

CHAPTER IV

RESULTS AND DISCUSSION

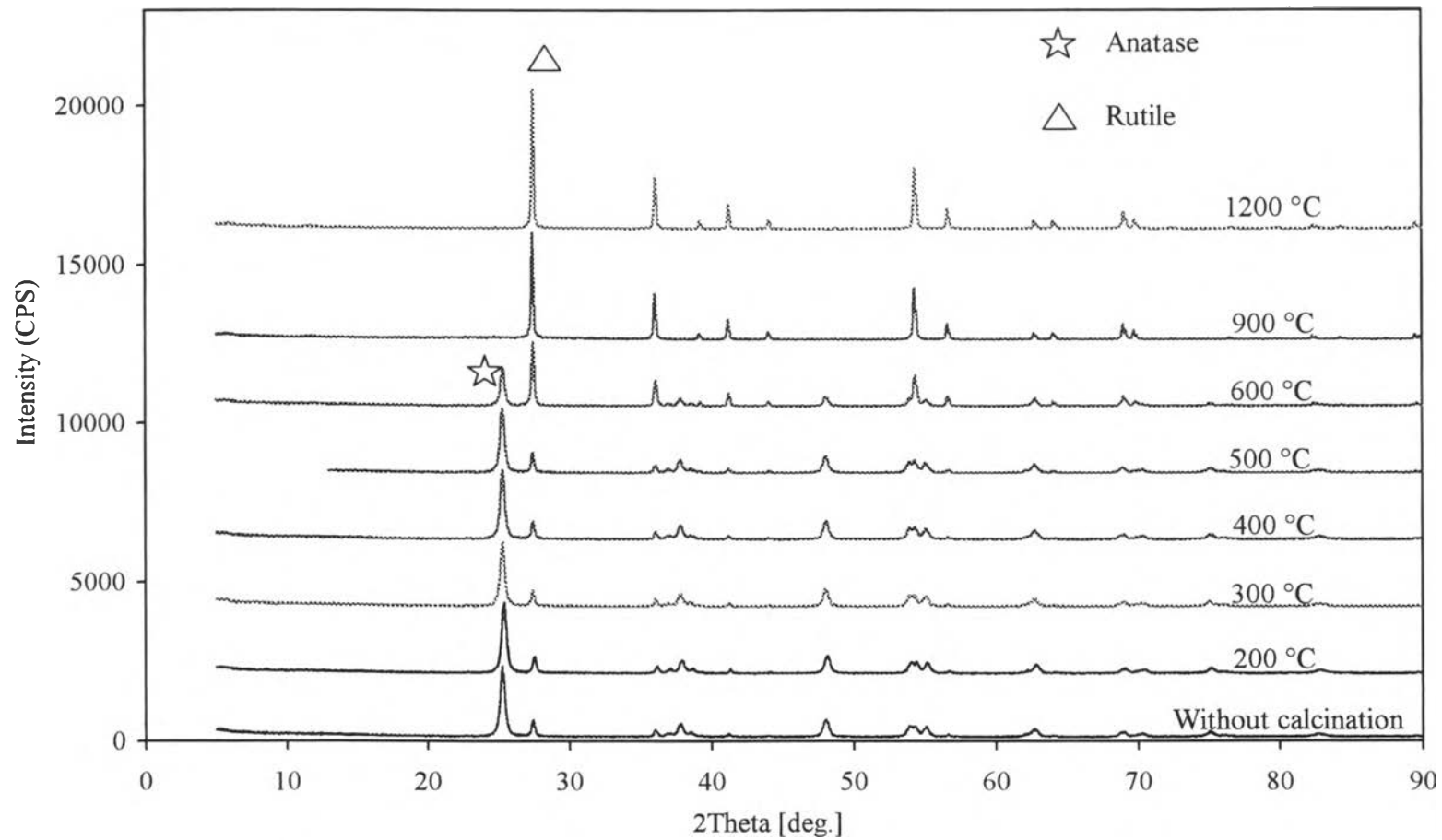
4.1 Catalyst Characterization

4.1.1 Crystal Structure

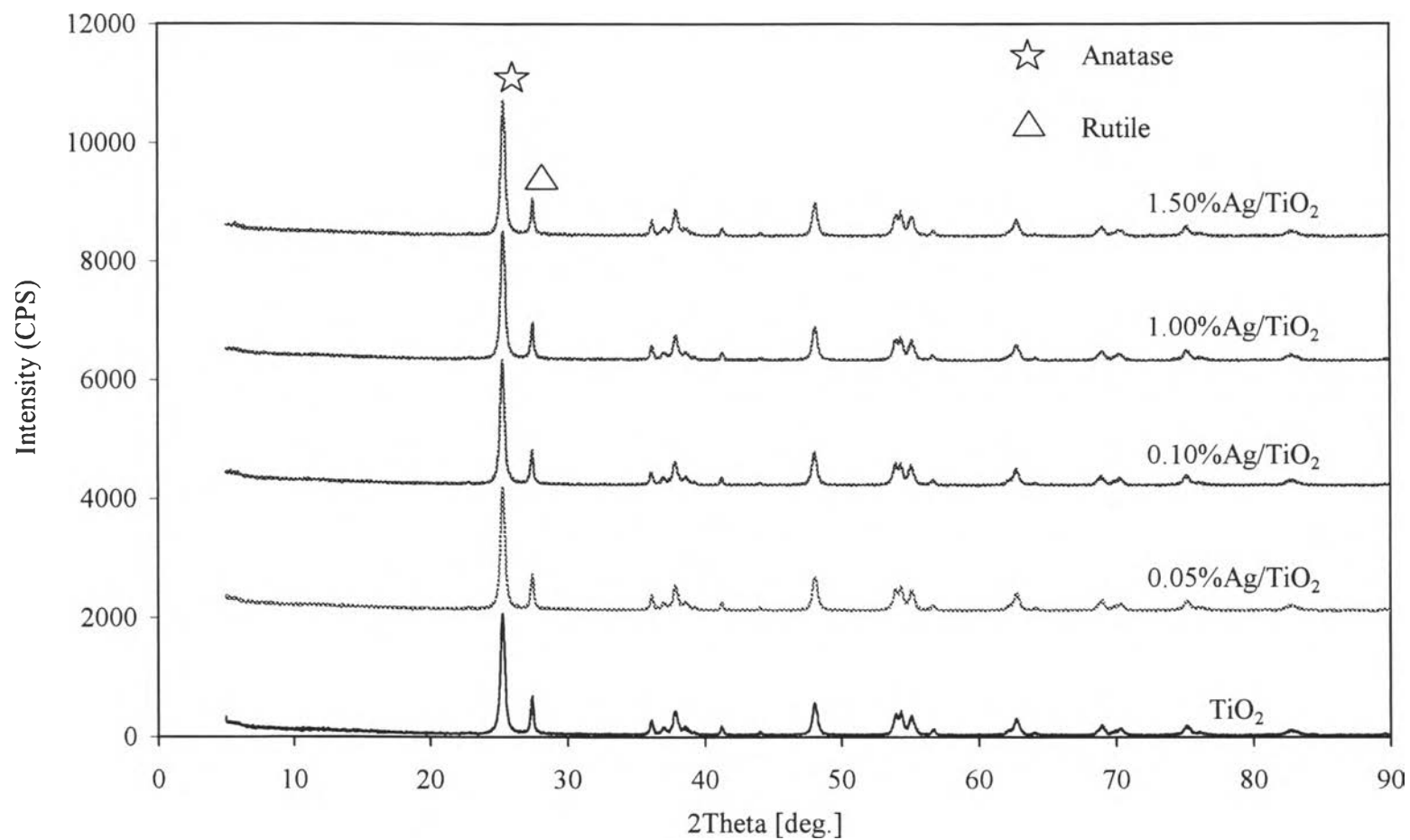
Figure 4.1 shows the XRD patterns of as-received TiO₂ (Degussa P25) and after calcination at 200, 300, 400, 500, 600, 900 and 1200 °C. For the XRD patterns of TiO₂, the main peaks of anatase, rutile and brookite are at $2\theta = 25.3^\circ$, 27.5° and 30.6° , respectively. The as-received TiO₂ (Degussa P25) shows two phases of anatase and rutile. The highest peak at $2\theta = 25.3^\circ$ shows that the major phase is anatase and rutile exists as the minor phase. With the increasing in the calcination temperature from 500 to 600 °C, the anatase peak intensity decreases while that of rutile increases. The anatase phase is transformed completely to rutile when the calcination temperature is higher than 900 °C.

The XRD patterns of Ag/TiO₂ and Au/TiO₂ at different metal loadings after the calcination at 500 °C are shown in Figures 4.2 and 4.3, respectively. The patterns indicate that there is no significant change in the crystal structure of TiO₂. No Ag and Au peaks are observed over the range of the Ag and Au doping. That may be due to the well dispersion of the metals on TiO₂ or low intensity of the metal signal.

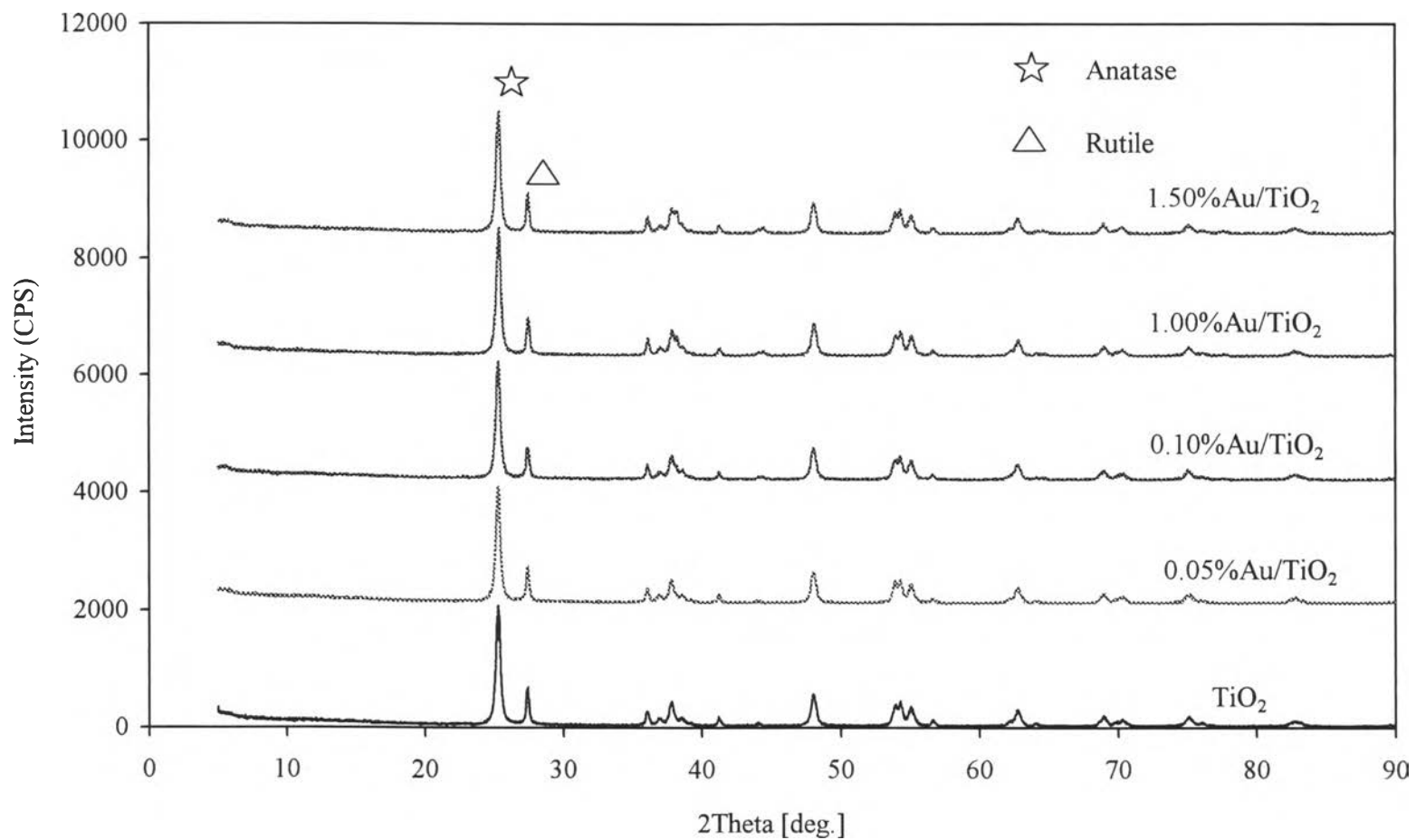
The crystallite sizes of the catalysts can be determined from the broadening of anatase main peak by Debye-Scherrer equation. The crystallite sizes of all catalysts are given in Table 4.1. The increasing in the calcination temperature and amount of metal doping does not significantly affect the crystallite size of TiO₂ in the rutile and anatase phase. The crystallite size of the anatase phase is much lower than that of the rutile phase.



Figures 4.1 X-ray diffraction patterns of as-received and after calcination TiO₂ (Degussa P25) at 200, 300, 400, 500, 600, 900 and 1200 °C for 3 hr.



Figures 4.2 X-ray diffraction patterns of 0.05%Ag, 0.10% Ag, 1.00%Ag, 1.5%Ag doped on TiO₂ and pure TiO₂ (Degussa P25) calcinated at 500 °C for 3 hr.



Figures 4.3 X-ray diffraction patterns of 0.05% Au, 0.10% Au, 1.00% Au, 1.5% Au doped on TiO₂ and pure TiO₂ (Degussa P25) calcinated at 500 °C for 3 hr.

Table 4.1 Crystallite sizes of TiO₂ (Degussa P25) at different calcination temperatures and variation of Ag and Au loading calcined at 500 °C for 3 hr

Catalyst	Crystallite Size (nm)	
	Anatase	Rutile
As-received TiO ₂	23.5	68.1
TiO ₂ (200 °C)	23.7	82.9
TiO ₂ (300 °C)	23.5	73.9
TiO ₂ (400 °C)	23.5	75.5
TiO ₂ (500 °C)	25.1	75.5
TiO ₂ (600 °C)	26.9	84.1
TiO ₂ (900 °C)	-	90.6
TiO ₂ (1200 °C)	-	86
0.05%Ag/ TiO ₂	25.1	71.2
0.10%Ag/ TiO ₂	26.9	77.2
1.00%Ag/ TiO ₂	23.6	80.9
1.50%Ag/ TiO ₂	25.2	79
0.05%Au/ TiO ₂	25.1	75.5
0.10%Au/ TiO ₂	25.1	71.2
1.00%Au/ TiO ₂	23.6	80.9
1.50%Au/ TiO ₂	22.2	90.2

4.1.1 Surface Morphology

TiO₂ (Degussa P25) film prepared on stainless steel by dip coating in the suspension of TiO₂ in methanol (1.0% w/v) for 15 times and drying at 100 °C overnight were characterized using SEM. The surface morphology of stainless steel and TiO₂ on stainless steel is shown in Figure 4.4. The SEM micrographs show that the stainless steel surface is quite smooth but the TiO₂ substrate is porous with high roughness and complexity. A separate experiment has shown that the TiO₂ film on

stainless steel with drying at 100 °C overnight has no significant detachment after being immersed in distilled water with stirring at 400 rpm overnight.

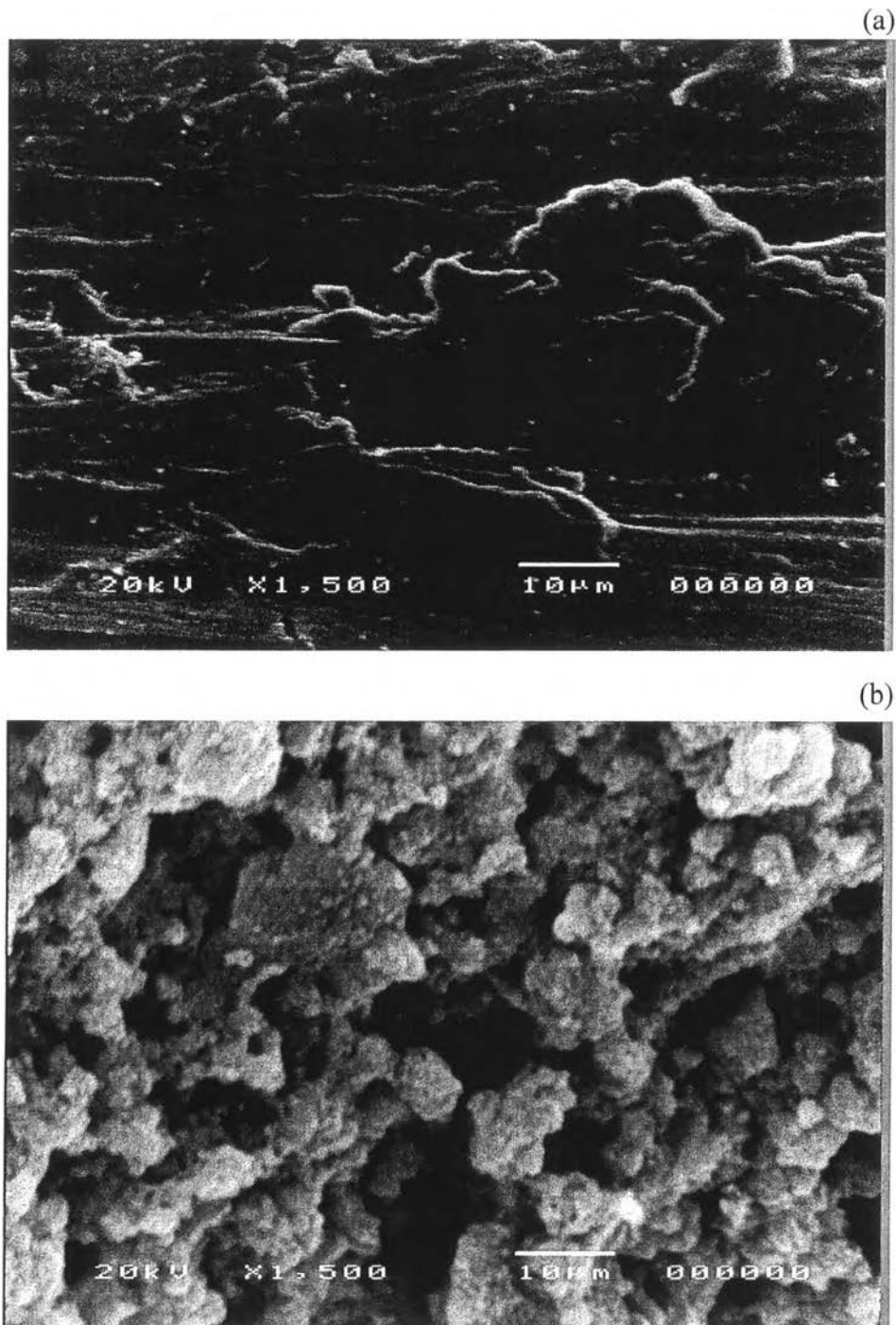


Figure 4.4 Scanning electron micrographs at 1500 x magnification of (a) stainless steel (b) TiO₂ on stainless steel.

4.2 Photocatalytic Degradation of 4-CP

Some nomenclatures used throughout this section are the remaining fraction of 4-CP (C/C_0) and the remaining fraction of TOC (TOC/TOC_0). C/C_0 is ratio of 4-CP concentration at any time to its initial concentration. Similarly, TOC/TOC_0 is the ratio of TOC concentration at any time to its initial concentration.

4.2.1 Photocatalytic Degradation in the Suspension System

4.2.1.1 Effect of Calcination Temperature

The photocatalytic degradations of 0.5 mM of 4-CP in aqueous solution by 0.5 g/l of the as-received or after calcination TiO_2 (Degussa P25) under UV-C radiation was further investigated and results are shown in Figure 4.5. Figure 4.5(a) and (b) shows the remaining fractions of 4-CP and TOC. The remaining fractions of 4-CP decrease rapidly and disappear after 3 hr for all catalysts. It is clearly seen that TiO_2 does not significantly affect the 4-CP degradation. Only UV lamp with short wavelength could destroy the chemical bond in the 4-CP molecule. However, the presence of a catalyst does reduce the TOC compared to the photolysis. The TOC degradation rate with the as-received catalyst shows the highest photocatalytic efficiency as indicated by the lowest TOC/TOC_0 with complete TOC removal after 5 hr. The photolysis could decrease TOC at the same extent as TiO_2 calcinated at 1200 °C, which is mainly rutile.

After the irradiation, HQ and HHQ are formed as intermediates in a consecutive reaction (Moonsiri *et al.*, 2004). The concentration of HQ and HHQ shown in Figure 4.4(a) and (b) initially increases and reaches the maximum before decreasing progressively. In the presence of the as-received- TiO_2 , HQ and HHQ completely disappear after the irradiation for 4 and 5 hr, respectively. For the photolysis, HQ and HHQ are not completely removed after the irradiation for 300 min and still exist at 0.09 mM and 0.16 mM. So the as-received- TiO_2 also improves the intermediate degradation dominantly compared to photolysis.

The increase in the calcination temperature decreases the TOC degradation rate because both crystallinity and catalytic surface area are decreased. When the calcination temperature is increased from 200 to 600 °C, the TOC degradation rate; and the concentration of HQ and HHQ decreases gradually because of the decreasing in the catalytic surface area (Satterfield, 1993). On the other hand, with the change in the temperature from 500 to 600 °C, the TOC degradation rate still decreases while the concentration of HQ and HHQ increases significantly because of the change in the crystal phase from anatase to rutile which is a non-active form (Cheng *et al.*, 1995). The catalyst calcinated at 1200 °C has no photocatalytic degradation effect. It can be concluded that the crystal structure is the most important parameter for the photocatalytic activity. The concentration of HQ and HHQ with the irradiation time for 6 hr and TiO₂ calcinated at 900 and 1200 °C is higher than those in the photolysis. The cause of this phenomenon is that the catalyst particles which have no activity obstruct 4-CP and its intermediate product from the UV-C irradiation.

4.2.1.2 Photocatalytic Degradation of 4-CP with Ag/TiO₂

The amount of Ag doped on TiO₂ (Degussa P25) prepared by incipient wetness impregnation was varied from 0.05-1.50 wt% to study effect of Ag attributed on the TiO₂. The degradation of 0.5 mM of 4-CP with TiO₂ calcinated at 500 °C and Ag/TiO₂ of 0.5 g/l was studied at different Ag dopings is shown in Figure 4.6. The figure shows that Ag deposited on TiO₂ particles does not alter the breakdown pathway of 4-CP compared to TiO₂ calcined at 500 °C.

The remaining fraction of 4-CP compared in Figure 4.6(b) implies that the amount of Ag doping does not significantly affect the 4-CP degradation. 4-CP completely disappears in 2 hr for all the catalysts tested. However, the effects on the intermediate products are clearly observed. It was found that after 6 hr the concentration of HQ and HHQ with 0.05 and 0.1%Ag/TiO₂ is lower than that resulted from using 500 °C calcined TiO₂. In addition, the concentration of HQ and HHQ with 1.00–1.50%Ag/TiO₂

increases with the increased in the amount of Ag. Similarly, the TOC degradation is affected as well. It was found that 0.05-0.01%Ag/TiO₂ facilitates the TOC degradation. The minimum TOC was observed with 0.10%Ag/TiO₂ after 6 hr. With the amount of Ag is higher than or equal to 1.00%Ag/TiO₂, the remaining fraction of TOC increases with increasing the Ag doping.

It is obvious that a small amount of Ag doping improves photocatalytic activity. The reason is that a small amount of Ag acts as a sink for photo induce carrier and acceleration of superoxide radical anion, O₂^{•-}, formation, which, in turn, increases the lifetime of holes and suppresses the electron-hole recombination process (Blazkova *et al.*, 1998). Another possible explanation is that Ag increases the rate of direct hole oxidation pathway leading to the improvement of the photocatalytic efficiency (Ilsz and Dombi, 1999). On the contrary, the addition of Ag also blocks the active site exposed to the UV light (Arabatzis, 2002). That is why the catalytic activity of 0.05%Ag/TiO₂ is less than that of 500°C calcined TiO₂ and that of 1%Ag/TiO₂ does not increase significantly. When the amount of Ag increases to a certain level, the photo electron will transfer from the semiconductor to metal particles while the accumulated negative charge is not consumed or not further transferred out of the metal. As a result, the particles become the recombination center (Arabatzis, 2002). So, the activity of the metal doping at higher and equal to 1.00%Ag/TiO₂ is lower than 0.05%Ag/TiO₂.

4.2.1.3 Photocatalytic Degradation of 4-CP with Au/TiO₂

Amounts of Au doped on TiO₂ (Degussa P25) were varied from 0.05 to 1.5 wt% and calcined at 500 °C for 3 hr. The degradation of 4-CP is shown in Figure 4.7.

The result of 4-CP degradation in Figure 4.7(a) shows that the amount of Au does not affect the degradation as in the Ag doping. However, its effects on the intermediate still exist. It was found that the optimum Au doping, 0.10%Au/TiO₂, gives the lowest TOC/TOC₀ compared with the other Au doping. However, the remaining fraction of TOC is higher

than that with 500°C calcined TiO₂. It is obvious that a small amount of Au doping affects the catalytic activity of TiO₂ but not to a desire level.

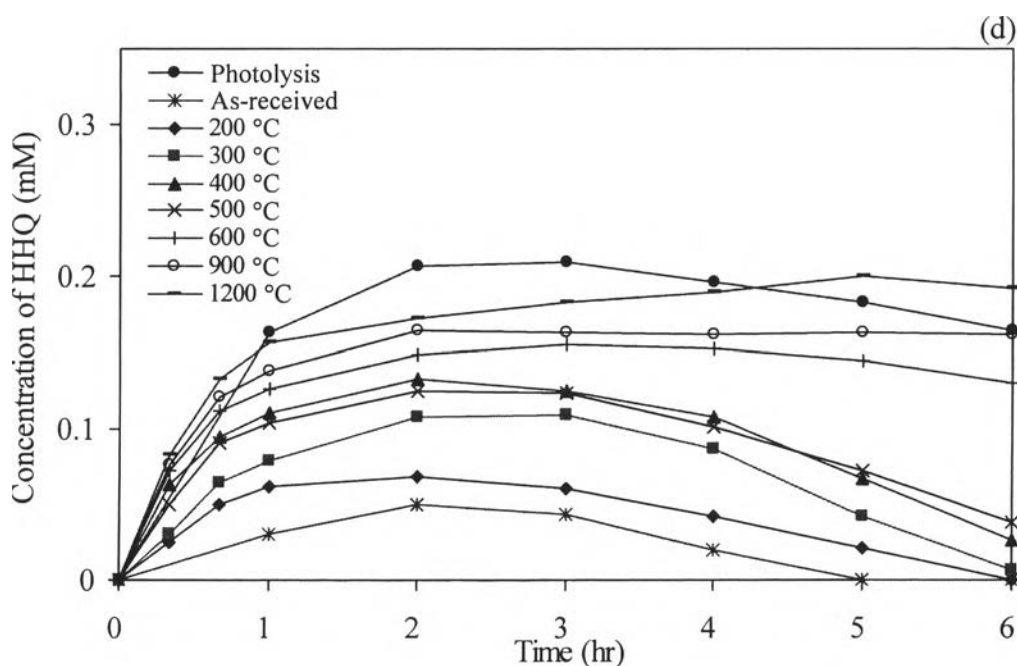
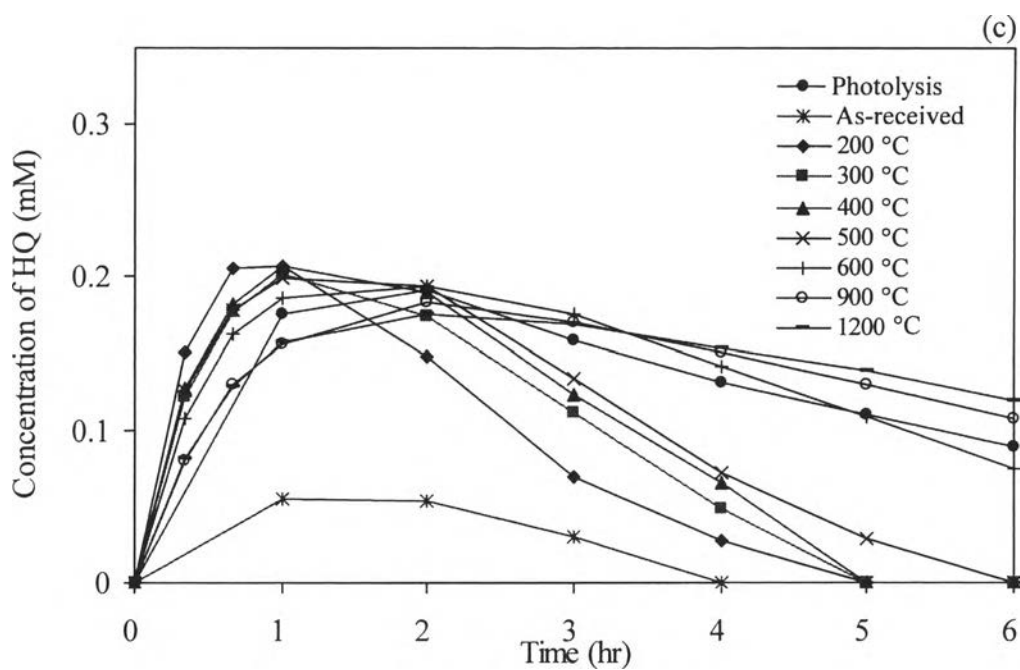
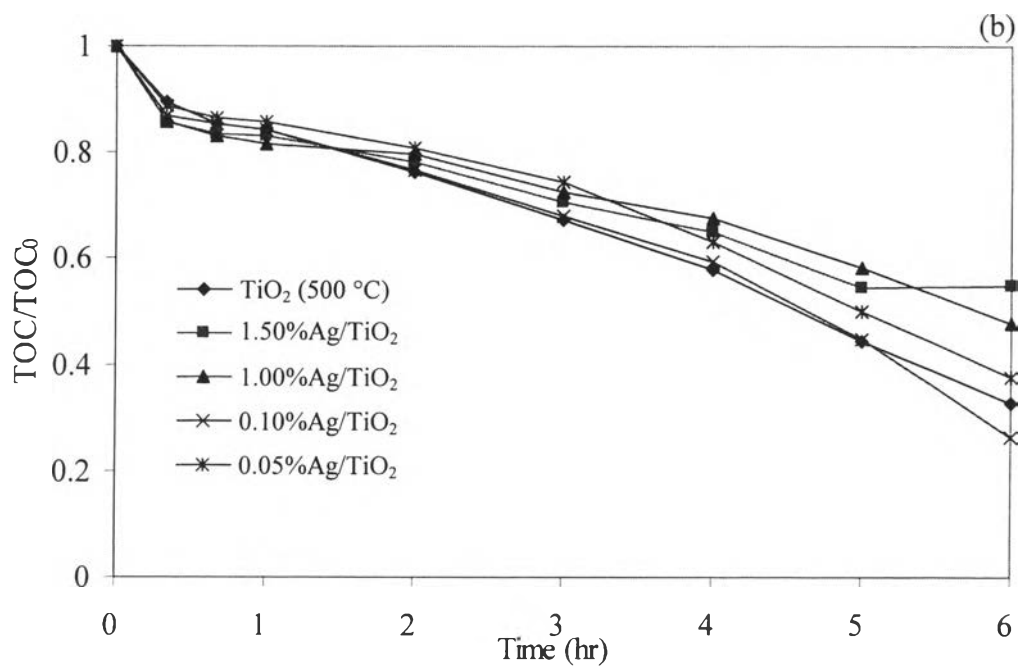
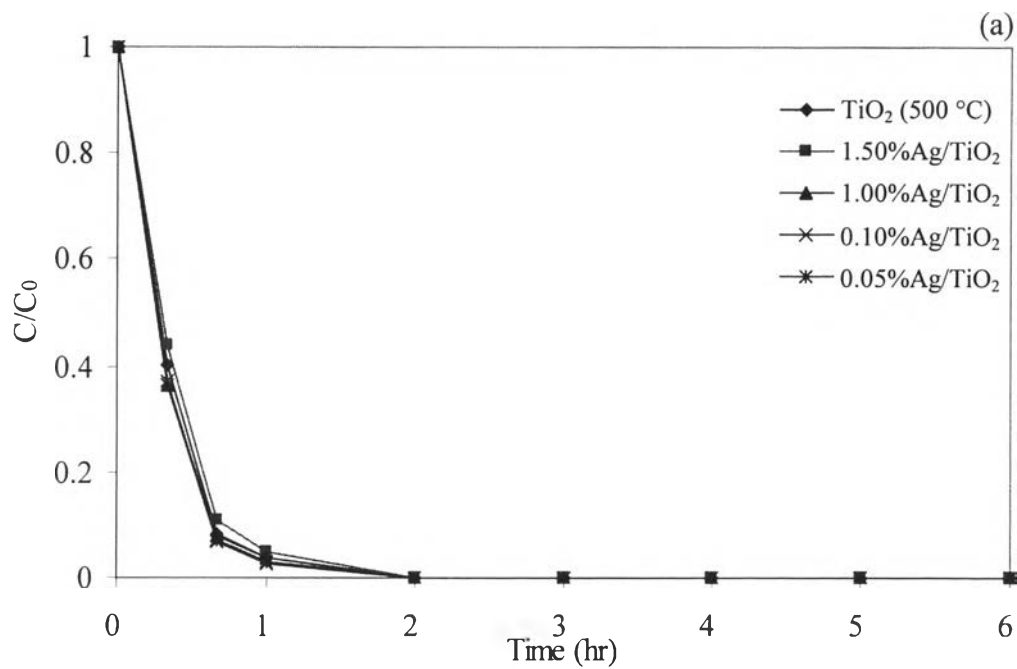


Figure 4.5 Photocatalytic degradation of 4-CP as a function of irradiation time using as-received and after the calcination TiO_2 at 200, 300, 400, 500, 600, 900 and 1200 °C (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.



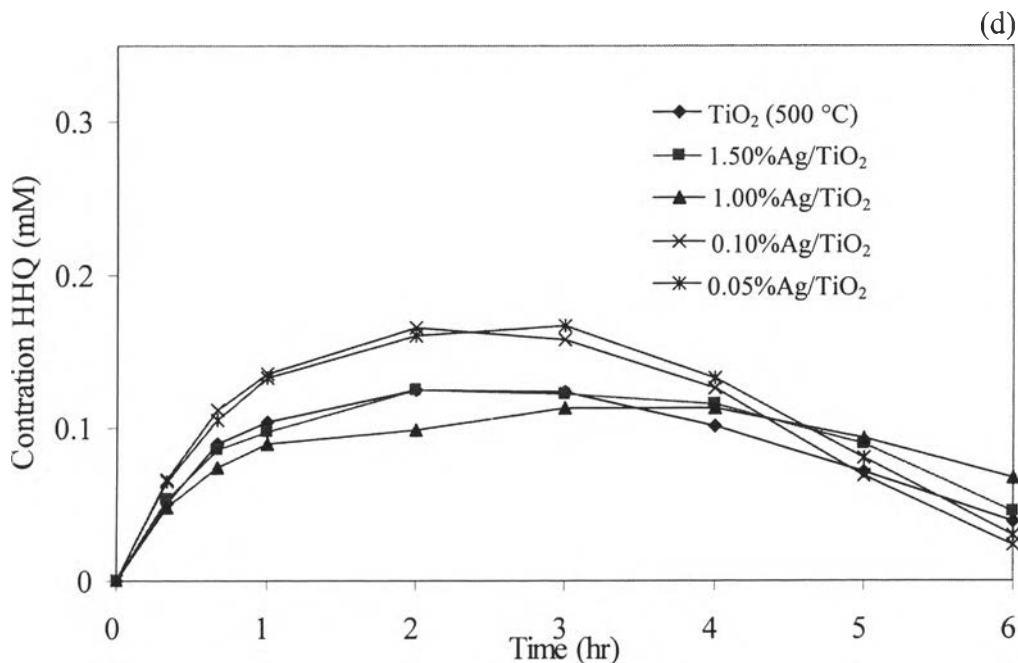
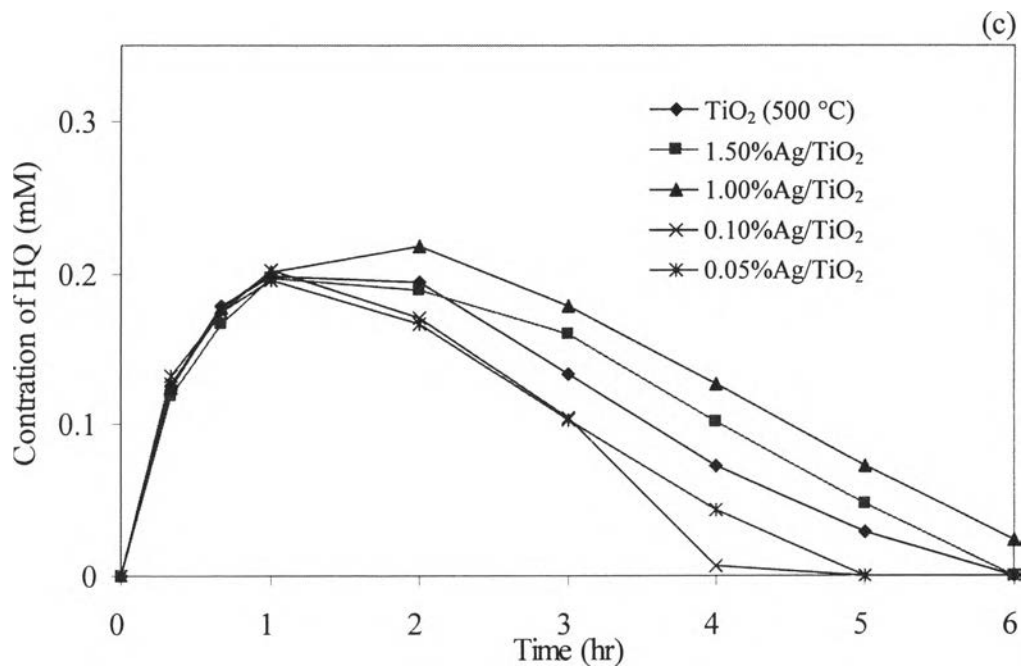
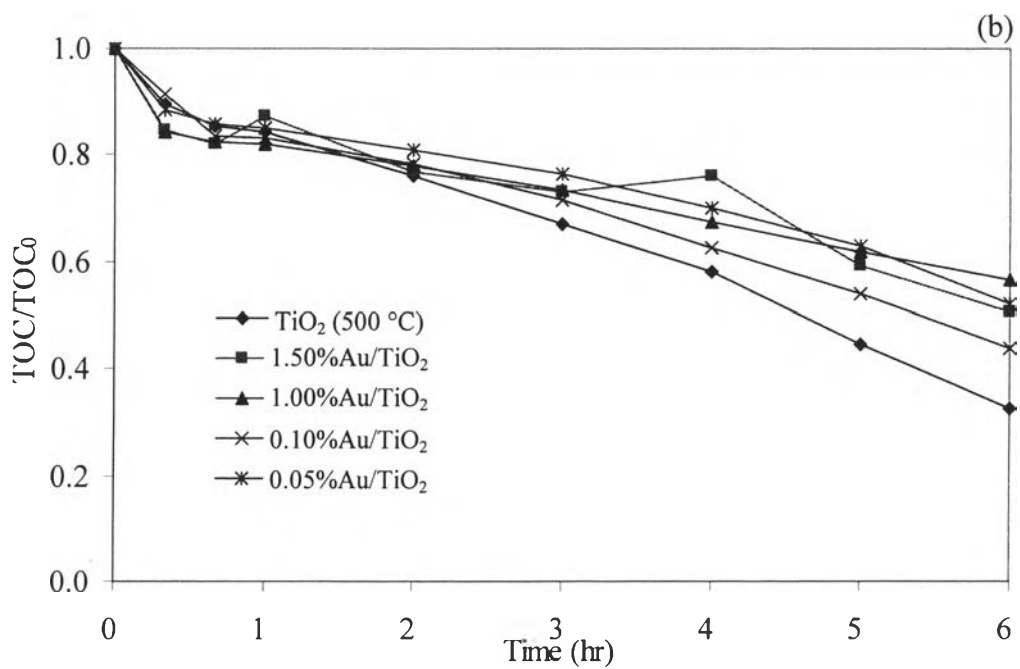
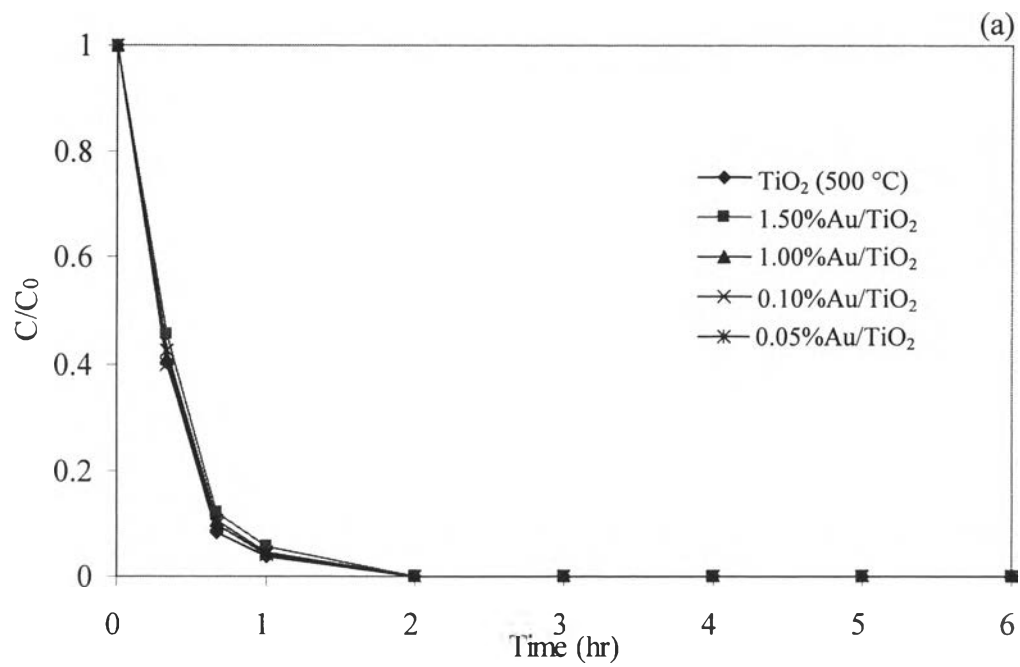


Figure 4.6 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.05%Ag/ TiO_2 , 0.10%Ag/ TiO_2 , 1.00%Ag/ TiO_2 , 1.50%Ag/ TiO_2 and TiO_2 calcined at 500 °C (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.



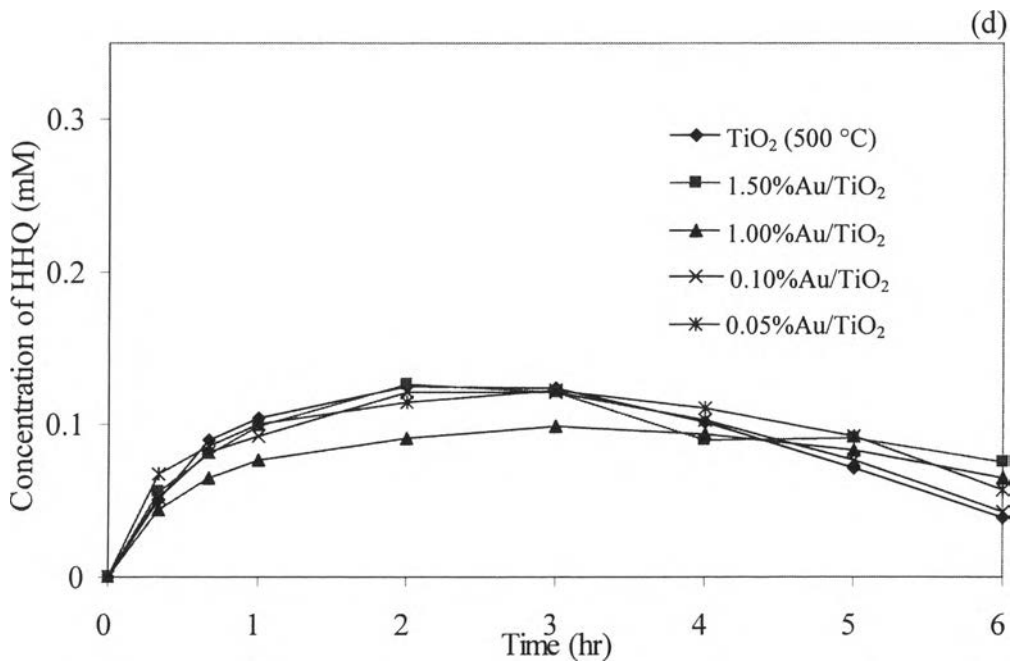
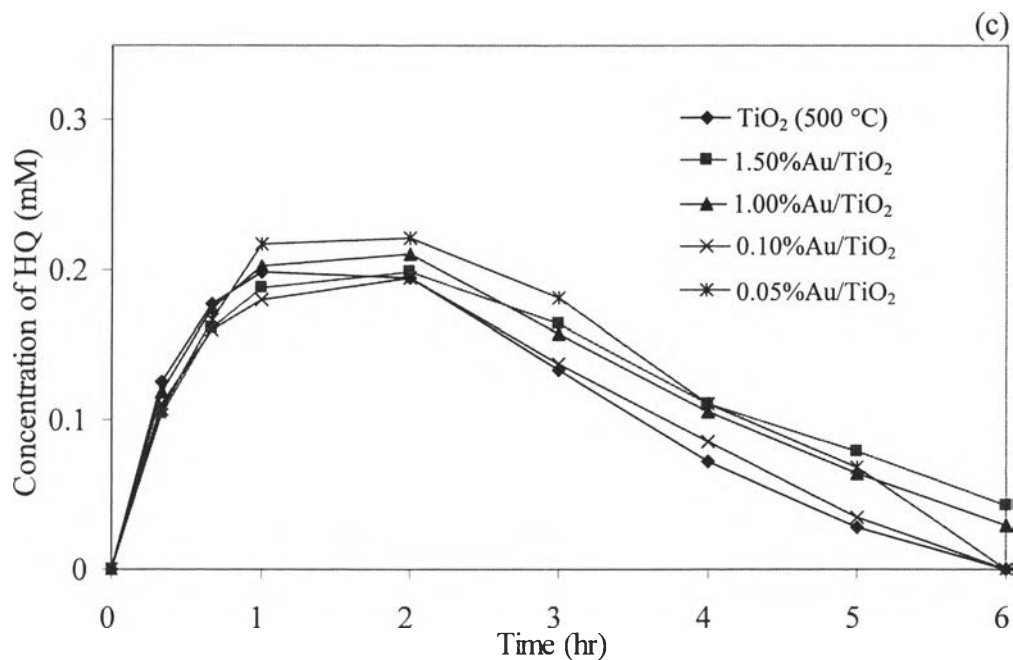


Figure 4.7 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.05%Au/ TiO_2 , 0.10%Au/ TiO_2 , 1.00%Au/ TiO_2 , 1.50%Au/ TiO_2 and TiO_2 calcined at 500 °C (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.

4.2.2 Photocatalytic Degradation in the Immobilized System

4.2.2.1 *Effect of Stage Number*

The photocatalytic reaction without TiO₂ immobilized on stainless steel is shown in Figure 4.8. As expected, the 4-CP degradation shown in Figure 4.8(a) increases with the increase in the number of stage number at any flow rate while the TOC degradation shown in Figure 4.8(b) is not significantly affected by the stage number. 4-CP degradation completely disappears with the solution flow rate equal to 25 ml/min or less. The HQ and HHQ concentration in Figure 4.8(c) and 4.8(d) shows that the concentration increases with the increase in the stage number when the solution flow rate equals to 25, 50 and 200 ml/min but for the flow rate of 12.5 ml/min the concentration reaches the maximum at the 2nd reactor and slightly decreases as the stage number increases. In other words, the stage number has a more pronounced effect on the degradation of 4-CP than that of HQ, HHQ. From another point of view, UV-C light helps in the degradation of 4-CP but not the intermediates.

With TiO₂ immobilized on stainless steel, the degradation of 4-CP, TOC, HQ and HHQ is shown in Figure 4.9. The 4-CP degradation shown in Figure 4.9(a) significantly increases as the flow rate decreases from 25.00 to 12.50 ml/min and slightly increases from 12.5 to 6.25 ml/min. It can be explained that 4-CP is mainly degraded by the UV-C radiation. The TOC degradation shown in Figure 4.9(b) is dominantly enhanced and TOC completely disappears with the solution flow rate of 6.25 ml/min in the 3rd reactor. The remaining TOC from the solution flow rates of 12.5 and 25.0 ml/min at the end of the 4th reactor are 50% and 11% of the photolysis, respectively. For the intermediate degradation, as expected, TiO₂ enhances the intermediate degradation. The intermediate concentration with 6.25 and 12.50 ml/min solution flow rates completely disappears in the 3rd and 4th reactors, respectively, as shown in the Figure 4.9(c) and 4.9(d). The results show that TiO₂ increases the degradation compared to the degradation without TiO₂.

4.2.2.2 Effect of Feed Flow Rate

For the reaction without TiO_2 , Figure 4.10 illustrates the effect of feed flow rate on the degradation of 4-CP. For any stage number, the 4-CP and TOC degradation increase with the decrease in the feed flow rate because an increase in the feed flow rate corresponds to the decrease in the resident time.

The degradation of 4-CP with TiO_2 immobilized on stainless steel is shown in Figure 4.11. At the low feed flow rates, 5 to 25 ml/min, the 4-CP and TOC degradation also increase with decreasing feed flow rate. In addition, the TOC degradation increases significantly when TiO_2 was added in the system.

The results imply that the photocatalytic reaction rate is low. That is why the activity is high at the low flow rate.

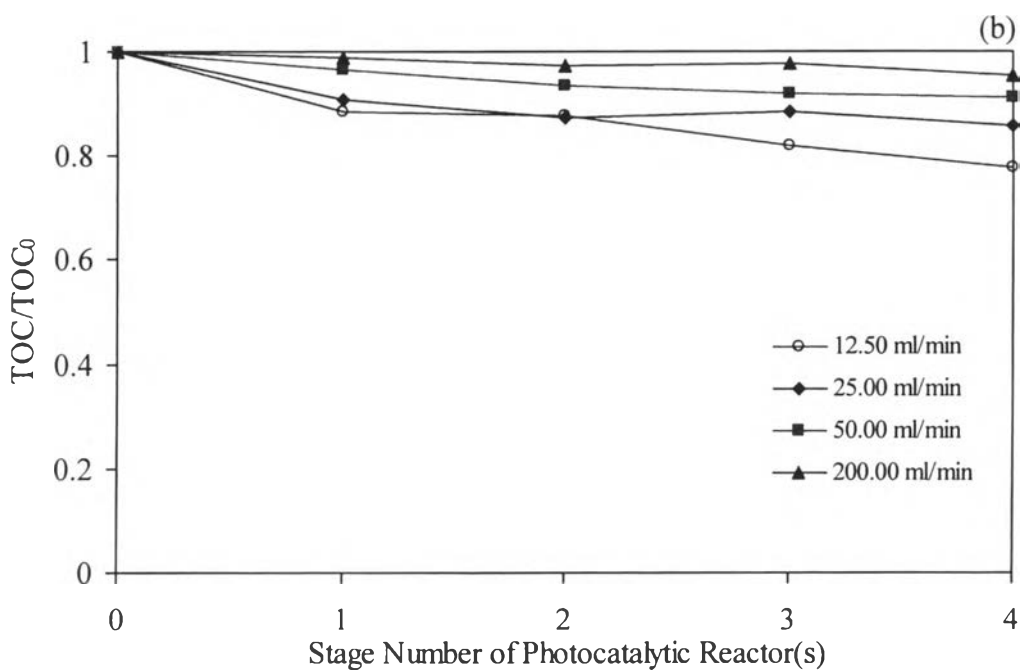
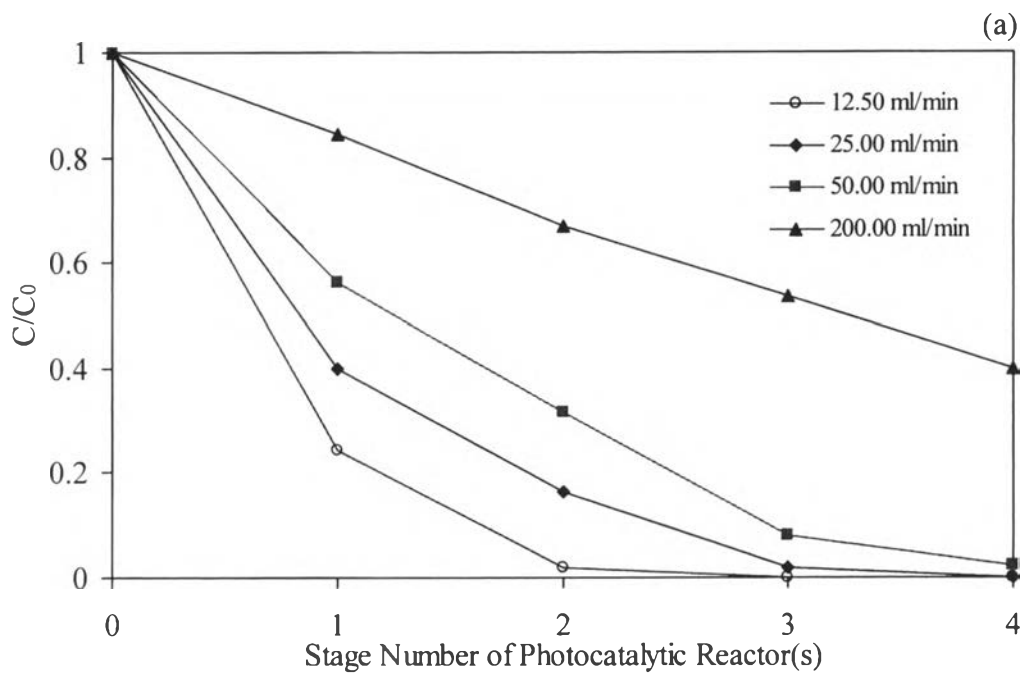
4.2.2.3 Effect of Stage Number of Reactor(s) at the Same Retention Time

The activity comparison of the degradation of 4-CP with TiO_2 and without TiO_2 at the same retention time in the 4 reactors is shown in Figures 4.12 and 4.13, respectively. As expected, the 4-CP degradation increases with increasing stage number of reactor(s). Interestingly, the TOC degradation is hardly affected by the increase in the stage number of reactor(s). The explanation is that during the 4-CP degradation, HQ, HHQ and unknown are formed and increased slightly with the stage number (Figure 4.12(c) and (d)).

4.2.2.4 Durability of TiO_2 on Stainless Steel

TiO_2 immobilized on stainless steel was examined in order to check their catalytic activity. The same catalyst was used in 1 and 3 consecutive irradiation experiments of freshly added 0.5 mM of 4-CP in aqueous solution with 12.5 ml/min flow rate. In each experiment, the catalyst was regenerated by flowing distilled water and O_2 through the packing and irradiating with UV-C. The results are shown in Figure 14.14. The TOC degradation of the 1st and 3rd consecutive experiments shows the same trend

and the TOC/TOC_0 values are relatively constant. It implies that the activity is not significantly deactivated with the catalytic cycles (Arabatzi *et al.*, 2002).



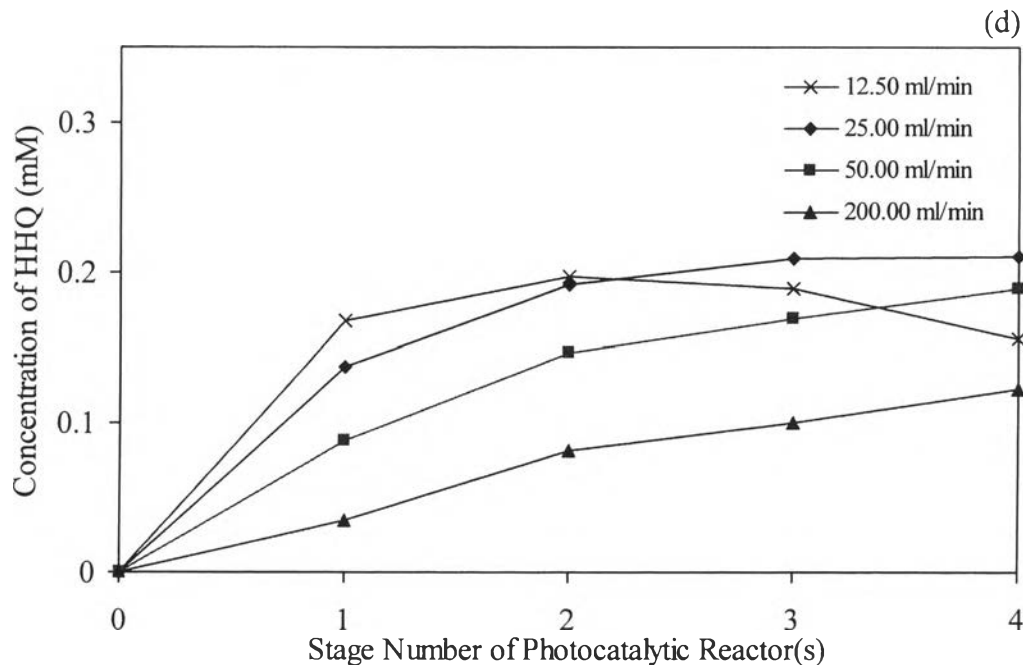
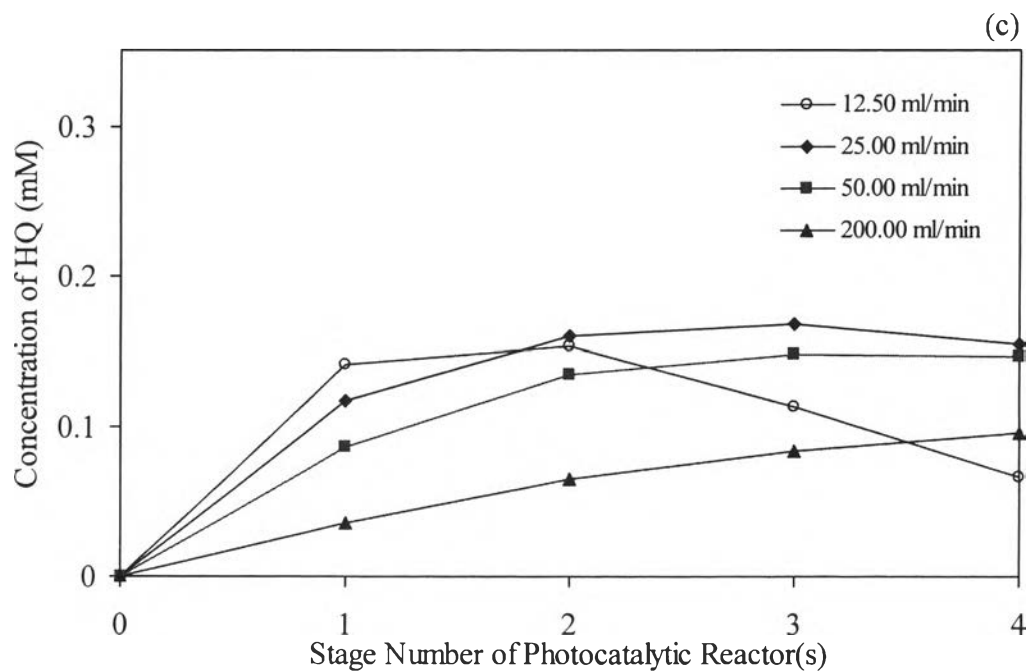
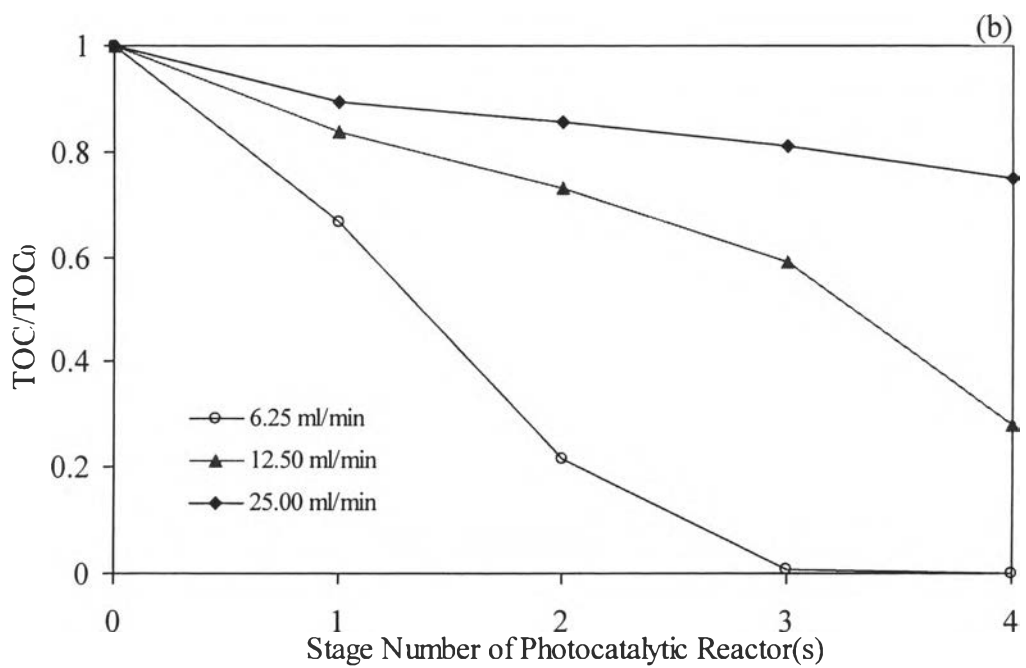
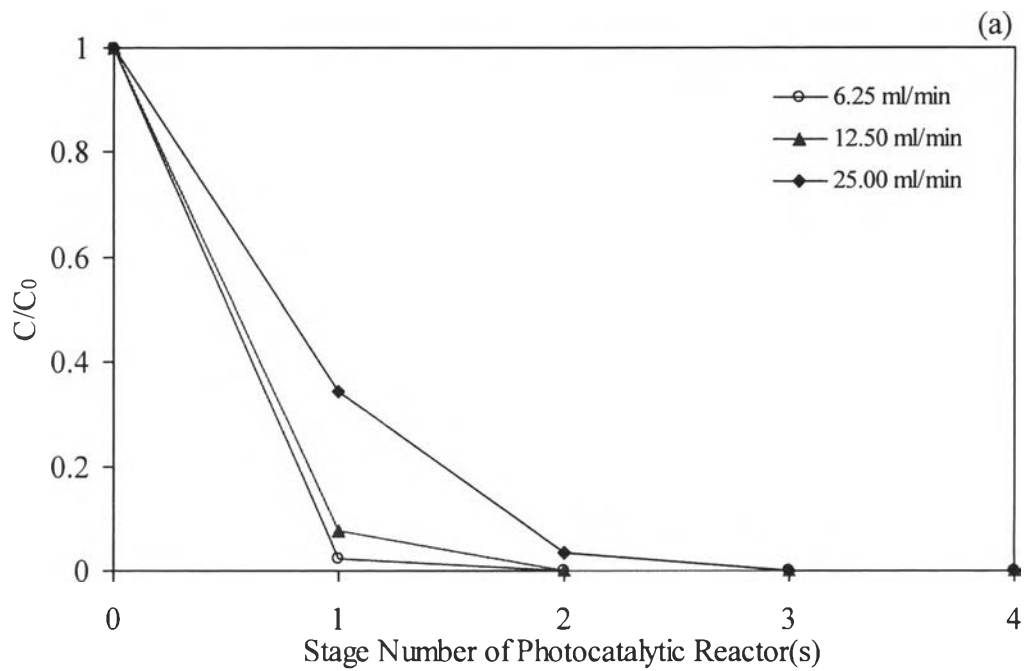


Figure 4.8 Photocatalytic degradation of 4-CP without TiO₂ as a function of stage number with different solution flow rate (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.



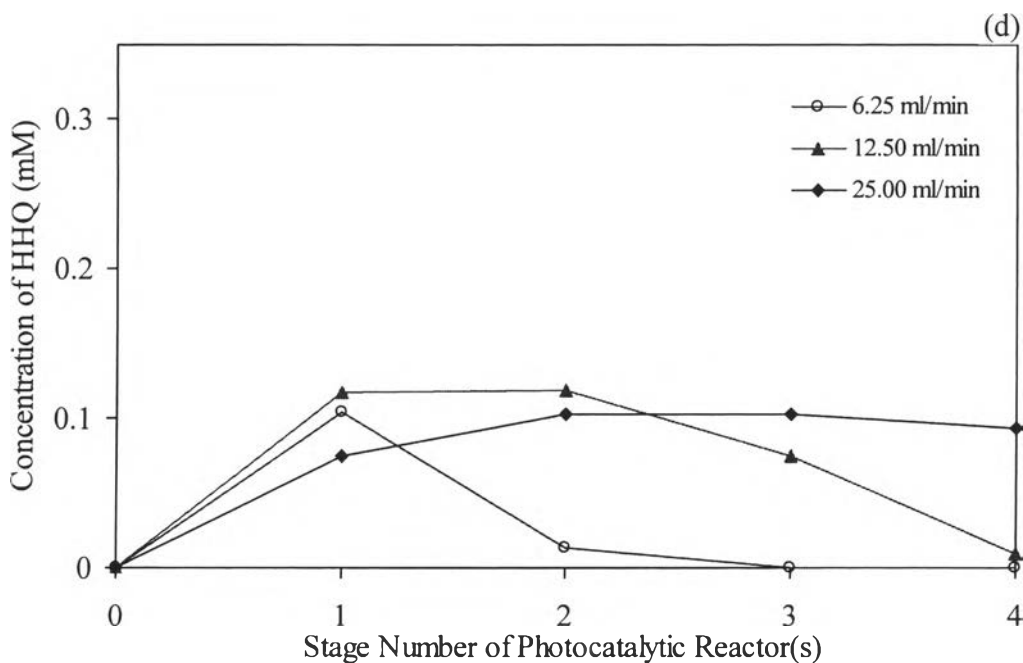
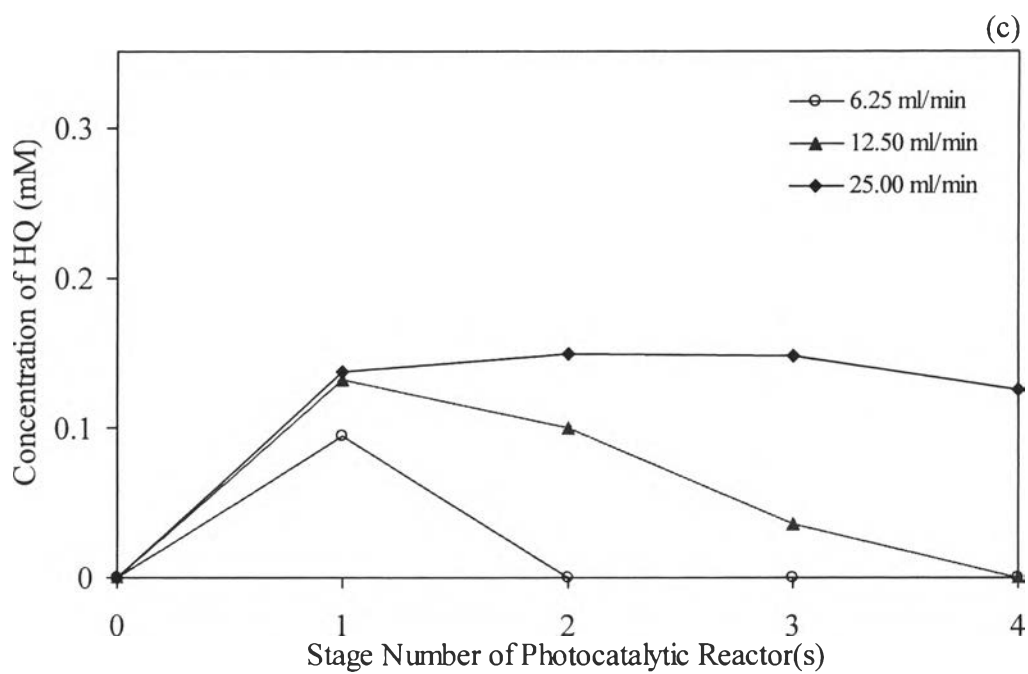


Figure 4.9 Photocatalytic degradation of 4-CP with TiO₂ as a function of stage number with different solution flow rate (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.

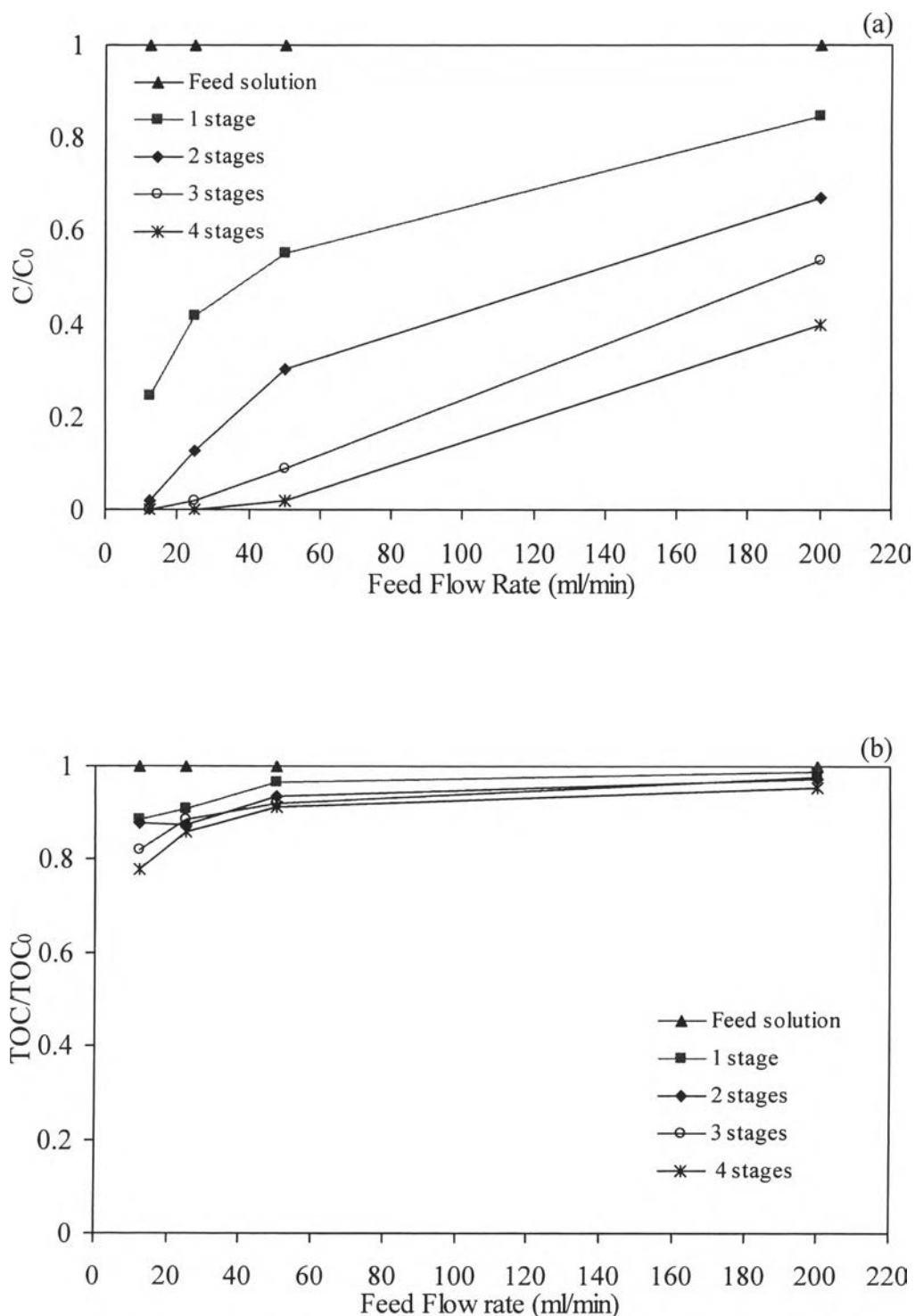


Figure 4.10 Photocatalytic degradation of 4-CP without TiO₂ as a function of feed flow rate with different solution flow rate (a) remaining fraction of 4-CP (b) remaining fraction of TOC.

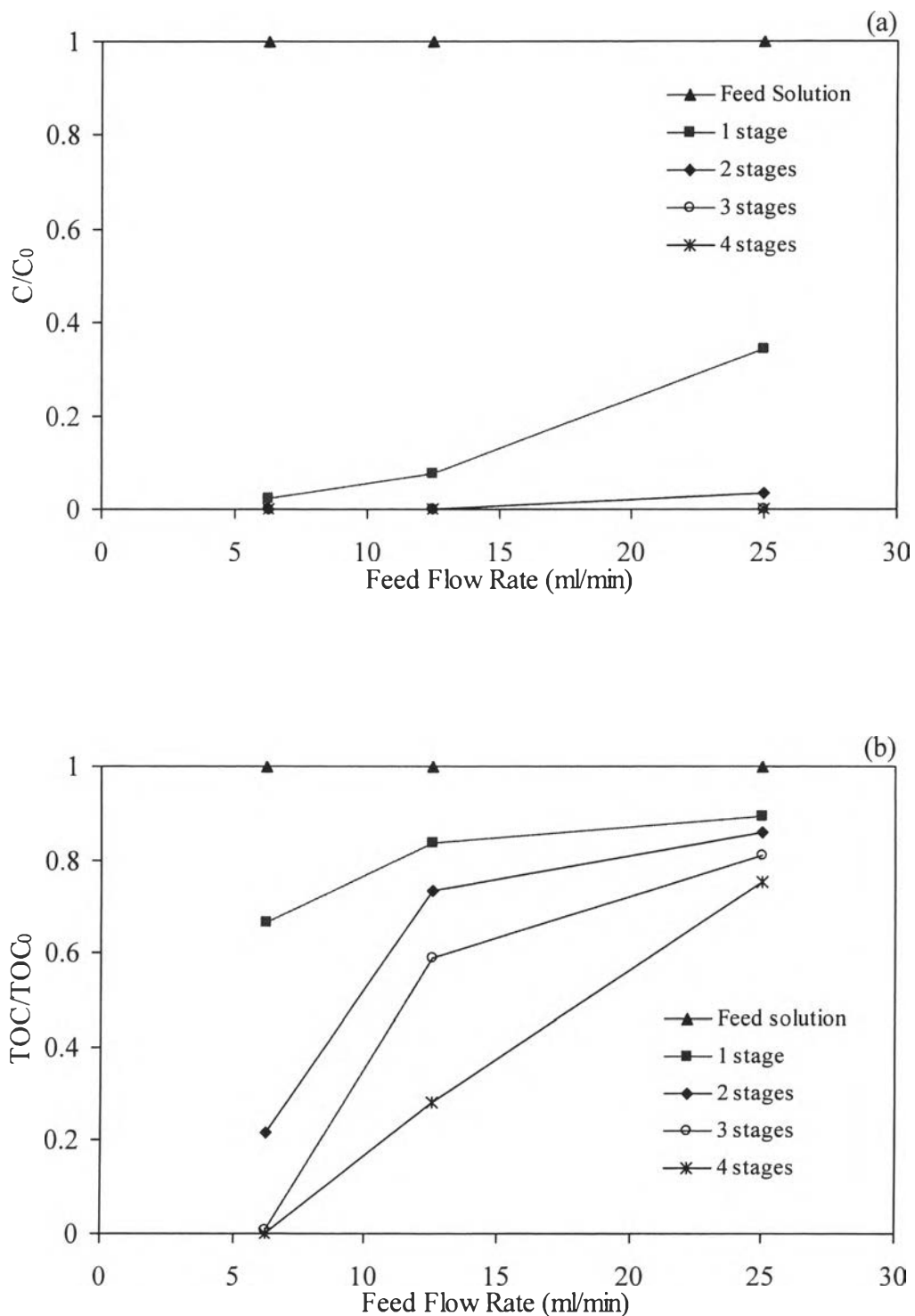
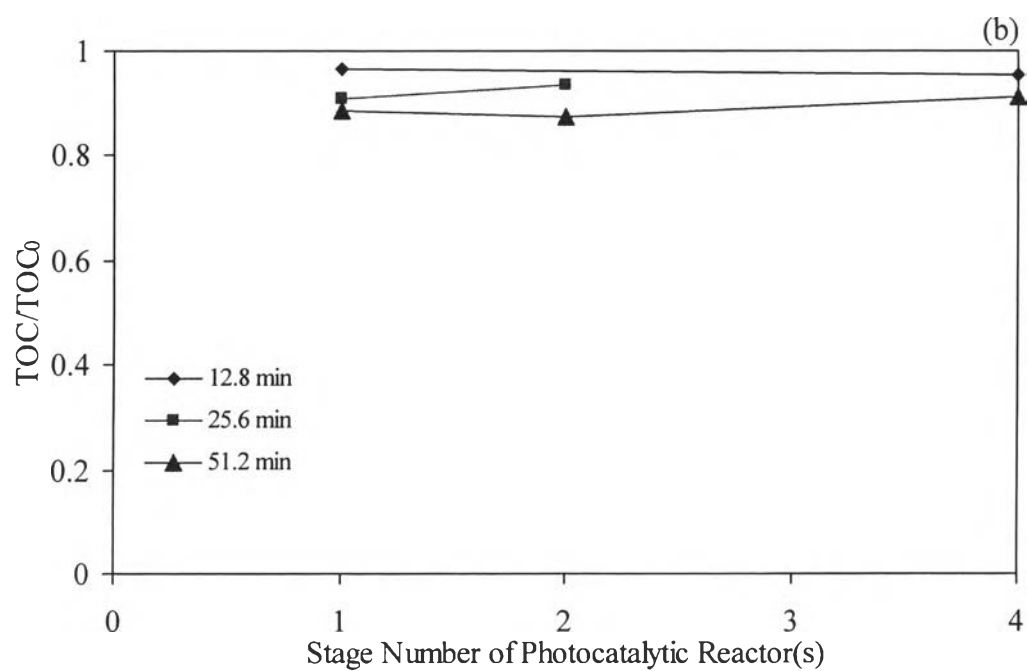
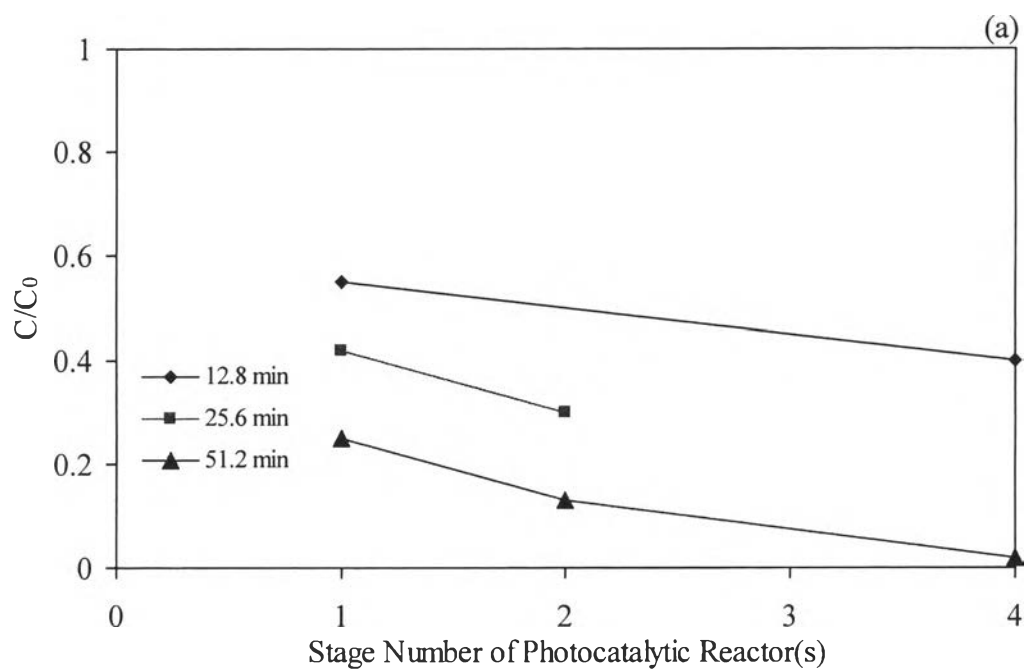


Figure 4.11 Photocatalytic degradation of 4-CP with TiO₂ as a function of feed flow rate with different solution flow rate (a) remaining fraction of 4-CP (b) remaining fraction of TOC.



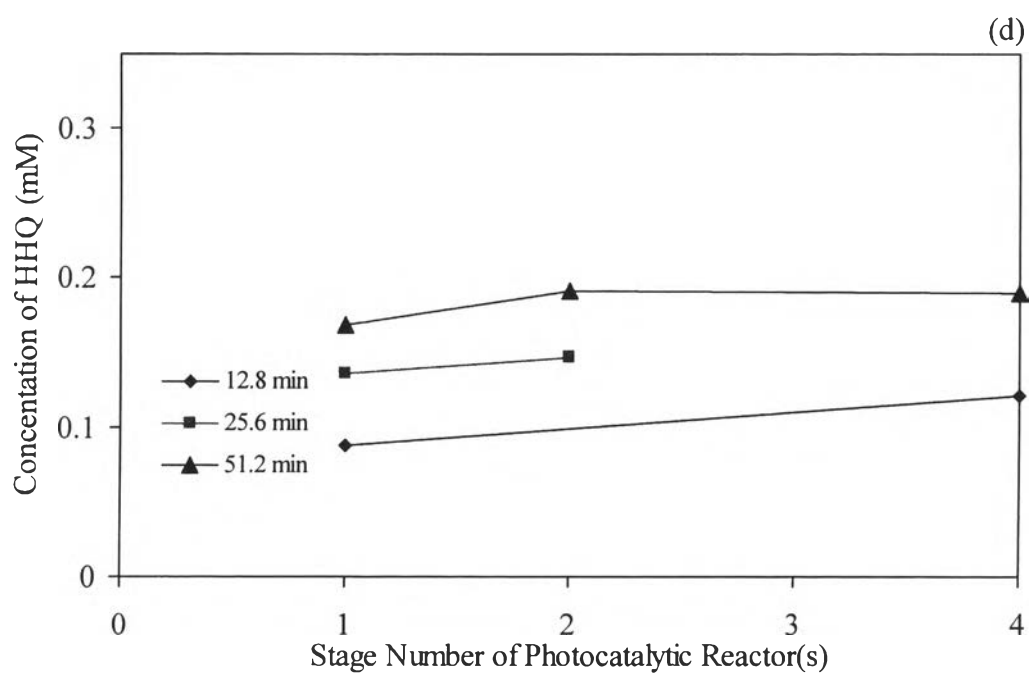
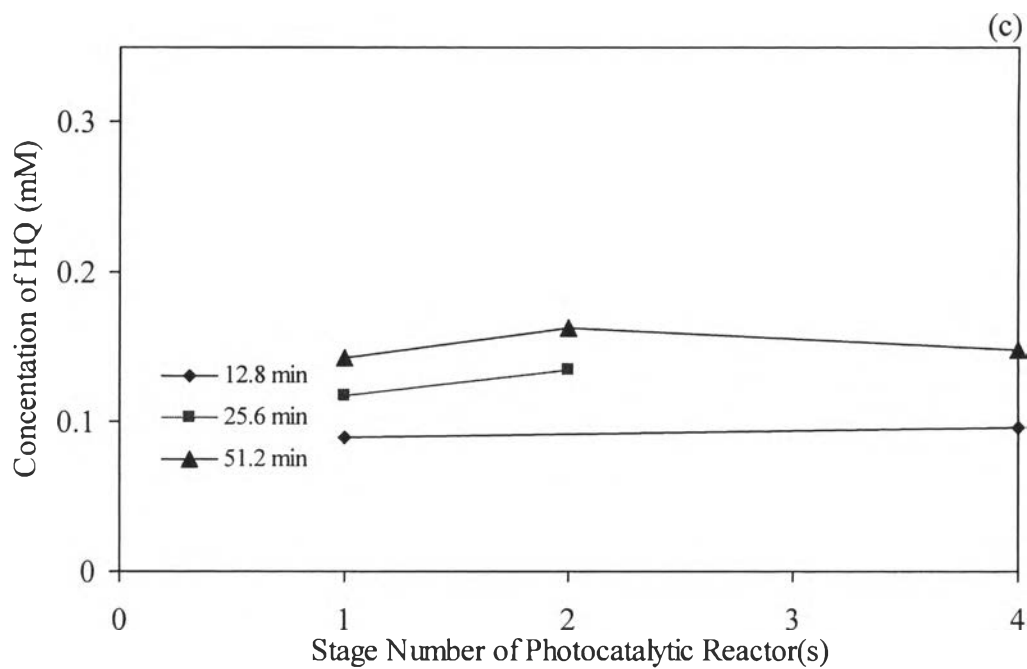
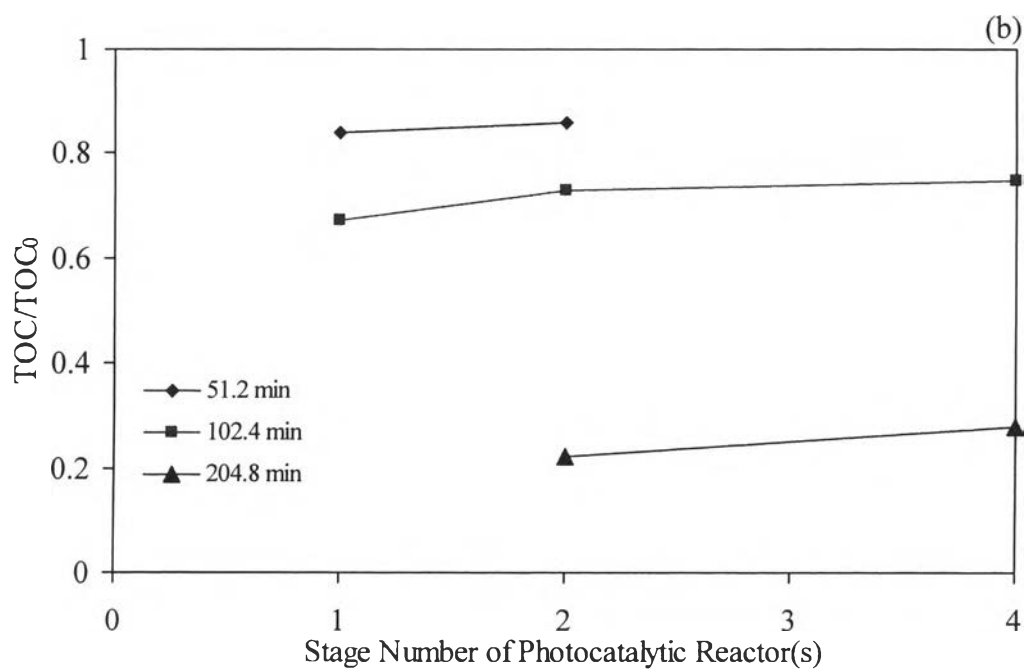
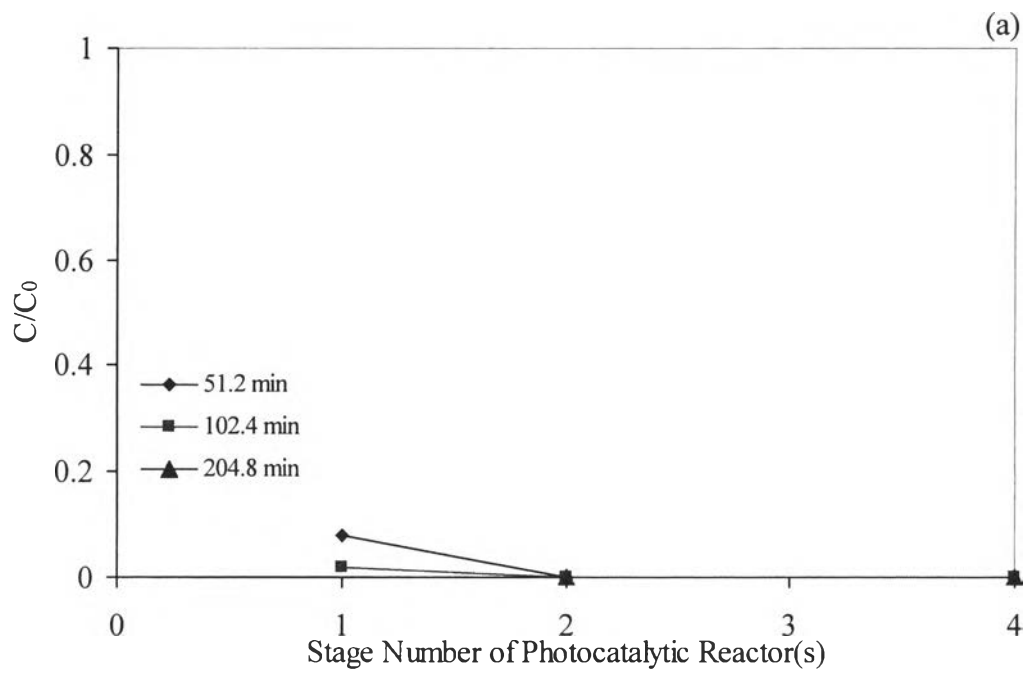


Figure 4.12 Photocatalytic degradation of 4-CP without TiO₂ as a function of stage number with different retention time (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.



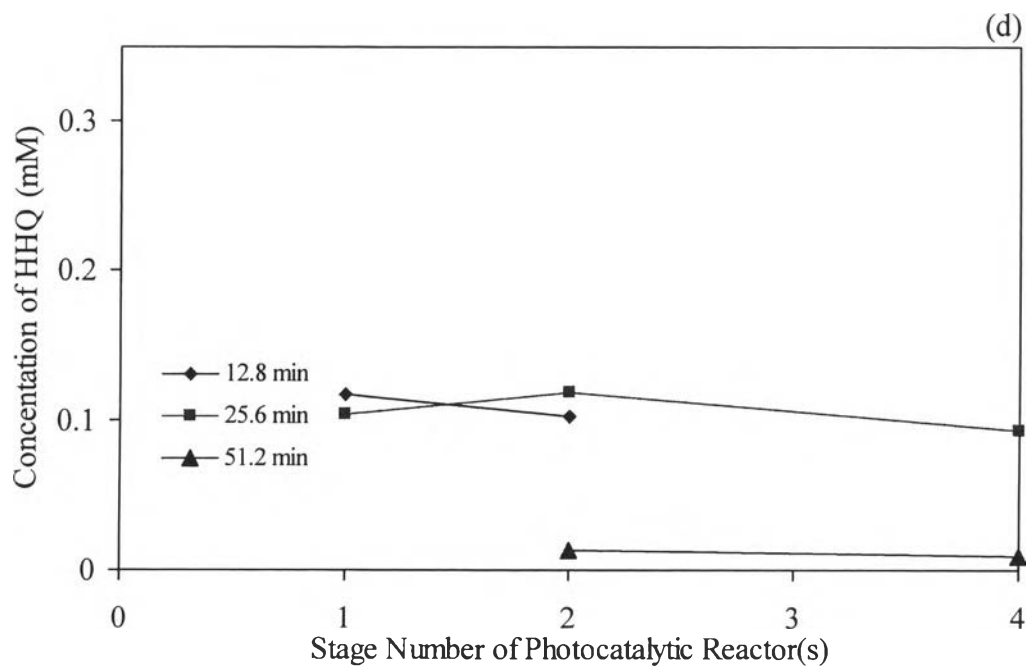
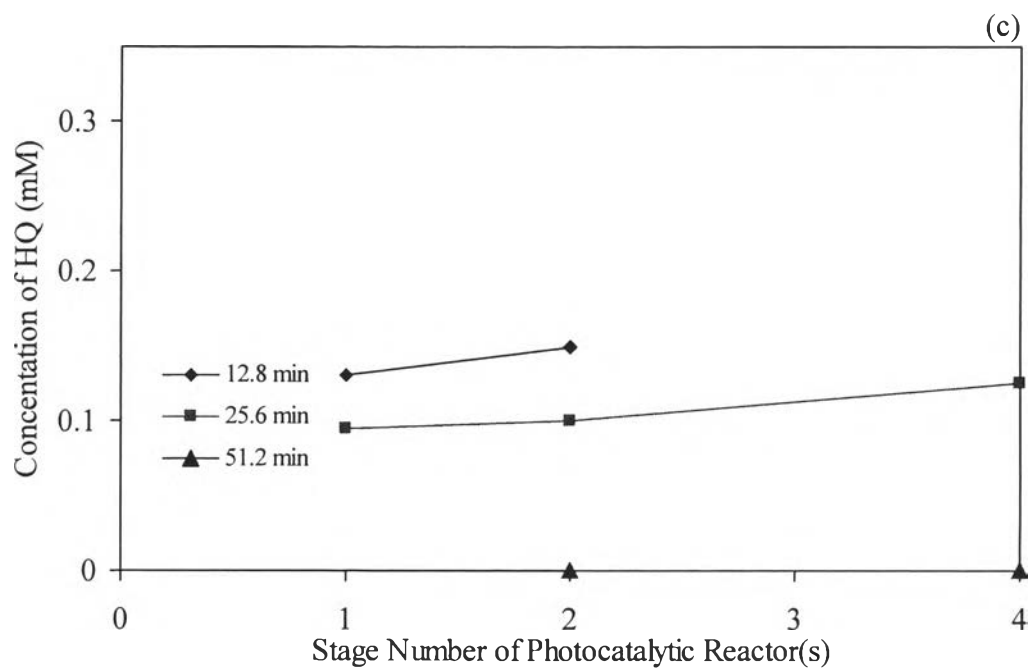


Figure 4.13 Photocatalytic degradation of 4-CP with TiO_2 as a function of stage number with different retention time (a) remaining fraction of 4-CP (b) remaining fraction of TOC (c) concentration of HQ (d) concentration of HHQ.

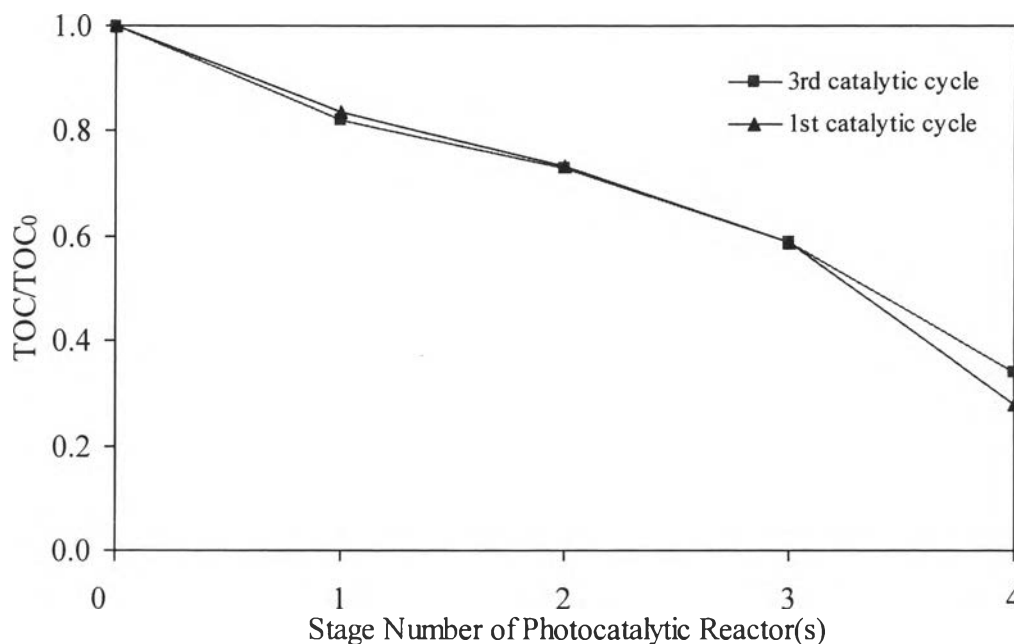


Figure 4.14 Durability of TiO₂ immobilized on stainless steel as a function of stage number and remaining fraction of TOC.

4.2.3 Rate Constant Comparison

The rate constant (k_{4-CP}) of 4-CP degradation was assumed to be the first-order reaction because of the low initial concentration (Theurich *et al.*, 1996). The results are shown in Tables 4.2-4.3. In the batch and suspended system, k_{4-CP} is shown in Table 4.2. k_{4-CP} slightly decreases as the calcination temperature of TiO₂ increases from 600 to 500°C because of the change in the crystal phase of TiO₂ from anatase, an active form, to rutile. The optimal metal (Ag and Au) doping of k_{4-CP} is 0.1 %.

Without TiO₂ in the continuous system, the decrease in the solution feed flow rate does not significantly change k_{4-CP} as shown in Table 4.3 because the increase in the UV-C light absorption time of 4-CP molecules by decreasing the feed flow rate does not affect the degradation of 4-CP. The addition of TiO₂, however, significantly increases k_{4-CP} at any flow rate compared with the photolysis. However, the decrease in the solution feed flow rate strongly increases the k_{4-CP} . It is obvious that the adsorption of 4-CP on TiO₂ is the rate-limiting step. The explanation is that the steps of

photocatalytic reaction are light absorption on catalyst, OH^\bullet formation and OH^\bullet oxidation, respectively. The light absorption on TiO_2 and the formation of OH^\bullet are independent on the solution flow rate but the adsorption of 4-CP on TiO_2 before oxidizing by OH^\bullet decreases with increasing the flow rate because of the decrease in the adsorption time.

$k_{4\text{-CP}}$ in the continuous and immobilized system is higher than that in the batch and suspended system when the solution flow rate is less than 12.5 ml/min. It may be due to the different configurations result in the difference in the UV-C light intensity and illuminated catalyst surface area.

Table 4.2 Rate constant ($k_{4\text{-CP}}$) of 4-CP degradation with Degussa P25 at different calcination temperatures and various Ag and Au dopings calcined at 500 °C for 3 hr

Catalysts	$k_{4\text{-CP}} (\text{min})^{-1}$	$k'_{4\text{-CP}} (\text{g}\cdot\text{min})^{-1}$
TiO_2 (200 °C)	0.0552	0.2453
TiO_2 (300 °C)	0.0565	0.2512
TiO_2 (400 °C)	0.0591	0.2619
TiO_2 (500 °C)	0.0575	0.2551
TiO_2 (600 °C)	0.0487	0.2160
TiO_2 (900 °C)	0.0488	0.2152
TiO_2 (1200 °C)	0.0464	0.2061
0.05 %Ag/ TiO_2	0.0610	0.2706
0.10 %Ag/ TiO_2	0.0634	0.2812
1.00 %Ag/ TiO_2	0.0575	0.2553
1.50 %Ag/ TiO_2	0.0527	0.2338
0.05 %Au/ TiO_2	0.0535	0.2374
0.10 %Au/ TiO_2	0.0549	0.2436
1.00 %Au/ TiO_2	0.0535	0.2374
1.50 %Au/ TiO_2	0.0501	0.2221

Table 4.3 Rate constant ($k_{4\text{-CP}}$) of 4-CP degradation with Degussa P25 immobilized on stainless steel at different solution feed flow rates

Solution Flow Rate (ml/min)	Without TiO ₂	With TiO ₂	
	$k_{4\text{-CP}}$ (min) ⁻¹	$k_{4\text{-CP}}$ (min) ⁻¹	$k_{4\text{-CP}}$ (g.min) ⁻¹
200	0.0723	-	-
50	0.0716	-	-
25	0.0619	0.0897	0.1682
12.5	0.0656	0.2461	0.4615
6.25	-	0.4003	0.7508