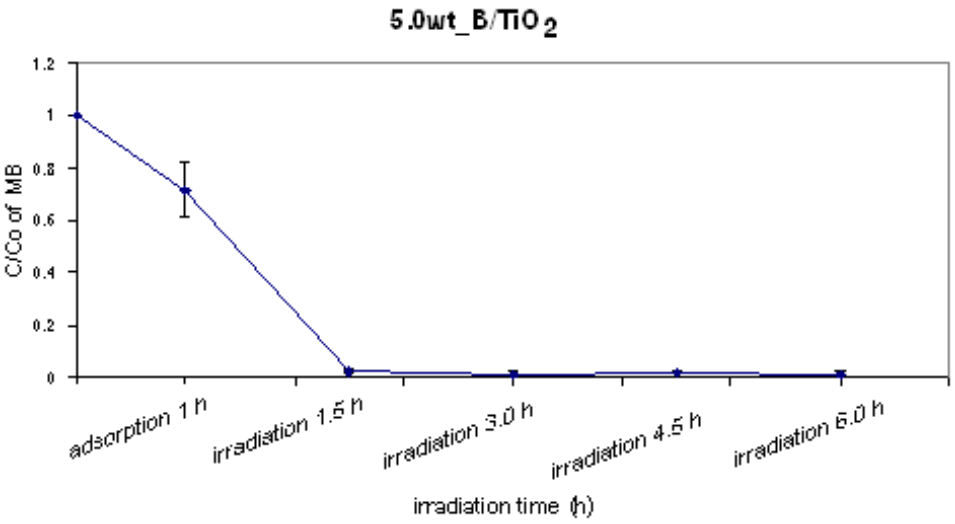


h) 5.0wt_B/TiO_2

1) C/C_o at 614 nm

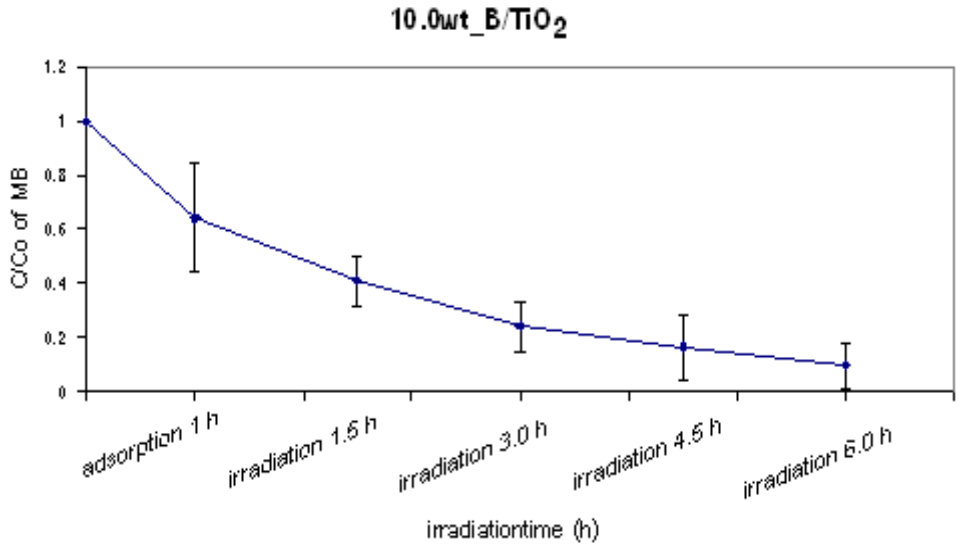


2) C/C_o at 656 nm

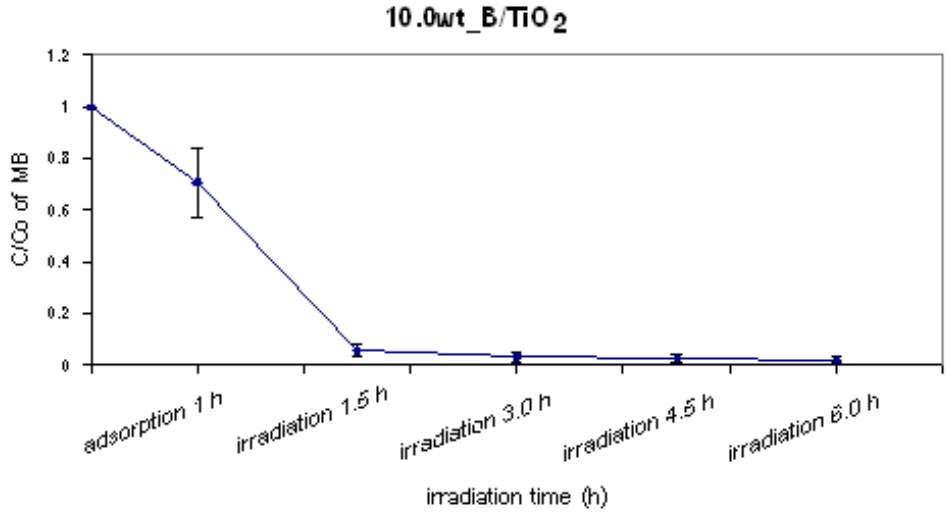


i) 10.0wt_B/TiO_2

1) C/C_o at 614 nm

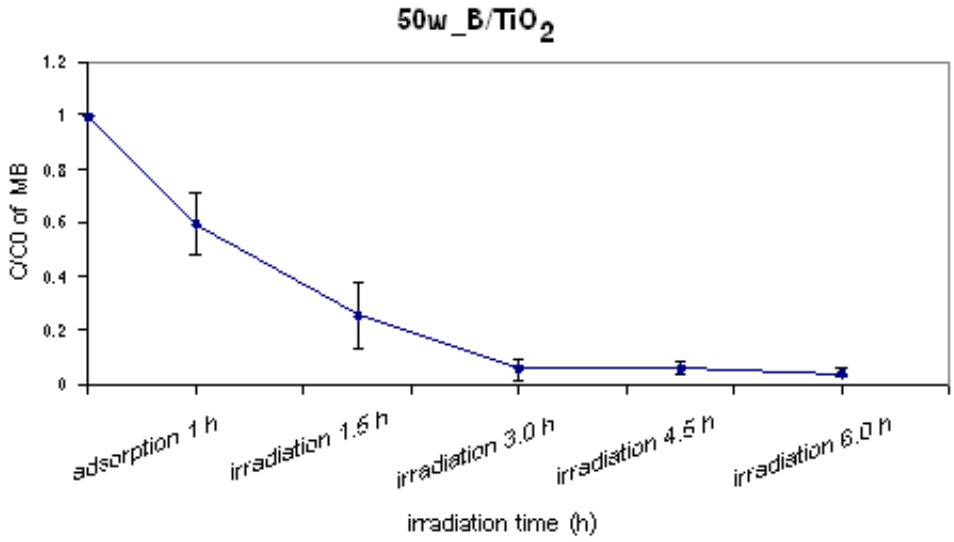


2) C/C_o at 656 nm

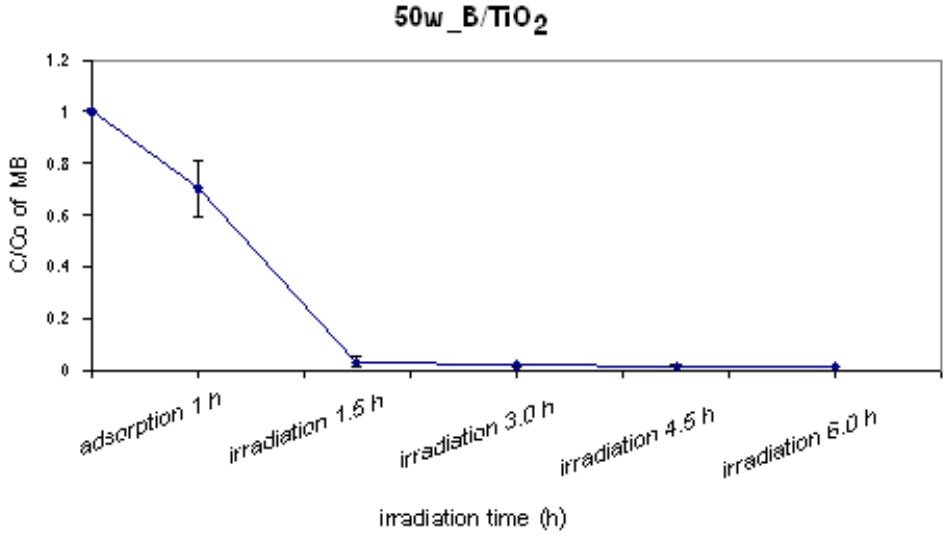


j) 50w_B/TiO_2

1) C/C_o at 614 nm

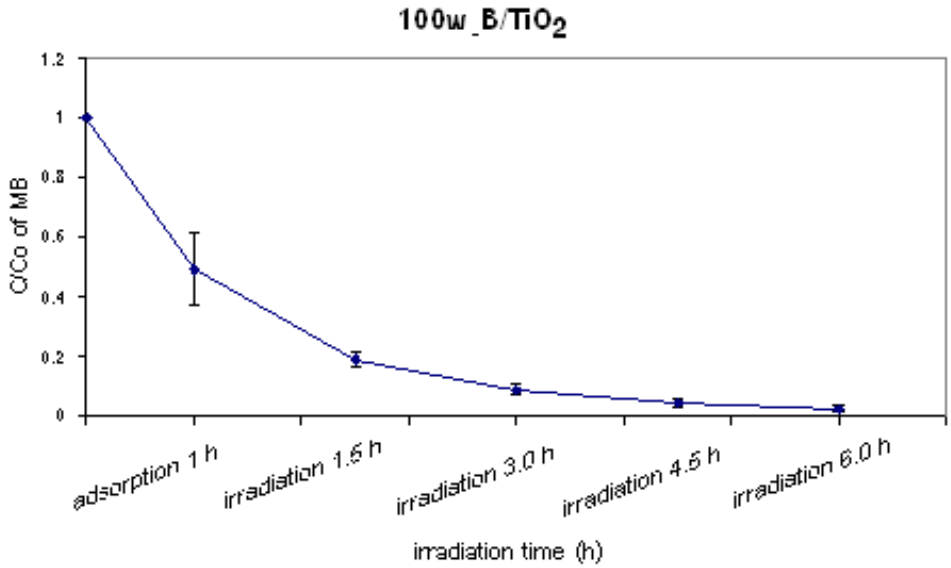


2) C/C_o at 656 nm

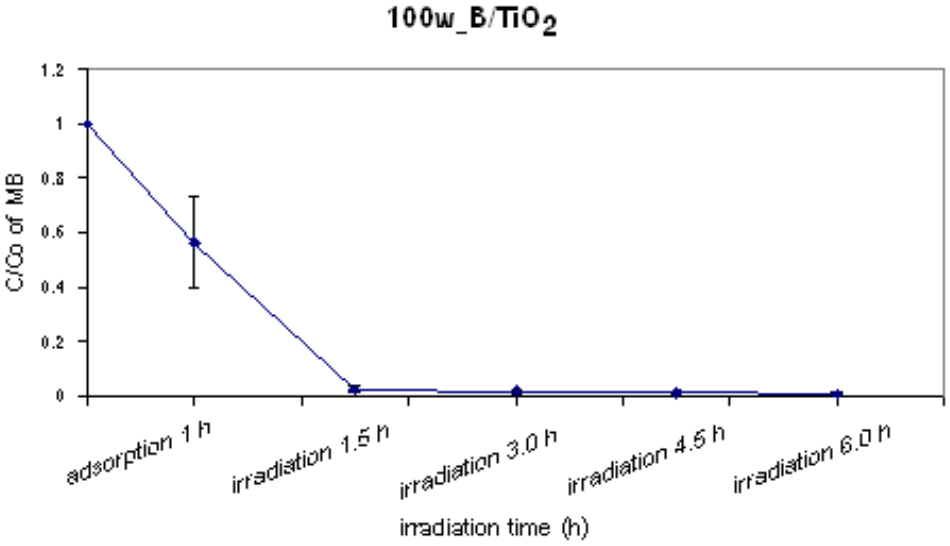


k) 100w_B/TiO_2

1) C/C_o at 614 nm

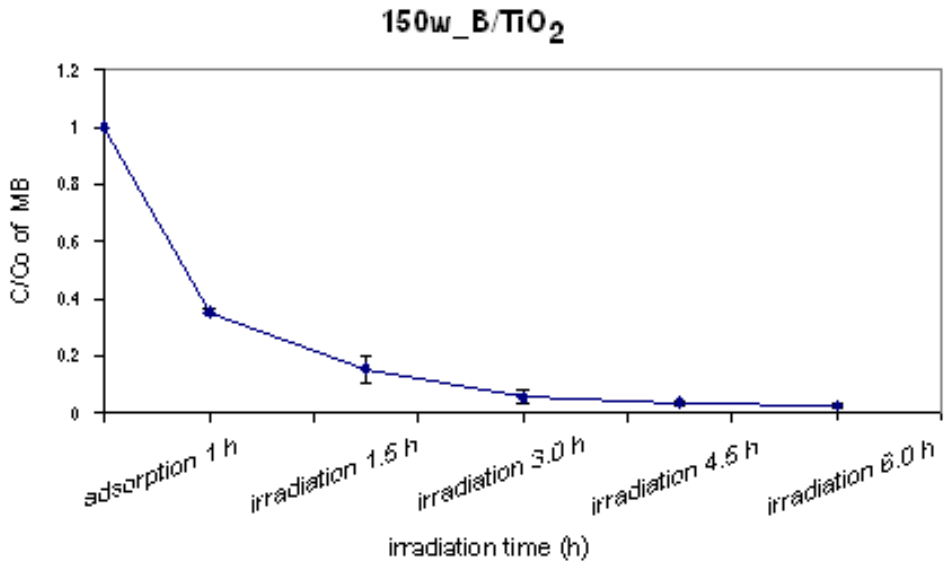


2) C/C_o at 656 nm

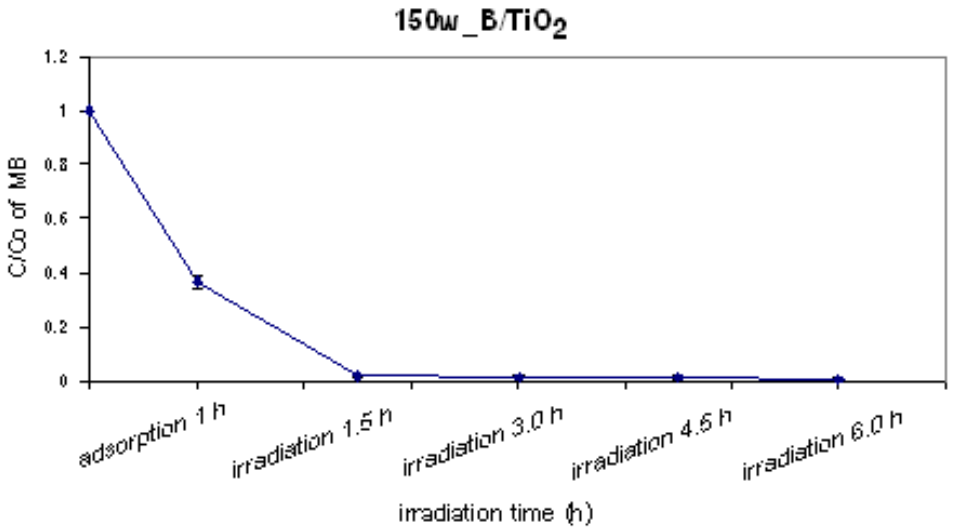


l) 150w_B/TiO_2

1) C/C_o at 614 nm

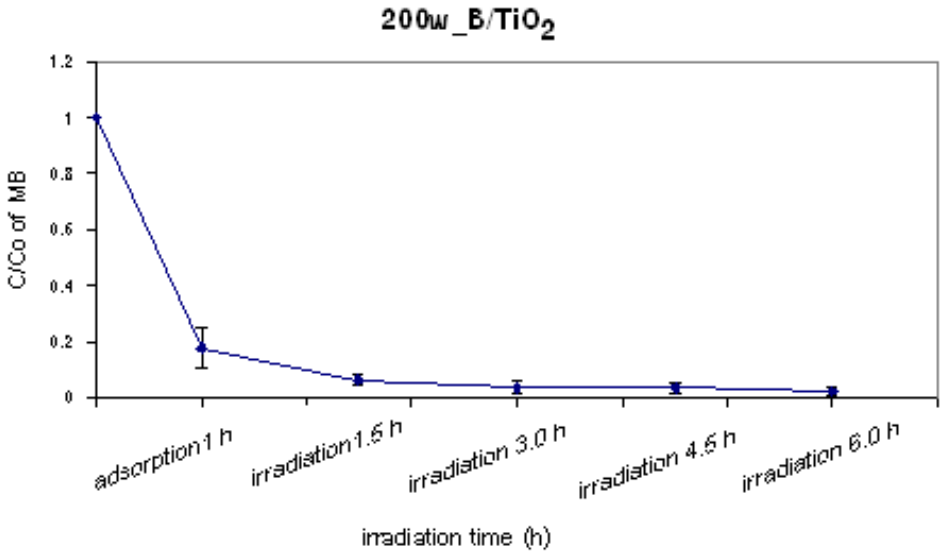


2) C/C_o at 656 nm

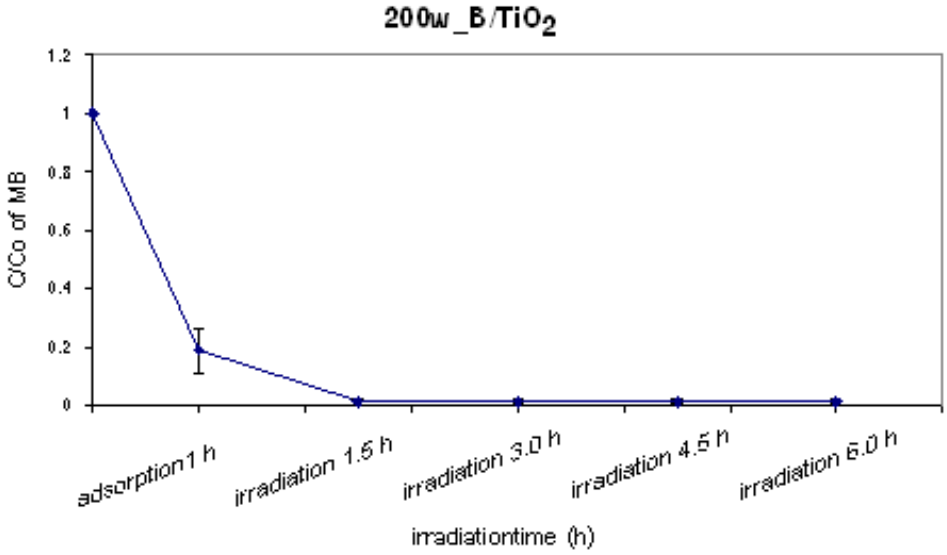


m) 200w_B/TiO_2

1) C/C_o at 614 nm

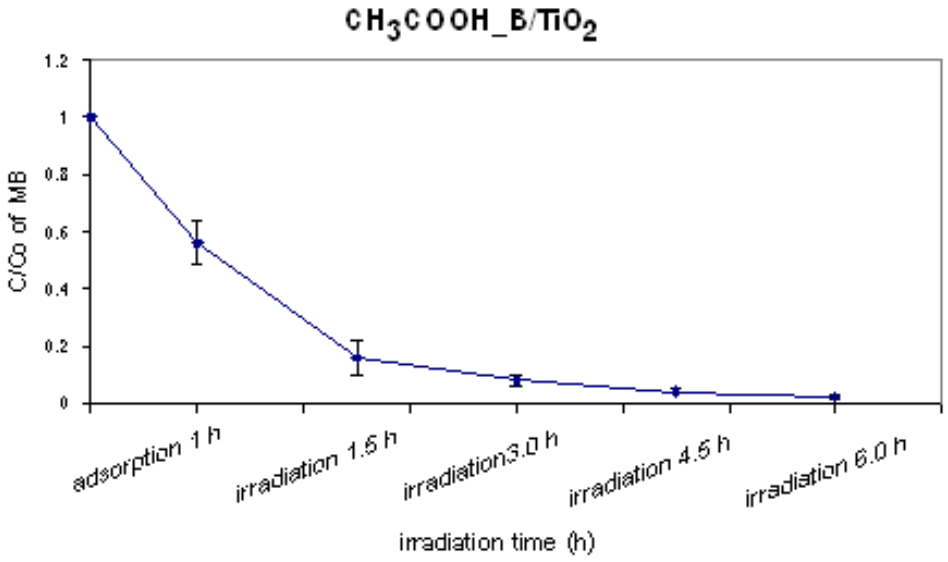


2) C/C_o at 656 nm

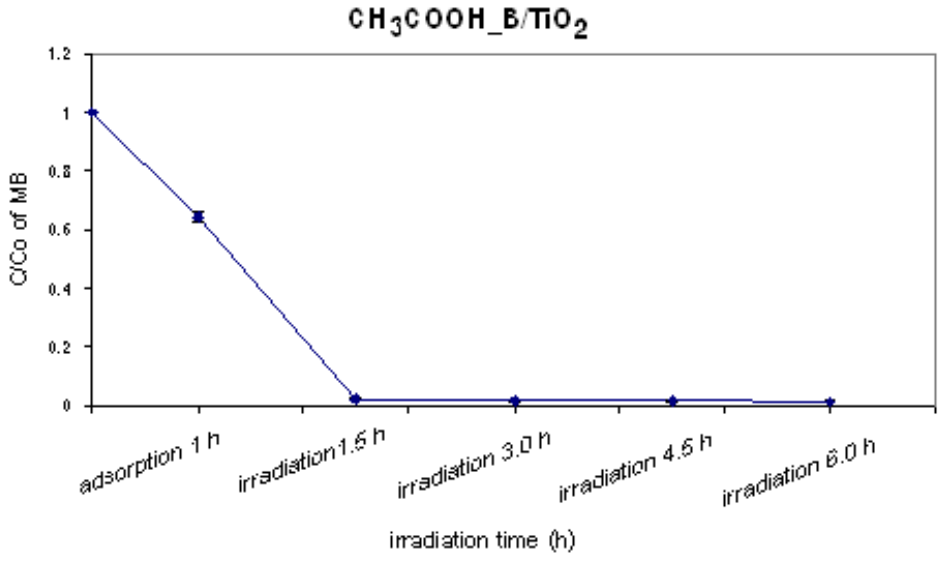


n) CH_3COOH_B/TiO_2

1) C/C_o at 614 nm

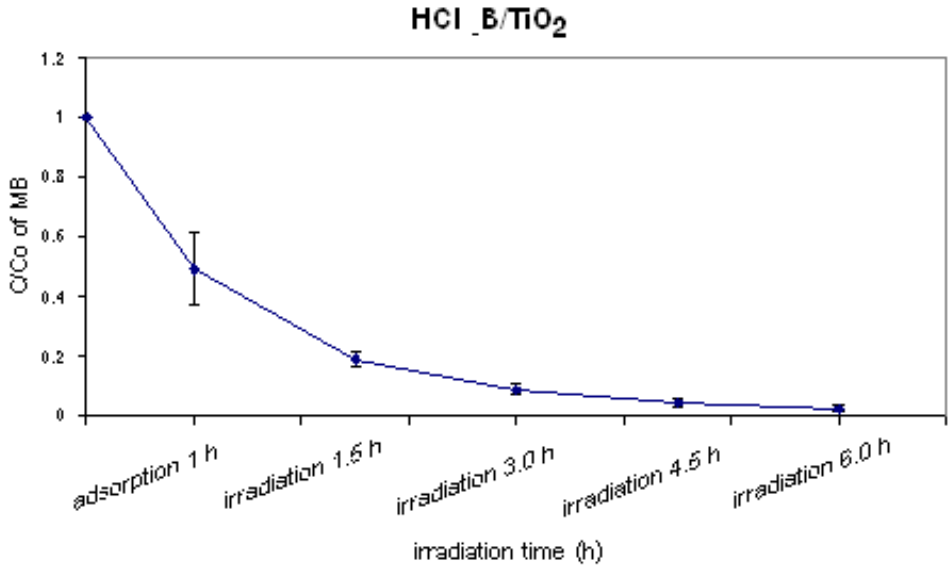


2) C/C_o at 656 nm

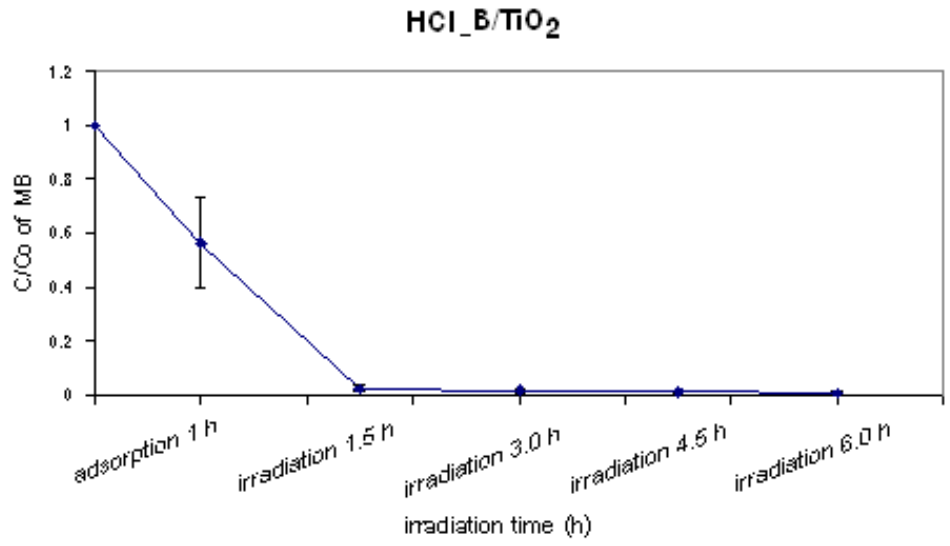


o) HCl_B/TiO_2

1) C/C_o at 614 nm

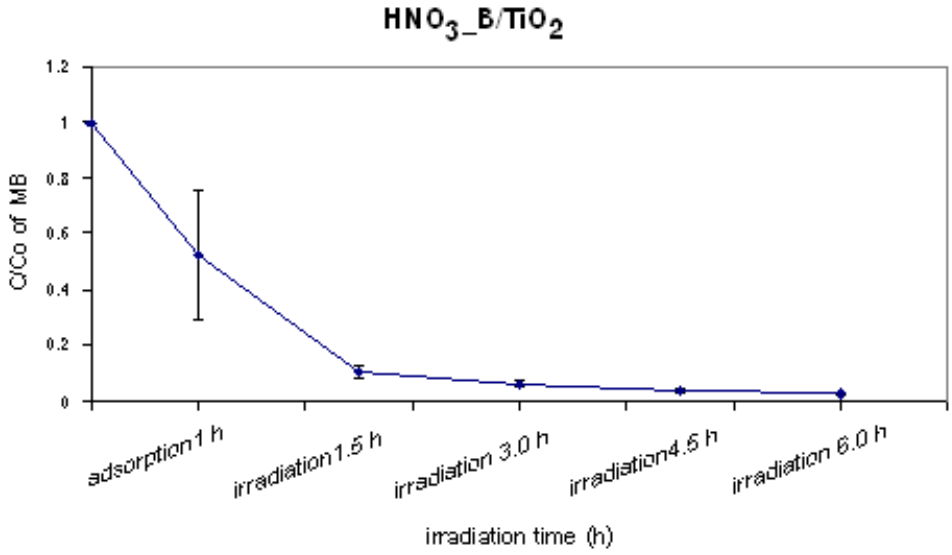


2) C/C_o at 656 nm

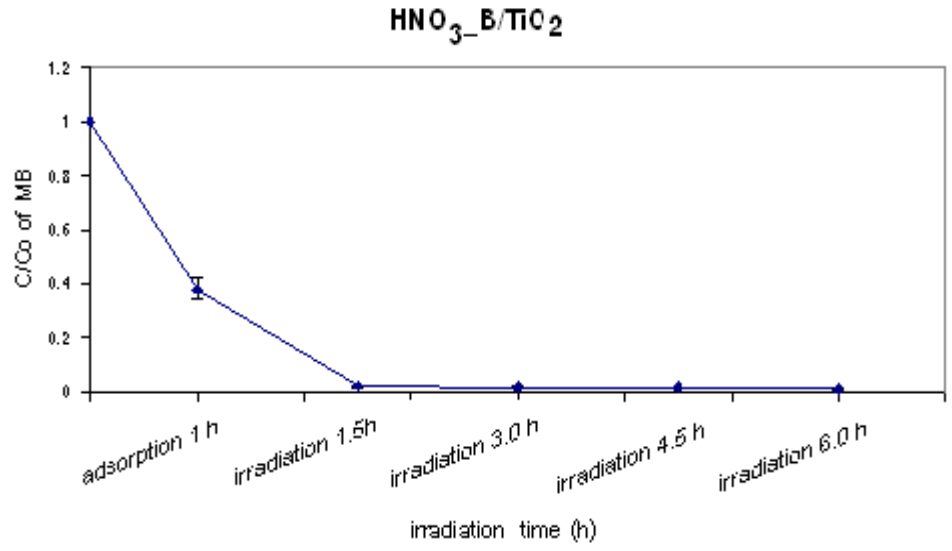


p) HNO_3_B/TiO_2

1) C/C_o at 614 nm

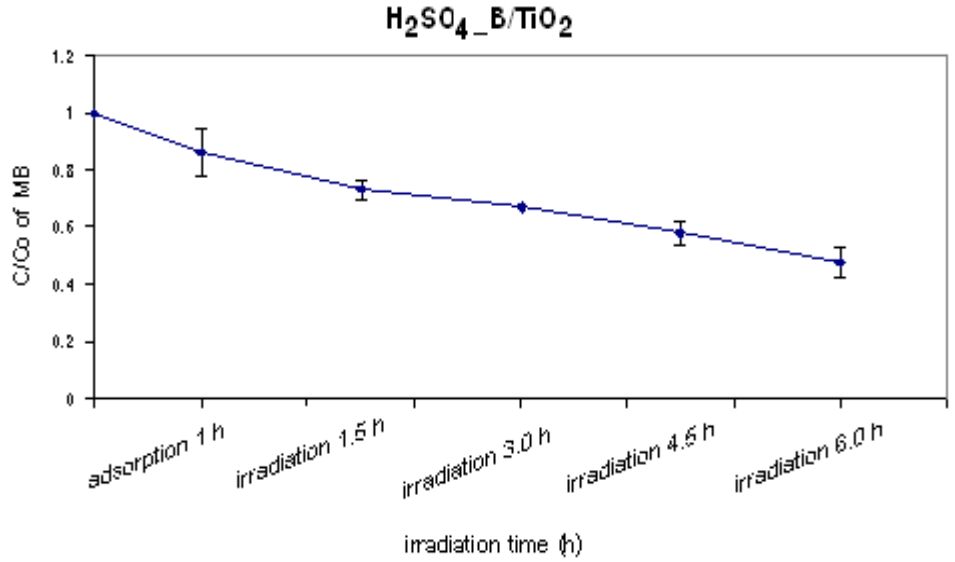


2) C/C_o at 656 nm

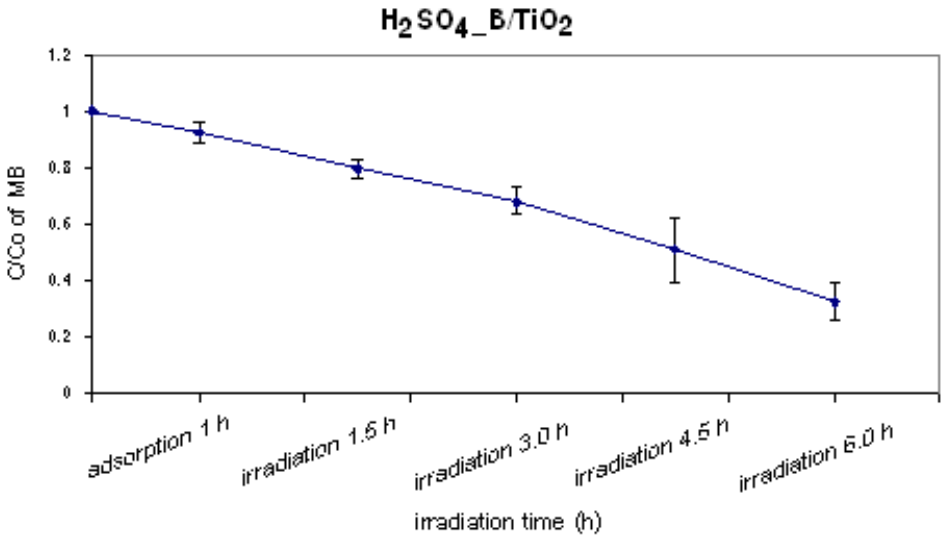


q) H_2SO_4_B/TiO_2

1) C/C_o at 614 nm

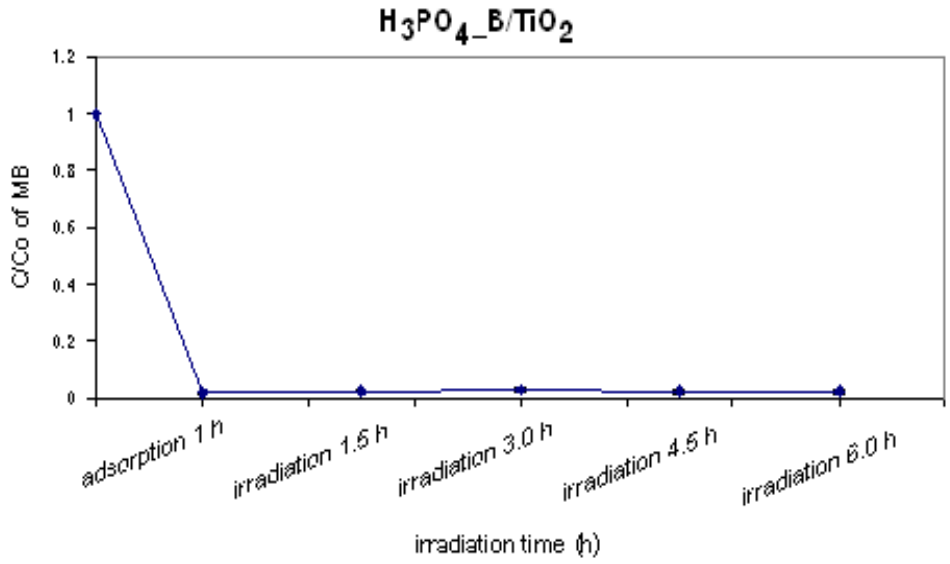


2) C/C_o at 656 nm

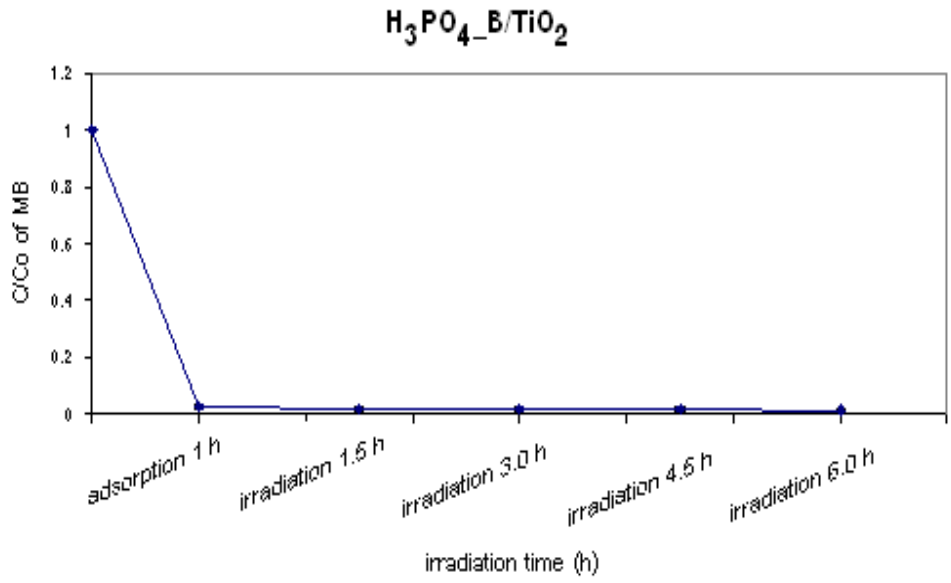


r) H_3PO_4_B/TiO_2

1) C/C_o at 614 nm

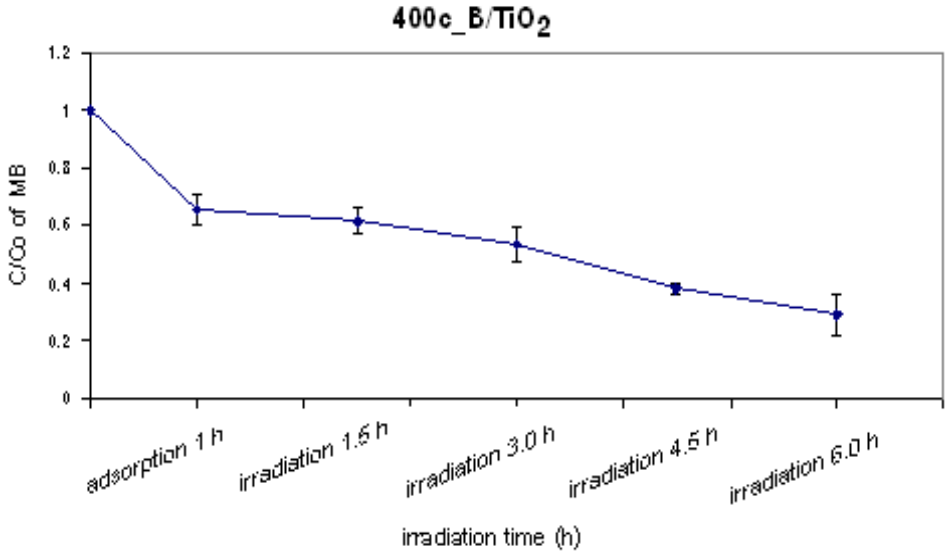


2) C/C_o at 656 nm

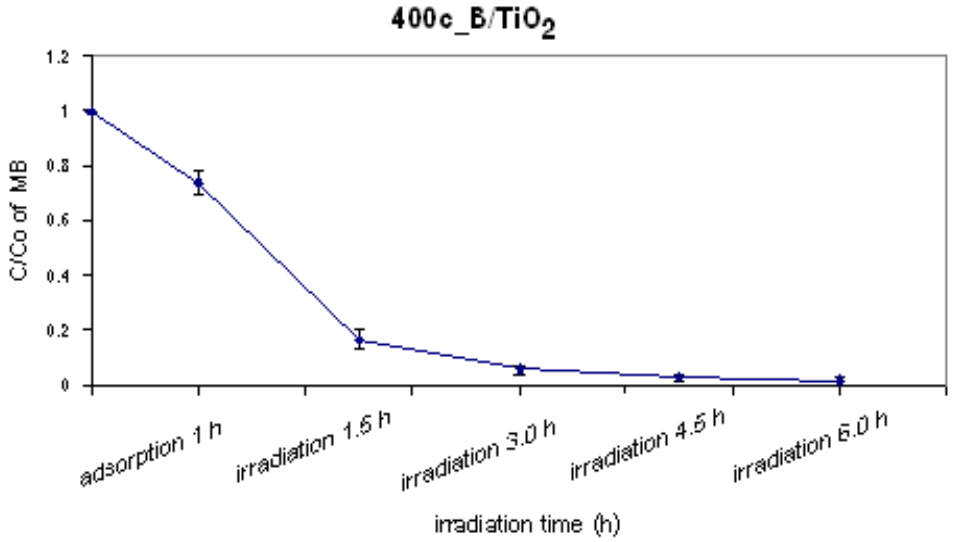


s) 400c_B/TiO_2

1) C/C_o at 614 nm

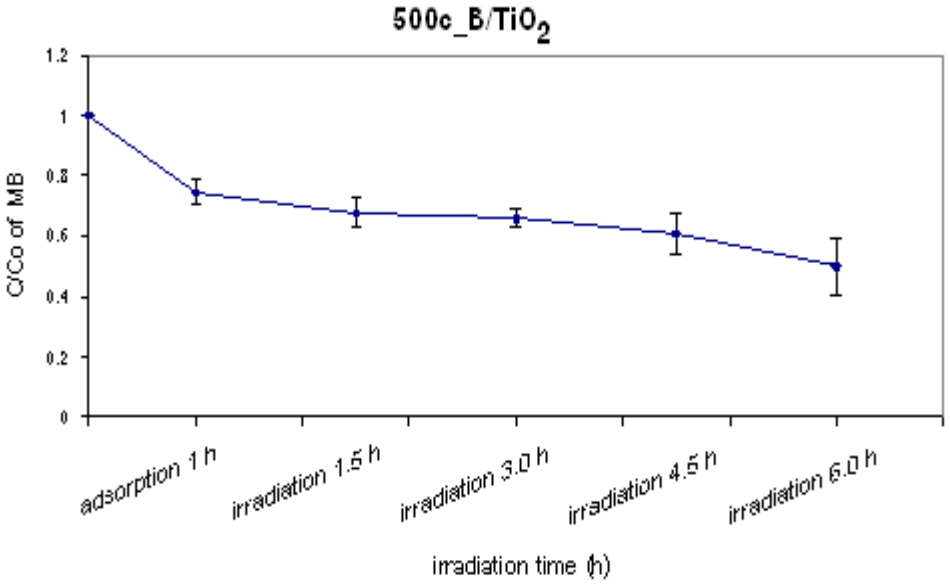


2) C/C_o at 656 nm

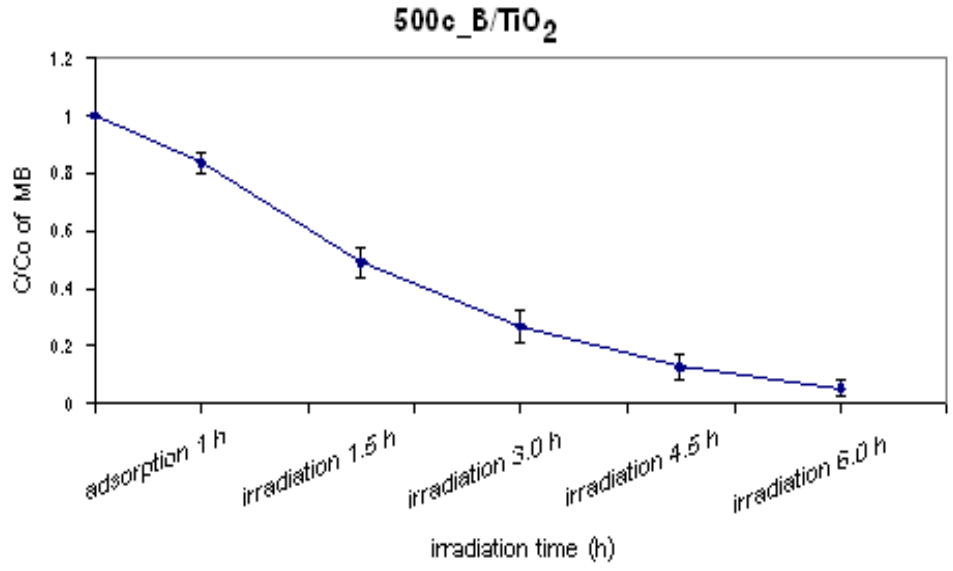


t) 500c_B/TiO_2

1) C/C_o at 614 nm

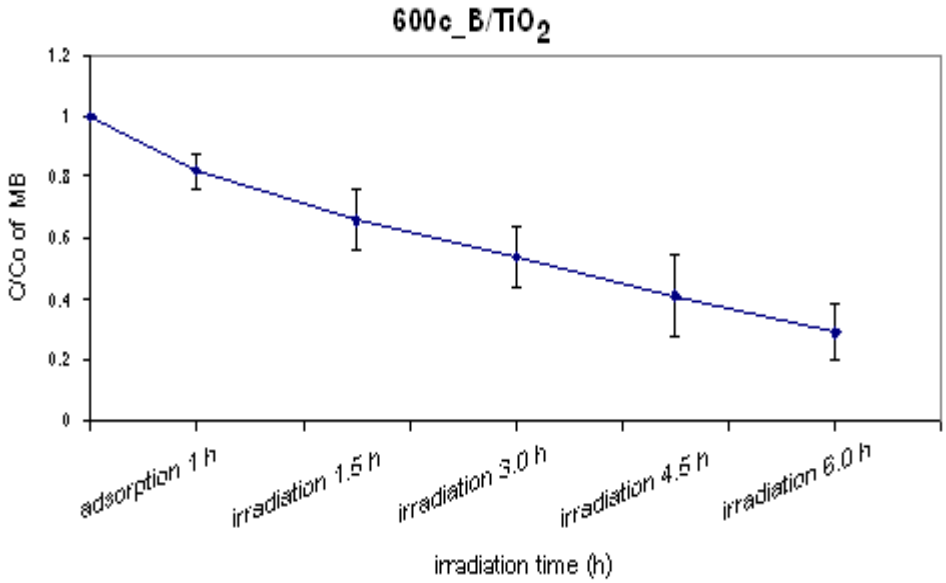


2) C/C_o at 656 nm

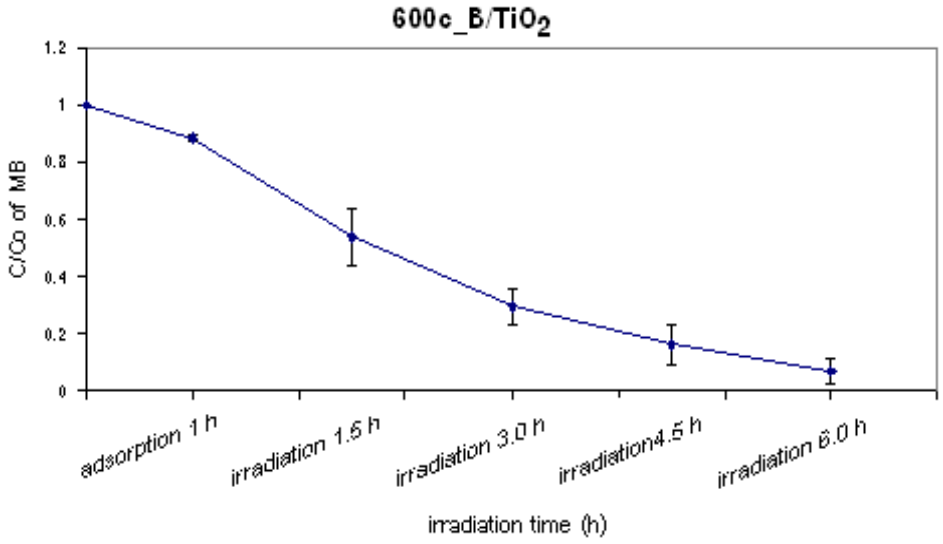


u) 600c_B/TiO_2

1) C/C_o at 614 nm

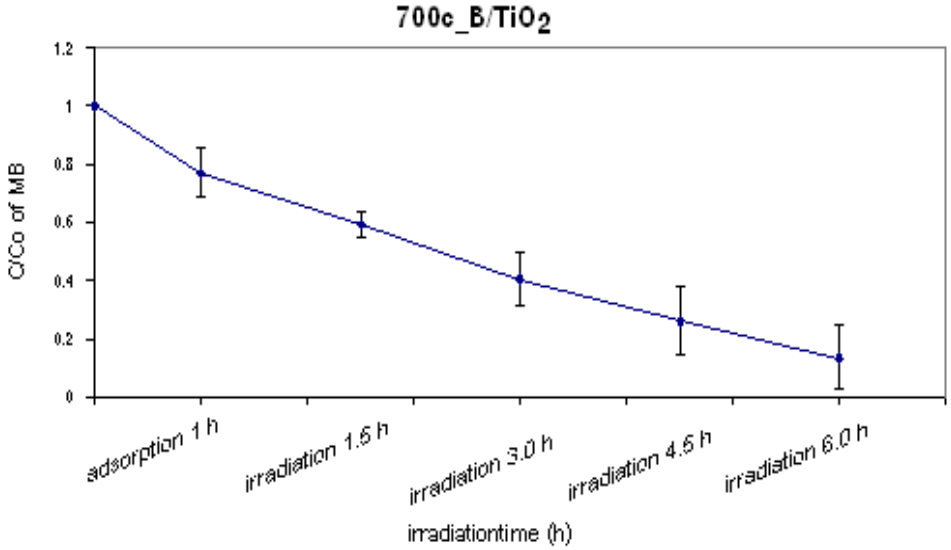


2) C/C_o at 656 nm

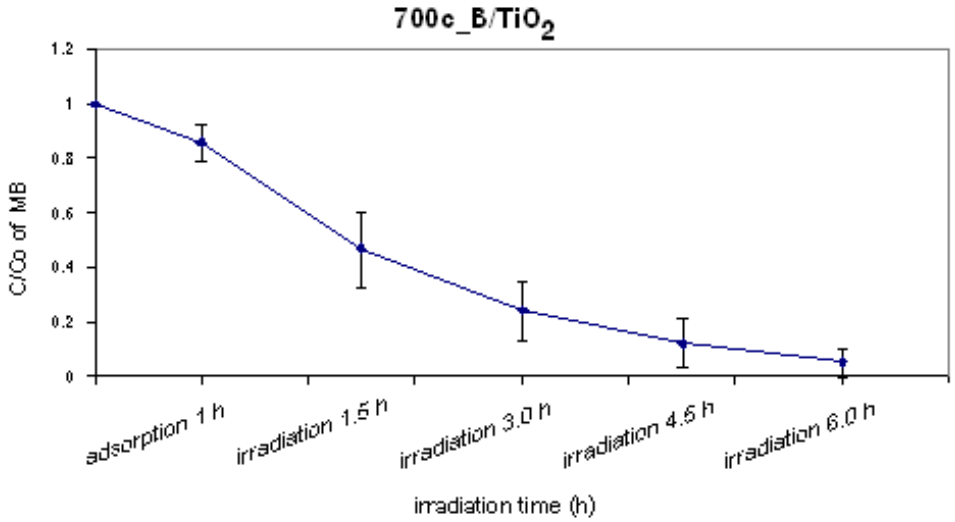


v) 700c_B/TiO_2

1) C/C_o at 614 nm

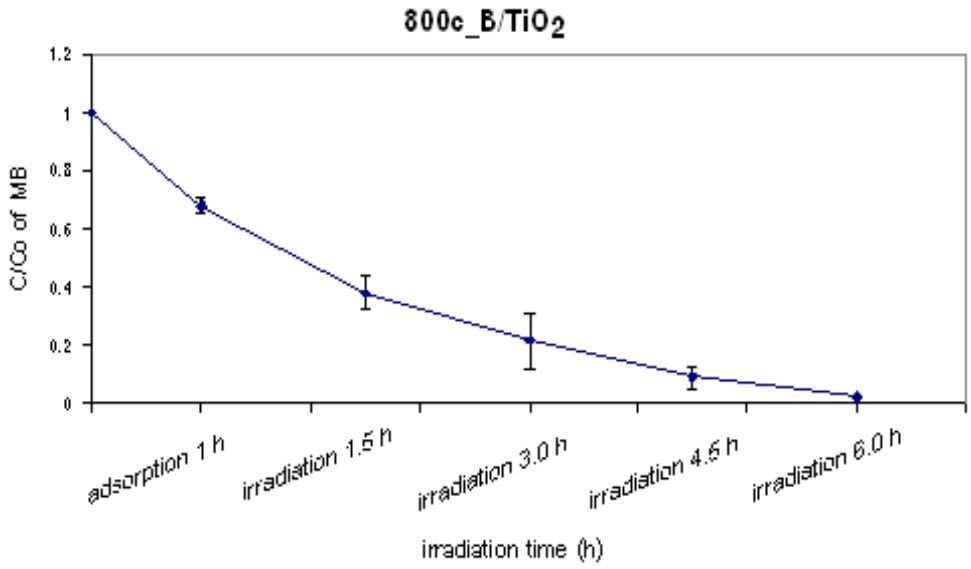


2) C/C_o at 656 nm



w) 800c_B/TiO_2

1) C/C_o at 614 nm



2) C/C_o at 656 nm

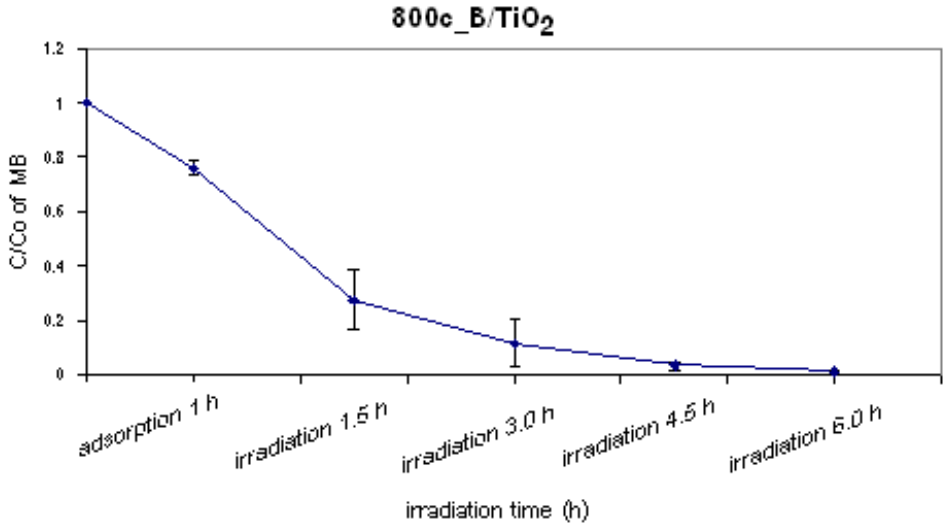


Figure 52 The reletive remained C/C_o of methylene blue in synthesized B-doped TiO_2 samples suspension as a function of time of irradiation.