CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

4.1.1 Crystal Structures

Figure 4.1 shows the XRD patterns of TiO_2 (sol-gel), immobilized TiO_2, 0.1% Au-0.1% Ag/TiO_2 and TiO_2 (Degussa P25). Generally, there are three different forms of TiO_2 namely anatase, rutile and brookite. For the XRD patterns of TiO_2, the main peaks at $2\theta = 25.3°$, $27.5°$ and $30.6°$ are for anatase, rutile and brookite, respectively. For TiO_2 (sol-gel), immobilized TiO_2 and 0.1% Au–0.1% Ag/TiO_2, there is only TiO_2 in the anatase form and no peaks of Au, at $2\theta = 38.3°$ and $44.5°$, and Ag, at $2\theta = 38.1°$ and $44.2°$, were observed. For the TiO_2 (Degussa P25), anatase and rutile phases were observed with anatase as the major phase and rutile as the minor phase. The anatase peak of TiO_2 (Degussa P25) has higher intensity than that of TiO_2 catalysts prepared by the sol-gel method. The XRD patterns of Au/TiO_2 and Ag/TiO_2 catalysts at different metal loadings are shown in Figures 4.2 and 4.3, respectively. For 1.5% and 1% Au/TiO_2, the patterns indicate TiO_2 in the anatase and rutile forms. The other catalysts only show the anatase phase. For all metal loading catalysts, the Au or Ag peaks cannot be observed indicating that Au and Ag can be dispersed well on TiO_2.

The crystallite size of the catalyst can be determined from the broadening of the anatase main peak by Debye-Scherrer equation. The crystallite sizes of all catalysts are given in Table 4.1. The crystallite size of the immobilized TiO_2 and TiO_2 (Degussa P25) are smaller than the TiO_2 (sol-gel). When compared to the TiO_2 (sol-gel), addition of either Au or Ag decreases the crystallite sizes. However, the metal loading does not significantly affect the crystallite sizes of the catalysts.
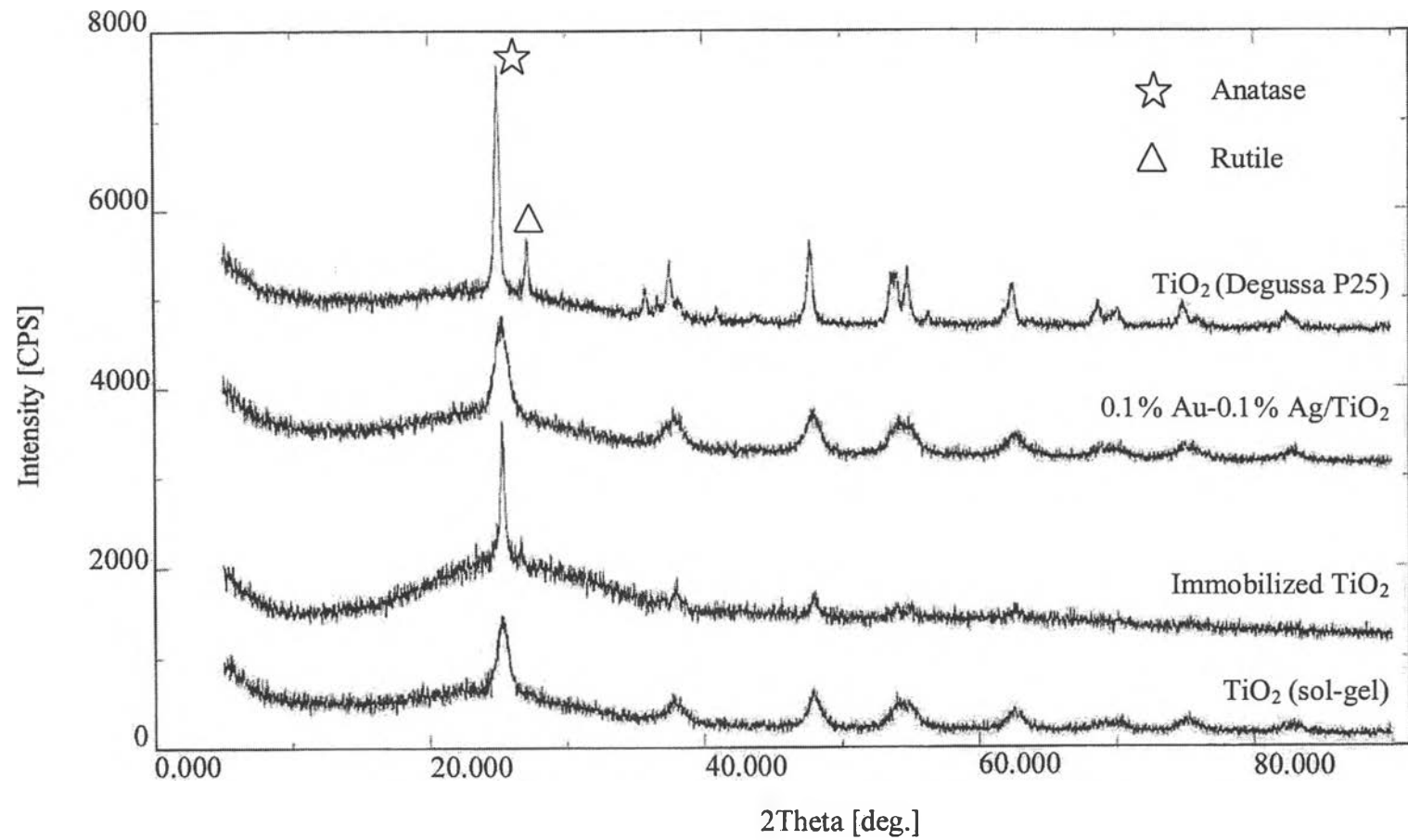
Figure 4.1 X-ray diffraction patterns of TiO₂ (sol-gel), Immobilized TiO₂, 0.1% Au-0.1% Ag/ TiO₂, TiO₂ (Degussa P25).
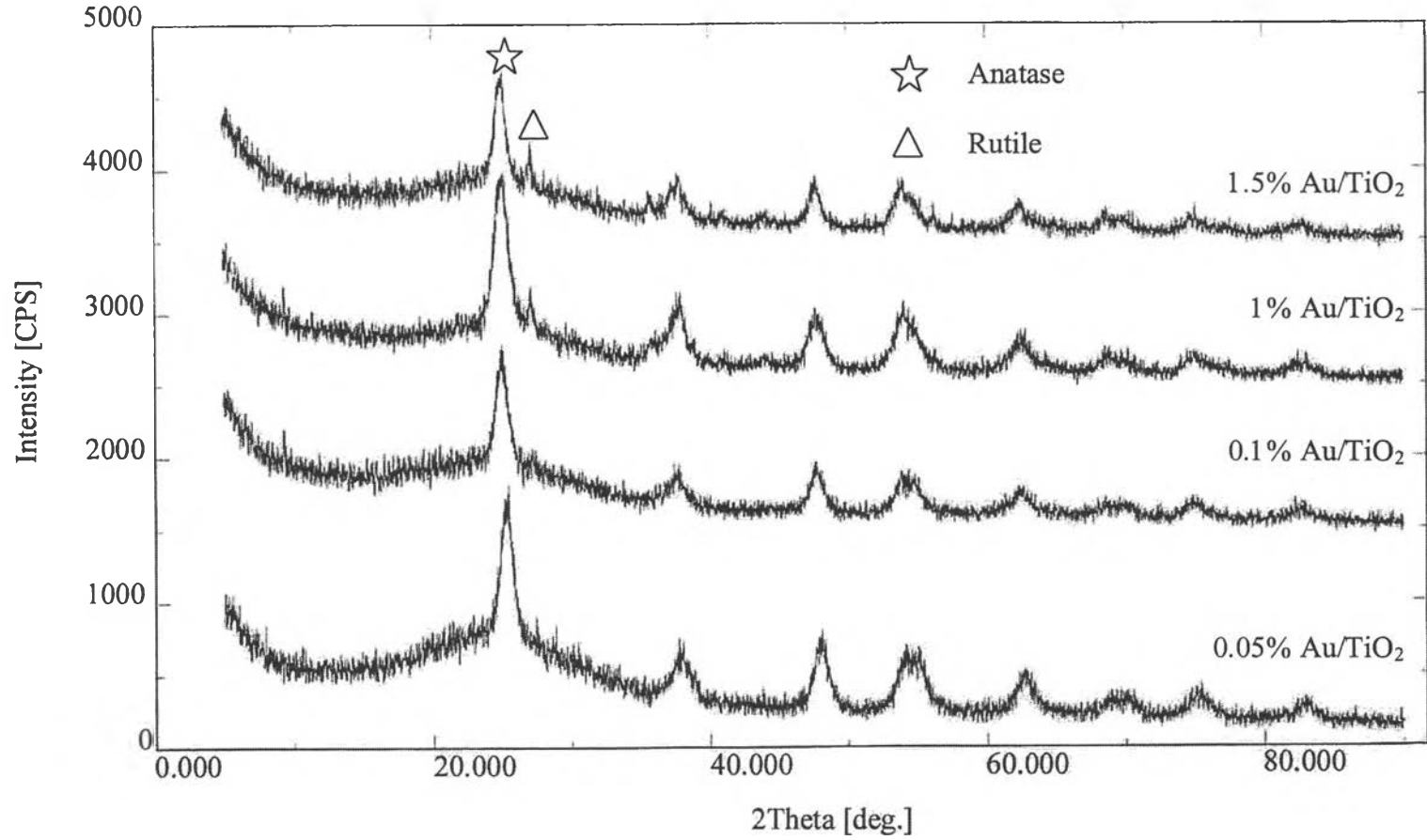
Figure 4.2 X-ray diffraction patterns of Au/ TiO₂ catalysts at different Au loadings.
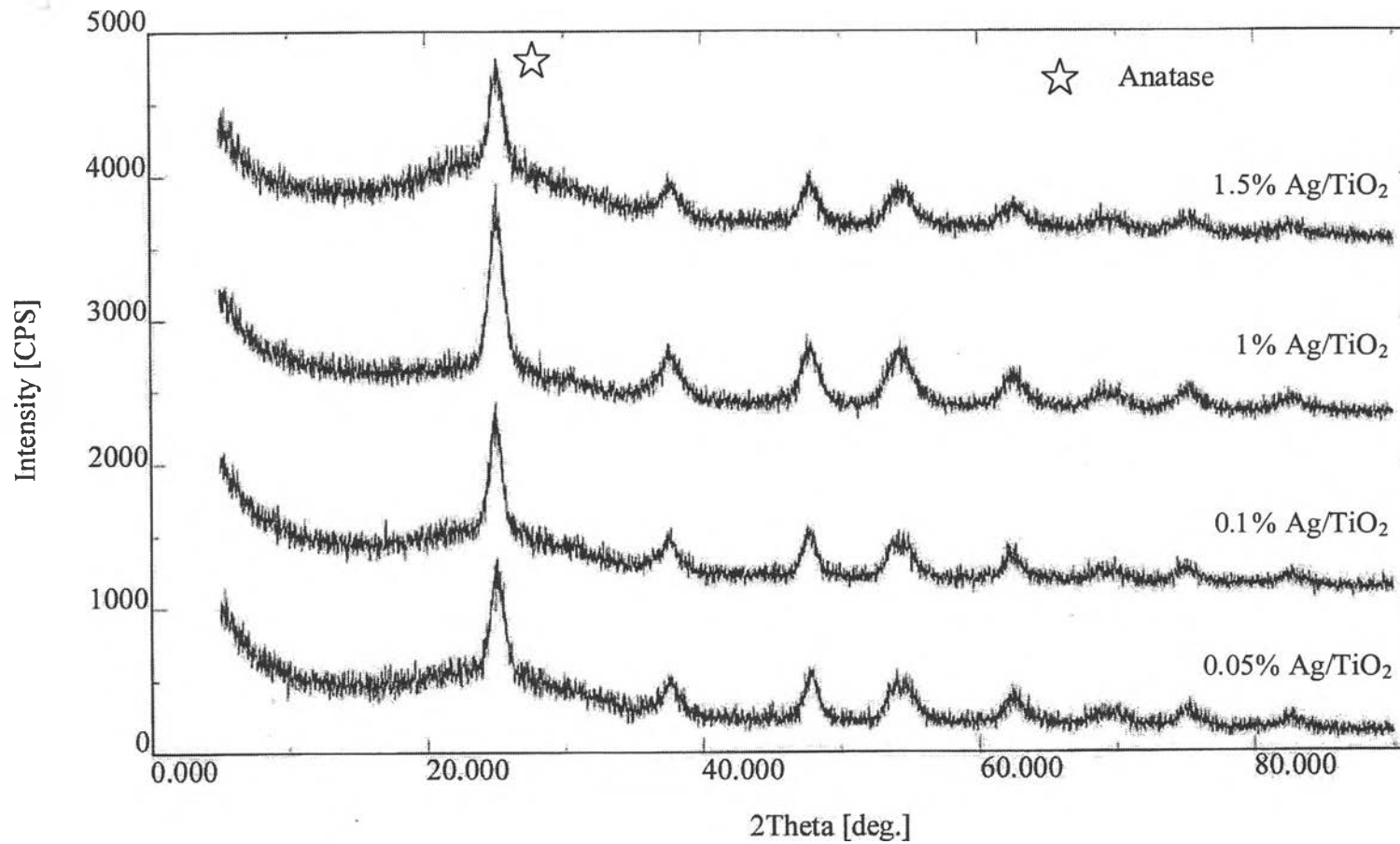
Figure 4.3 X-ray diffraction patterns of Ag/ TiO₂ catalysts at different Ag loadings.

Table 4.1 Calculated crystallite sizes of the studied catalysts

Catalyst	Crystallite Size (nm)
TiO_2 (Degussa P25)	26.90
TiO_2 (sol-gel)	34.90
Immobilized TiO_2	28.89
0.05% Au/TiO_2	8.56
0.1% Au/TiO_2	10.43
1% Au/TiO_2	8.95
1.5% Au/TiO_2	19.76
0.05% Ag/TiO_2	7.67
0.1% Ag/TiO_2	8.75
1% Ag/TiO_2	7.66
1.5% Ag/TiO_2	8.93
0.1% Au/0.1% Ag/ TiO_2	7.81

4.1.2 Surface Morphology of Prepared Catalysts

The BET surface areas of all studied catalysts are shown in Table 4.2. Almost all catalysts prepared by the sol-gel method have higher BET surface areas than that of TiO_2 (Degussa P25). An addition of Ag into TiO_2 increases the BET surface area up to the maximum level of 175.3 m^2/g at 1% Ag. It is possible that Ag is dispersed well on the TiO_2 surface. However, a further increase in the Ag loading to 1.5% results in decreasing BET surface area. That could be a result from the agglomeration effect. In contrast, an increase in an amount of Au decreases the BET surface area. It is possible that the increase in the amount of Au loading results in blocking the pores of the catalyst. In the case of the bimetallic loading catalyst, Ag has stronger effect than Au on the BET surface area.

Table 4.2 Surface areas of the studied catalysts

Catalyst	BET Surface Area (m^2/g)
TiO_2 (Degussa P25)	79.9
TiO_2 (sol-gel)	103.6
0.05% Au/TiO_2	137.8
0.1% Au/TiO_2	120.3
1% Au/TiO_2	98.4
1.5% Au/TiO_2	73.8
0.05% Ag/TiO_2	123.1
0.1% Ag/TiO_2	155.6
1% Ag/TiO_2	175.3
1.5% Ag/TiO_2	150.7
0.1% Au/0.1% Ag/ TiO_2	158.5

4.2 Photocatalytic Degradation of 4-CP

Some nomenclatures used throughout this section are the remaining fraction of 4-CP (C/C_o) and the remaining fraction of TOC (TOC/TOC_o). C/C_o is a ratio of 4-CP concentration at any time to its initial concentration. Similarly, TOC/TOC_o is a ratio of TOC concentration at any time to its initial concentration. The experimental data of the photocatalytic activities of all studied catalysts are shown in Appendix B.

4.2.1 Photocatalytic Degradation of 4-CP with TiO_2

4.2.1.1 Effect of TiO2 (Degussa P25)

Photocatalytic degradation of 0.5 mM 4-CP solution was carried out with a TiO_2 (Degussa P25) loading of 0.5 g/l under UV irradiation. Samples were taken every 30 minutes for the quantitative and qualitative analysis of 4-CP and other products. Figure 4.4 shows the remaining fractions of 4-CP and TOC and the concentration profiles of the intermediate products without any catalyst.
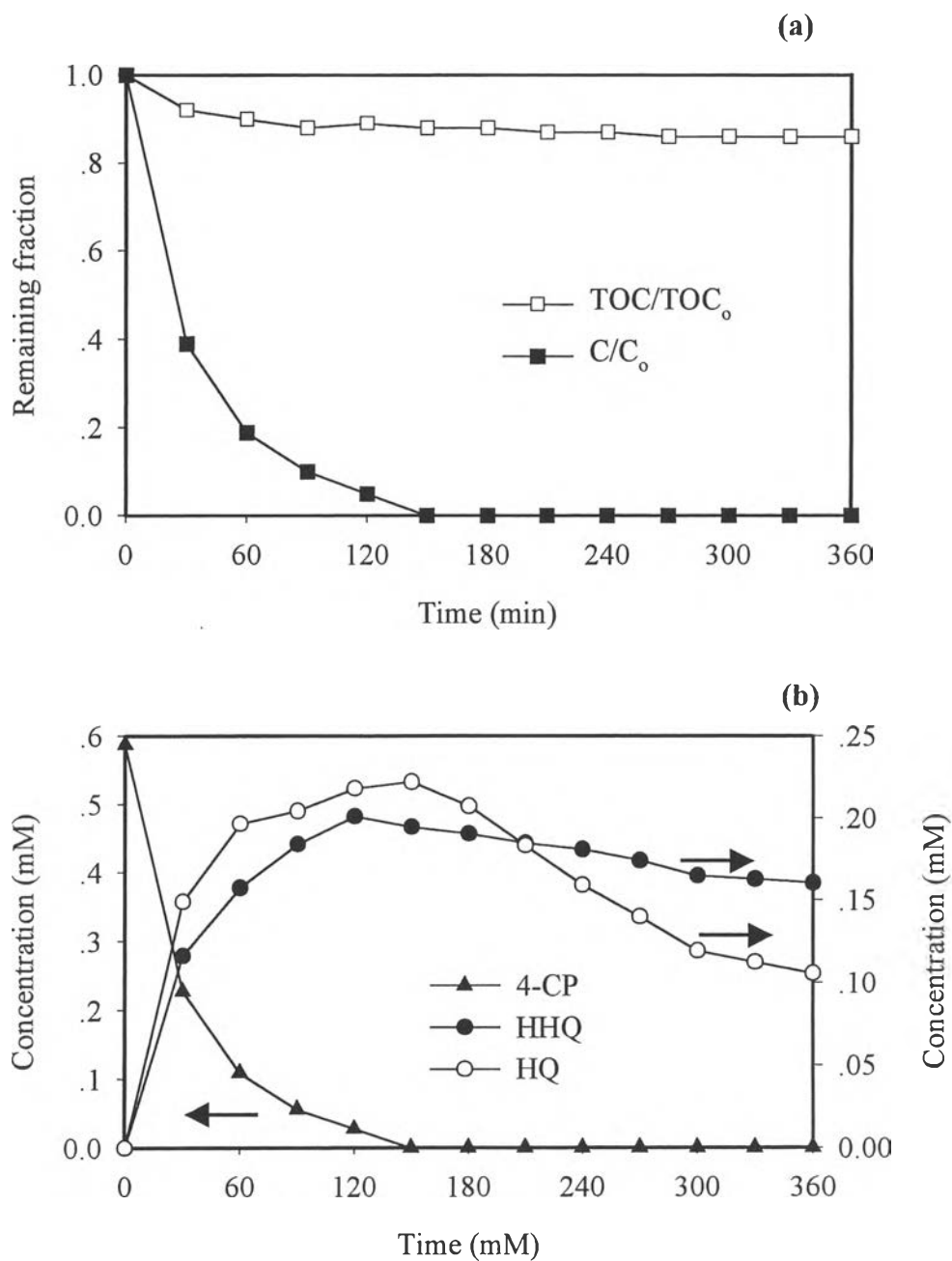
Figure 4.4 Photocatalytic degradation of 4-CP as a function of irradiation time without catalyst (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.

4-CP decreased moderately and disappeared after 150 minutes but the TOC decreased only 14% after the irradiation for 360 minutes. In the presence of TiO_2 (Degussa P25), 4-CP decreases slightly and disappears after 180 minutes while the TOC decreases 97% from the initial TOC after the irradiation for 360 minutes as shown in Figure 4.5. Figure 4.5 (b) indicates that the concentration of hydroxyhydroquinone (HHQ) increases sharply and reaches the maximum level at an irradiation time of 120 minutes while the concentration of hydroquinone (HQ) increases and reaches a maximum after 60 minutes before its concentration decreases progressively. The shapes of the HHQ and HHQ curves are typical for compounds formed as intermediates in a consecutive reaction (Moonsiri, 2002). In addition, the concentrations of the intermediate products were much lower than those without catalyst. It can be concluded that the energy of the short wavelength generated from the UV lamp is strong enough to destroy the chemical bond of the 4-CP molecule to form the intermediate products rather than CO_2. In the presence of TiO_2, hydroxyl radical is generated on the TiO_2 surface excited by UV. As a result, the rate of 4-CP degradation is increased and the intermediate products (HHQ and HQ) are further oxidized to CO_2 and H_2O.

4.2.1.2 Effect of TiO₂ (sol-gel)

The photocatalytic degradation of 4-CP using TiO_2 prepared by the sol-gel method is shown in Figure 4.6. Compared with the commercial TiO_2 (Degussa P25), the decrease of 4-CP concentration with TiO_2 (sol-gel) was much faster and the 4-CP concentration disappeared within 90 minutes. However, the TOC degradation rate with TiO_2 (Degussa P25) was higher than that with the TiO_2 (sol-gel) catalyst. From the results, it can be concluded that the degradation rate of 4-CP with TiO_2 (sol-gel) is higher than that with TiO_2 (Degussa P25). In contrast, the degradation rates of the intermediate products with TiO_2 (Degussa P25) are higher than those with the TiO_2 (sol-gel) catalyst. The reason is the high surface area of the TiO_2 (sol-gel) catalyst results in a large amount of 4-CP adsorbed on the catalyst surface leading to the higher degradation rate of 4-CP as compared to the commercial TiO_2 (Degussa P25). TiO_2 (Degussa P25) gives a higher degradation rate in terms of TOC than TiO_2 (sol-gel) because of its higher crystalinity than TiO_2 (sol-gel), which, in turn, inhibits the e^-/h^+ recombination. When the recombination
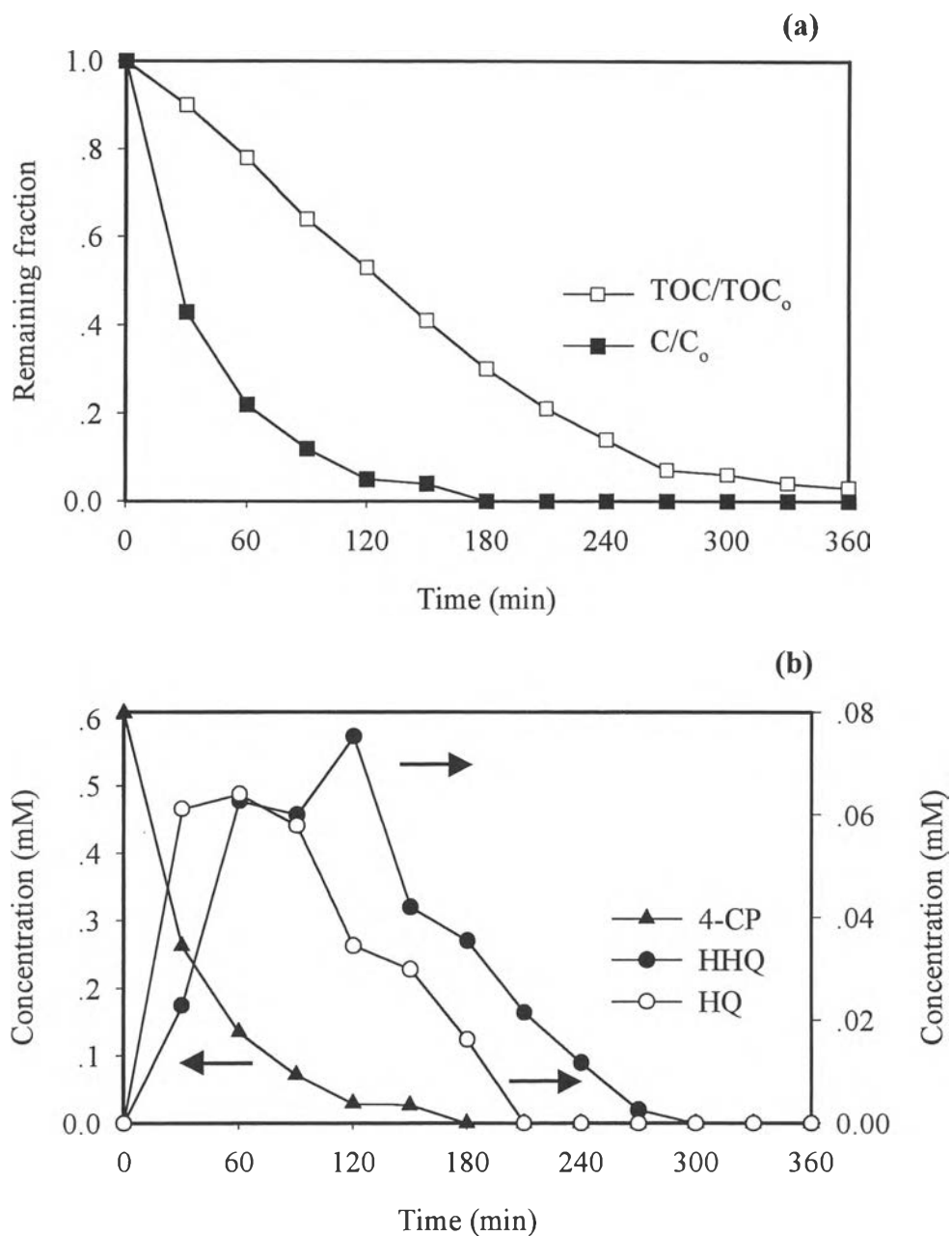
Figure 4.5 Photocatalytic degradation of 4-CP as a function of irradiation time using TiO_2 (Degussa P25) (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
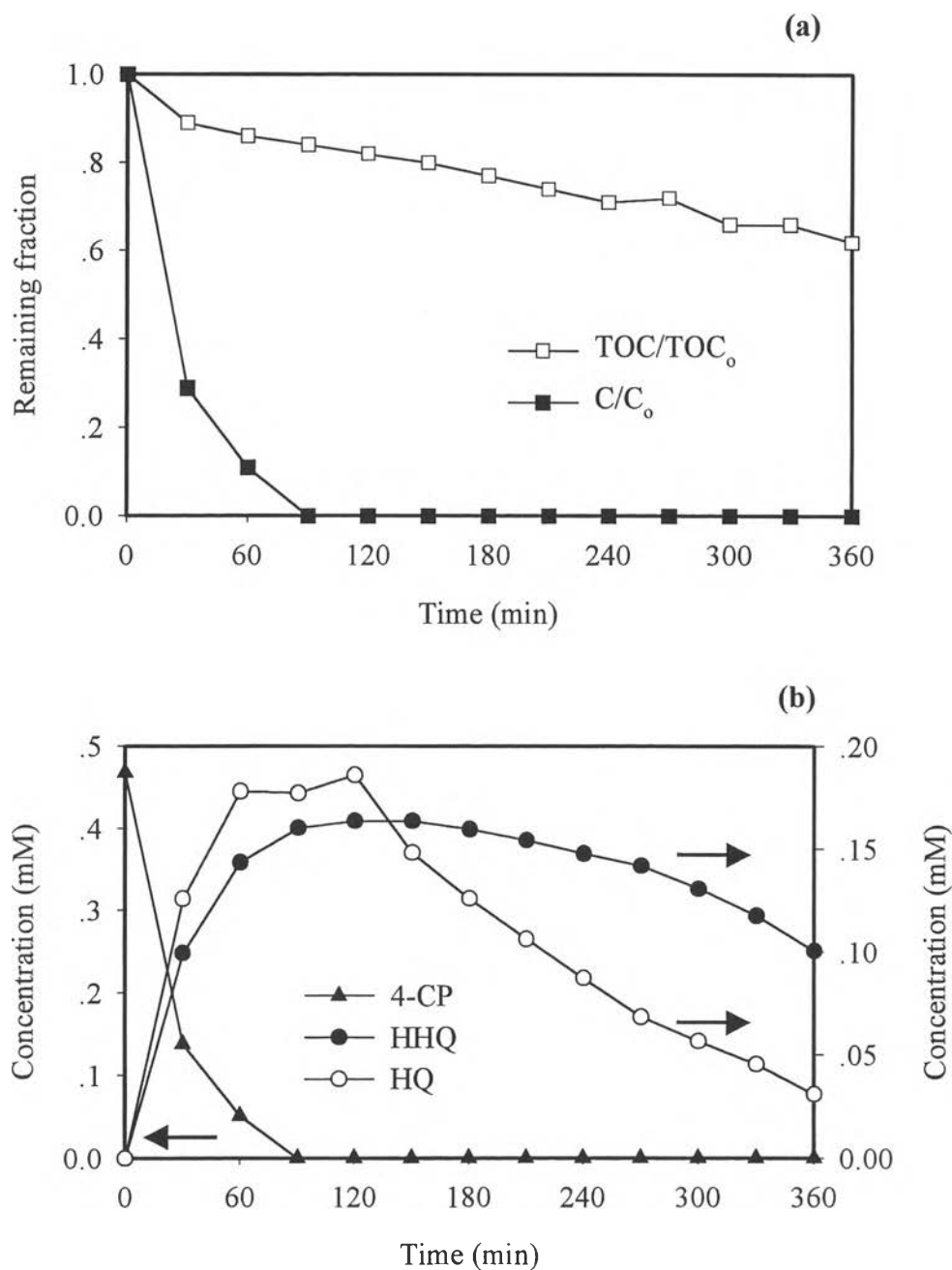
(a)

(b)

Figure 4.6 Photocatalytic degradation of 4-CP as a function of irradiation time using TiO_2 (sol-gel) (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.

decreases, there are more electrons and holes diffusing to the catalyst surface and reacting with the substrate molecules adsorbed on the surface at the faster rate (Jung and Park, 2000 and Tharathonpisutthikul, 2000). The results are also consistent with the work by Guillard *et al.* (1999), who investigated the 4-CP degradation using different TiO_2 catalysts including Degussa P25. Although Degussa P25 has the lowest surface area, it gave the highest TOC degradation rate. It was explained that TiO_2 (Degussa P25) decreased the readsorption rate of the intermediate products.

4.2.2 Photocatalytic Degradation of 4-CP with Au/TiO_2

For this study, the photocatalytic degradation of 0.5 mM 4-CP on a series of Au/TiO_2 with various amounts of Au from 0.05-1.5 wt.% was carried out. Figures 4.7-4.10 show the 4-CP degradation with different Au loadings. 4-CP degradation with 1% and 1.5% Au/TiO_2 shows the same results as pure TiO_2 catalysts. HQ is first formed and reaches the maximum before degrading to HHQ. In addition, maximum concentration of HQ was found to be higher than HHQ. In contrast, the 4-CP degradation with 0.05% and 0.1% Au/TiO_2 showed different results, i.e., concentration profiles of HQ and HHQ are parallel without an intersection and the maximum concentration of HHQ was higher than HQ. The results imply that HQ is degraded into HHQ rapidly with 0.05% and 0.1% Au/TiO_2 catalysts because of the high surface areas of these two catalysts (see Table 4.2) resulting in the increase of the intermediate products adsorption on the catalyst surface.

The remaining fractions of 4-CP at different Au loadings are compared in Figure 4.11. It is clearly seen that the amount of Au does not significantly affect the 4-CP degradation. Figure 4.12 shows the remaining fraction of TOC at 360 minutes as a function of Au loading. It was found that the amount of Au loadings affected the intermediate products and TOC degradation. 0.1% Au/TiO_2, could degrade 4-CP faster than the other Au/TiO_2 catalysts and had the minimum TOC at 360 minutes. With Au loadings greater than 0.1%, the remaining TOC increased with increasing the Au loadings. The less TOC indicates that more organic compounds react and convert into CO_2. The results indicate that a small amount of Au added can slightly improve the photocatlytic activity of TiO_2 and the
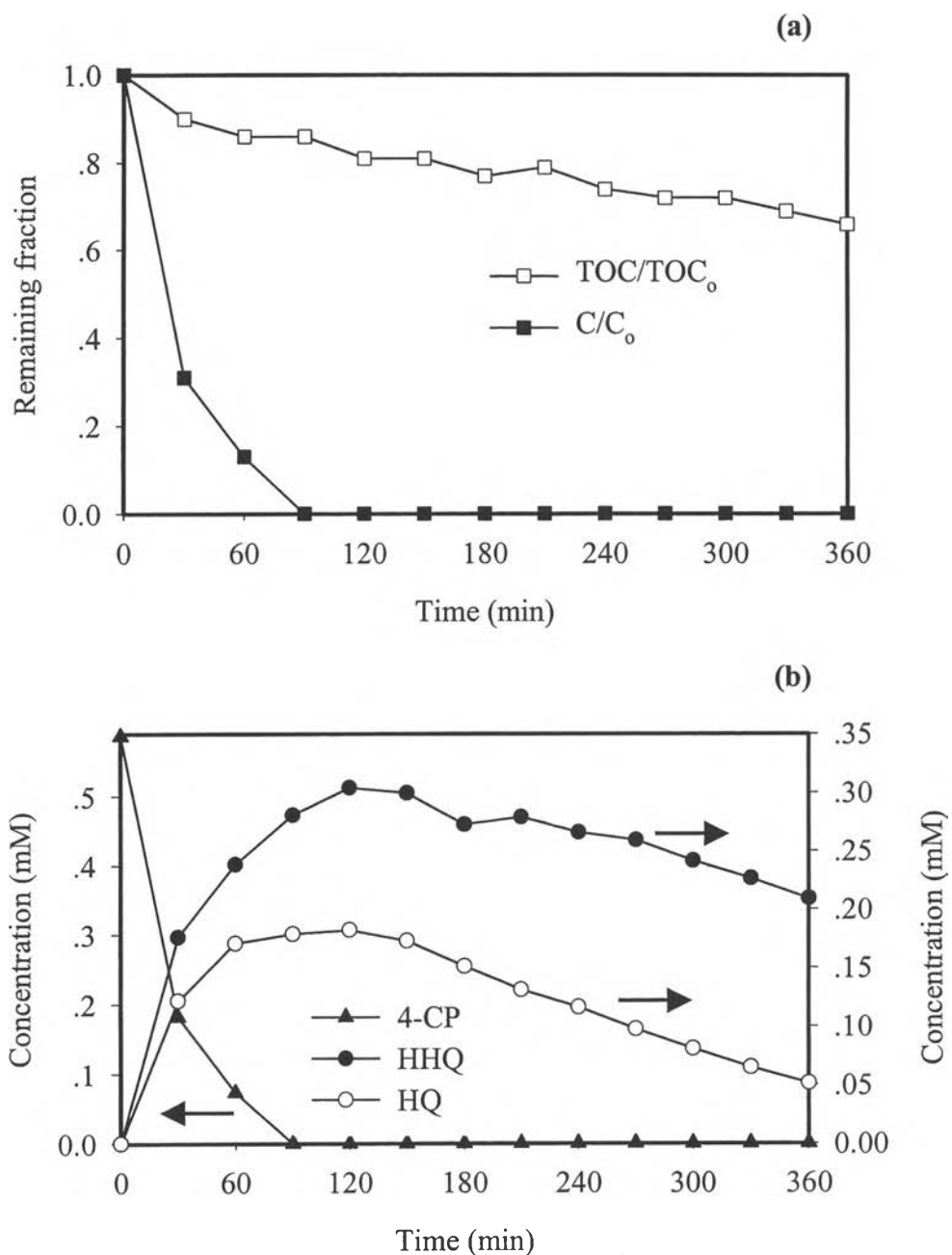
Figure 4.7 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.05% Au/TiO$_2$ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
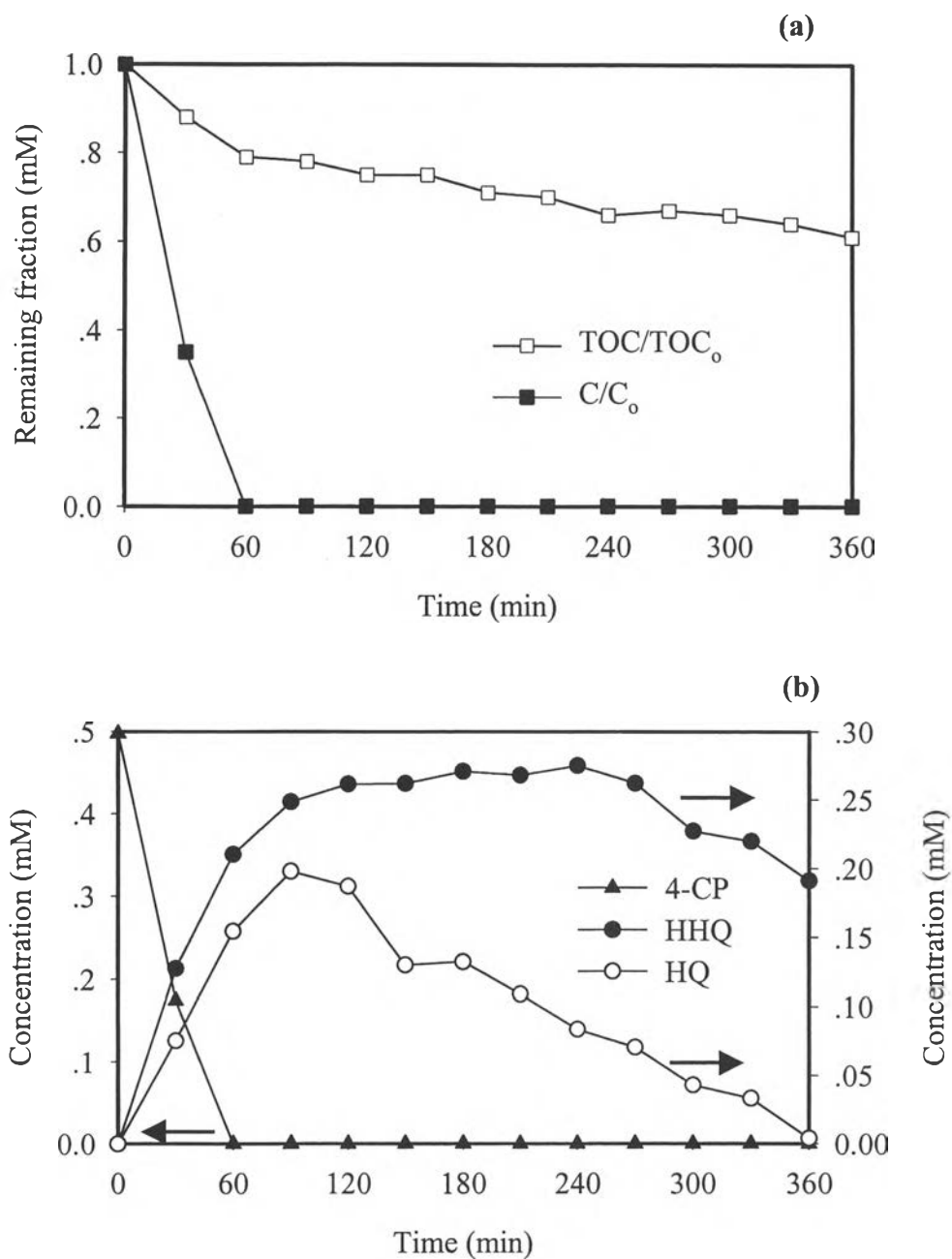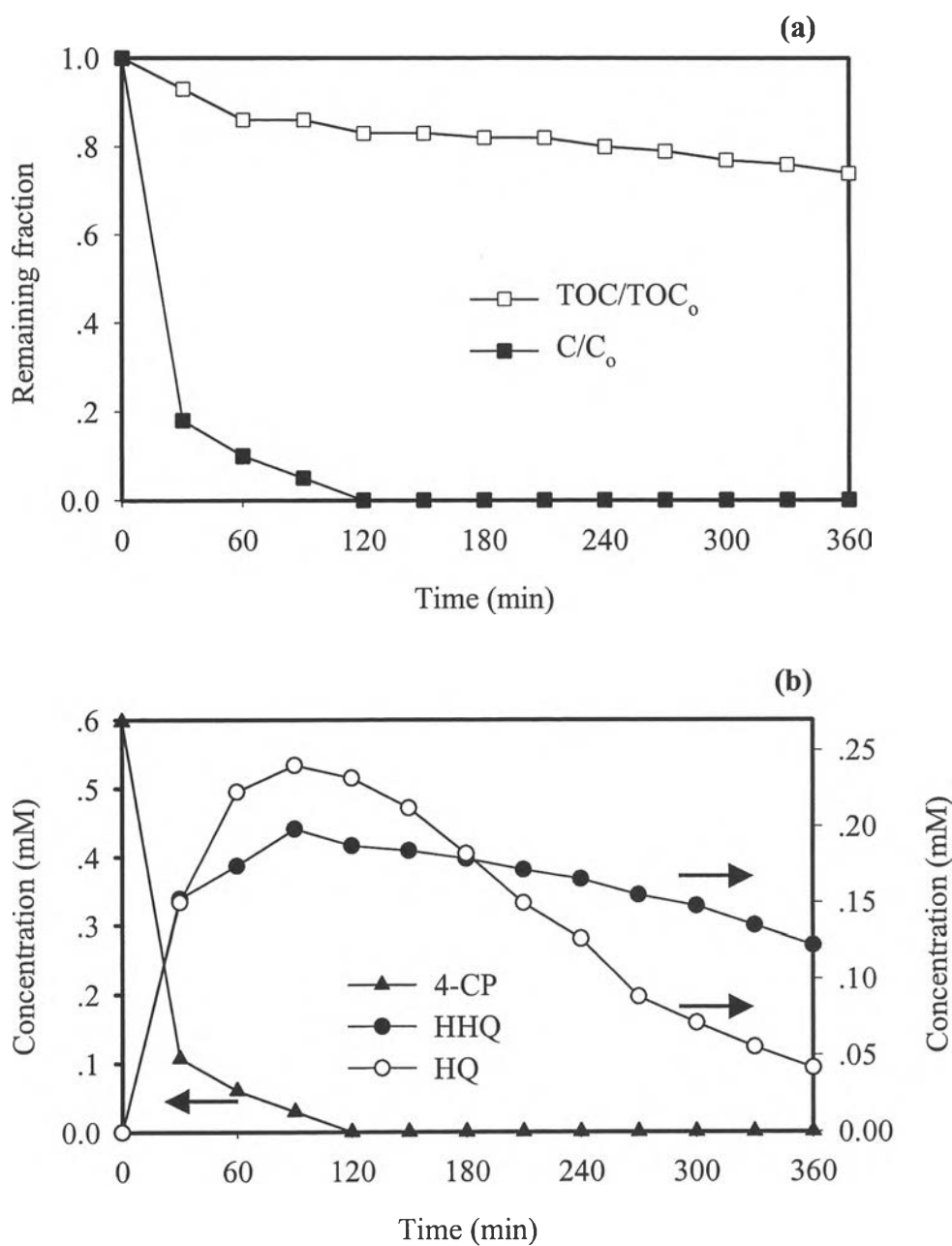
Figure 4.8 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.1% Au/TiO_2 (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
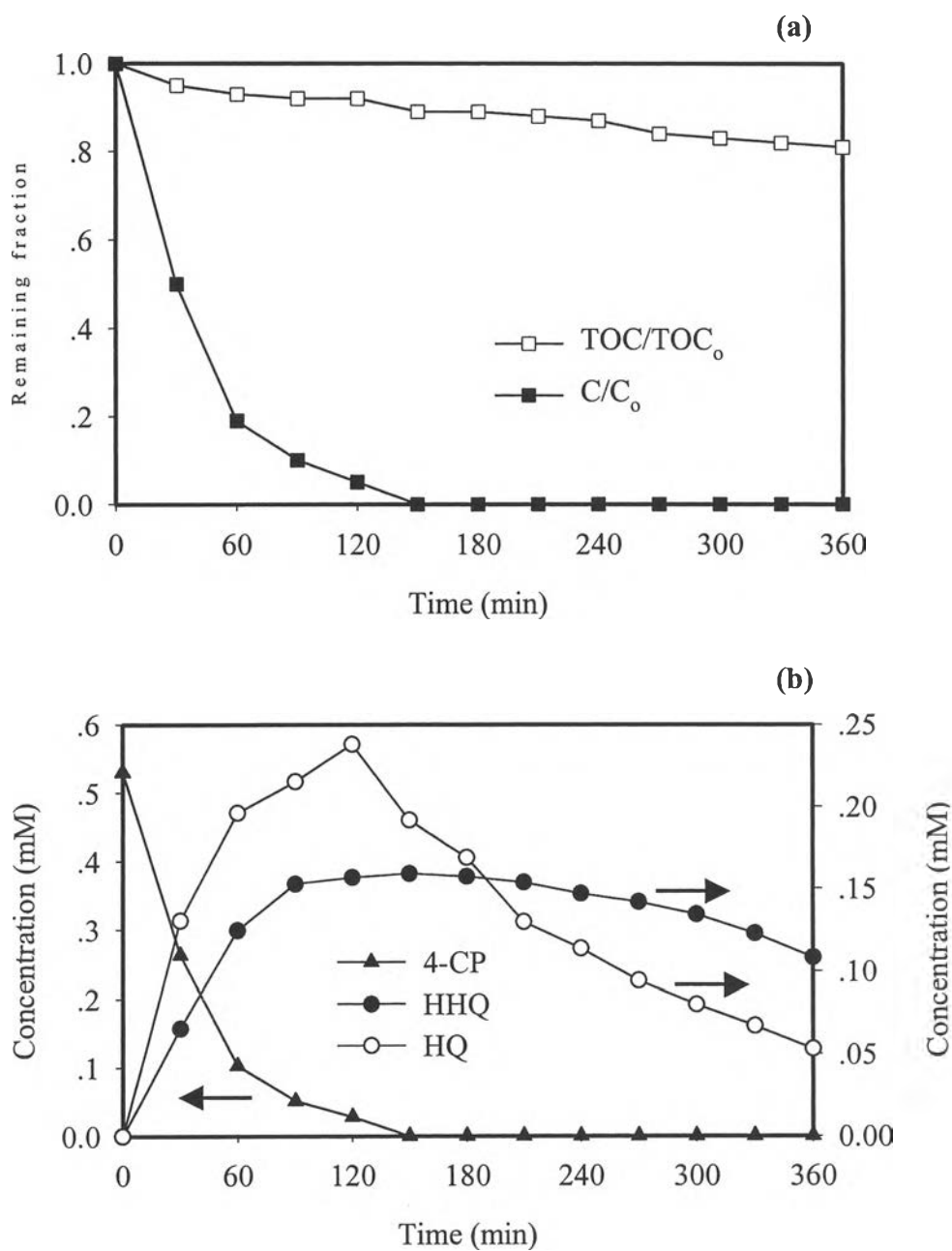
Figure 4.9 Photocatalytic degradation of 4-CP as a function of irradiation time using 1% Au/TiO₂ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
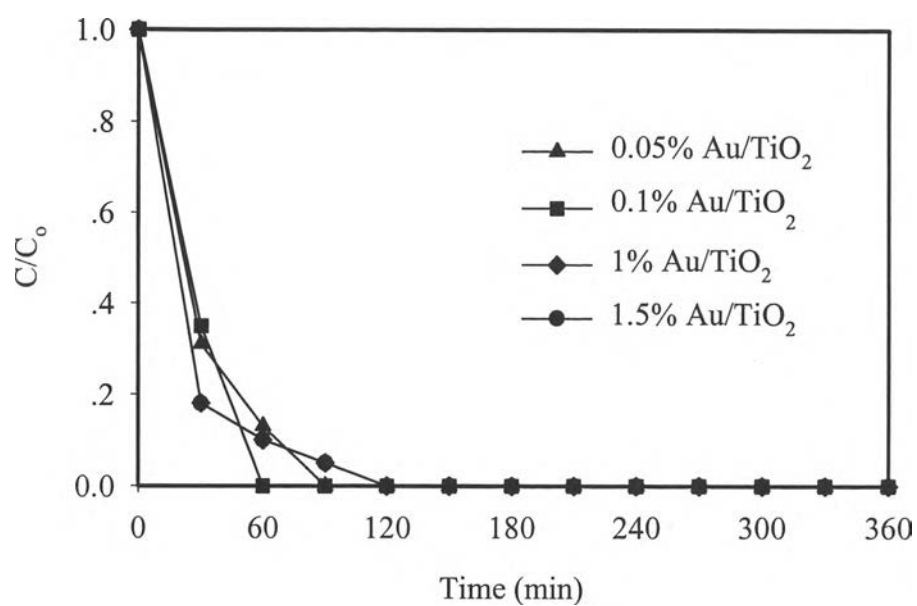
(a)

(b)

Figure 4.10 Photocatalytic degradation of 4-CP as a function of irradiation time using 1.5% Au/TiO$_2$ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.

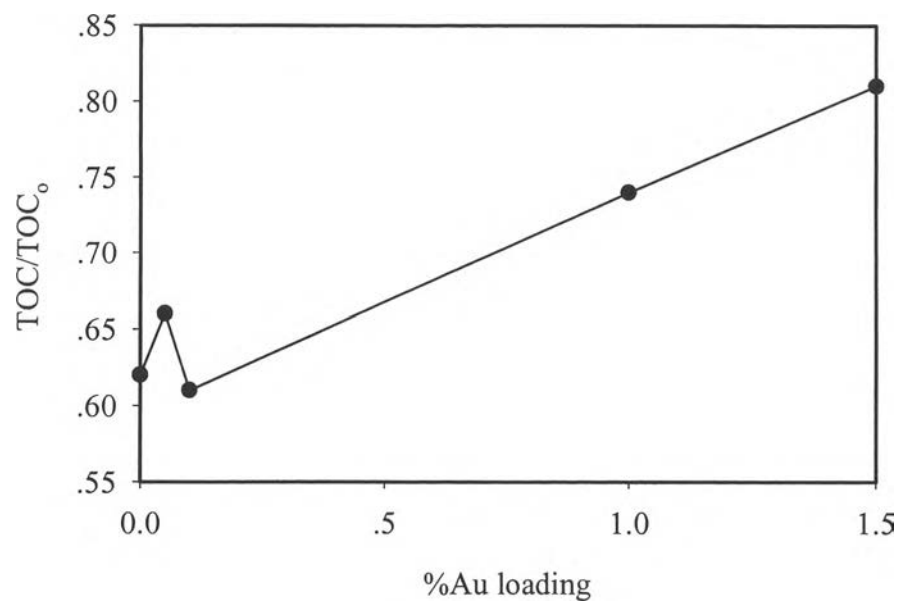**Figure 4.11** Comparison of remaining fraction of 4-CP at different %Au loadings.

Figure 4.12 Remaining fraction of TOC at 360 minutes for different %Au loadings in TiO_2.

optimum amount of Au loading is 0.1%. It can be explained that the Au particles on the TiO$_2$ surface cause a strong increase of the rate of oxygen reduction in the reduction route of the photoreaction. However, the small decrease of the photoactivity at a higher metal loading (>0.1%) is caused by the so-called screening effect that the deposited metal makes part of the catalyst surface less accessible for photons (Dobosz and Sobcznski, 2001).

4.2.3 Photocatalytic Degradation of 4-CP with Ag/TiO$_2$

Effects of adding Ag in TiO$_2$ on the degradation of 4-CP were investigated systematically. A series of Ag/TiO$_2$ was prepared at different Ag loadings from 0.2-1.5%. The degradation rates of 4-CP at different Ag loadings are shown in Figures 4.13-4.16. As shown in the figures, the addition of Ag in TiO$_2$ does not alter the breakdown pathway of 4-CP (See Appendix A) compared to 0.05% and 0.1% Au/TiO$_2$ catalysts. There was, however, a slight difference in the intermediate products formed between with 1-1.5% Au/TiO$_2$ and Ag/TiO$_2$. For the two Au-loaded TiO$_2$ catalysts, during the reaction, HQ concentration was higher than HHQ, which is opposite to what was observed with all Ag-loaded TiO$_2$ catalysts. It is not clear at this point how both metals contribute to such the difference. In any case, 4-CP was first degraded into HQ, after that HQ degraded rapidly into HHQ resulting from the high surface areas of the Ag/TiO$_2$ catalysts as compared to Au/TiO$_2$ catalysts especially at Au loadings.

The remaining fractions of 4-CP at different Ag loadings are compared in Figure 4.17. As can be seen in Figure 4.17, the amount of Ag does not significantly affect the degradation of 4-CP. The remaining fractions of TOC at 360 minutes and the metal loadings are plotted to compare the effect of the Ag loadings on the TOC reduction rates as shown in Figure 4.18. As can be seen in Figure 4.18, the amount of Ag has the effect on the intermediate products and TOC degradation. The minimum TOC at 360 minutes was achieved with 0.1 % Ag/TiO$_2$ catalyst. The remaining TOC further increased with increasing Ag loading. The results indicate that a small amount of Ag added could improve the photocatalytic activity of TiO$_2$ and the optimum amount of Ag loading is 0.1%. The reason is that a small amount of Ag on TiO$_2$ attributes to the acceleration of superoxide radical anion, $O_2^{\bullet-}$,
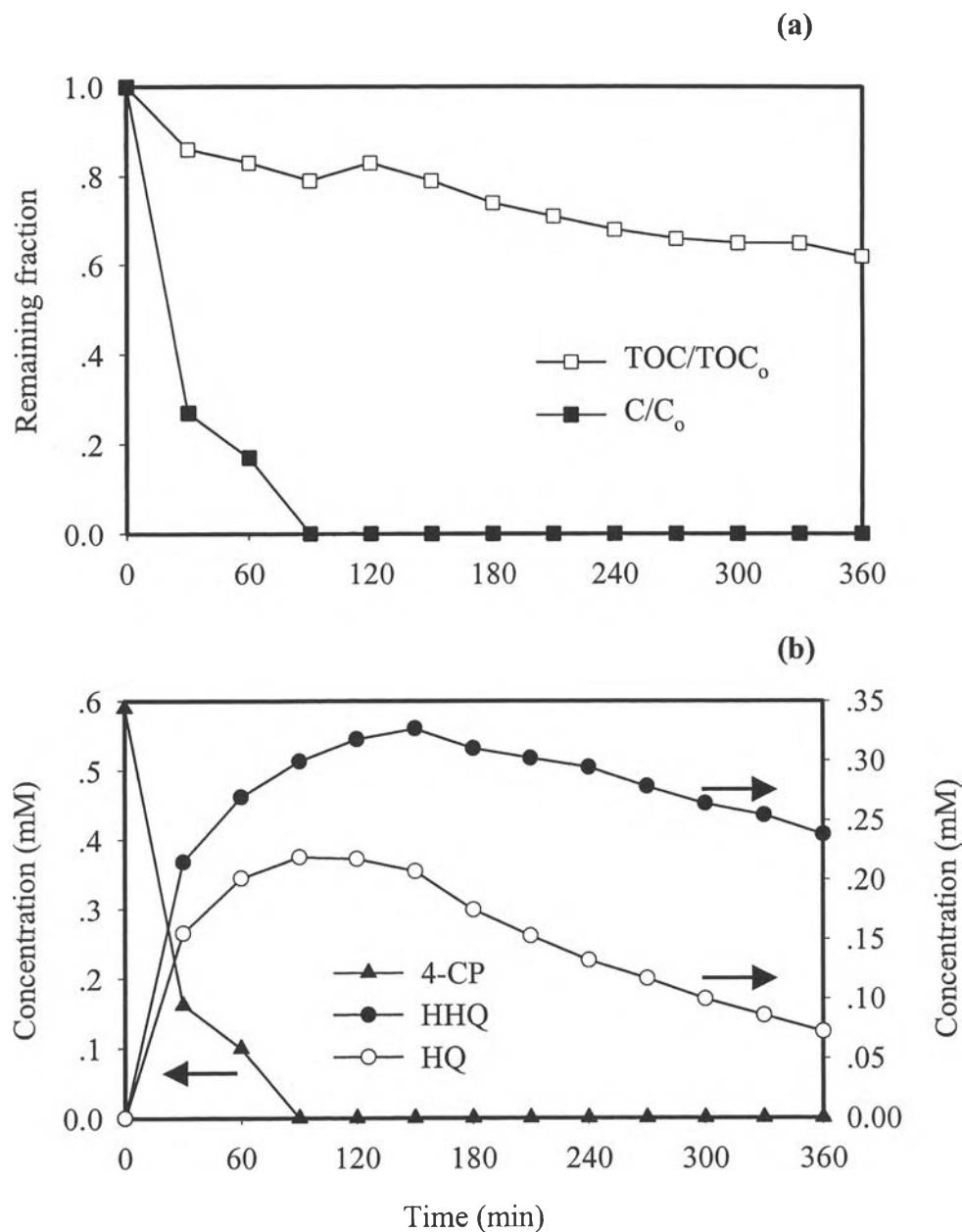
Figure 4.13 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.05% Ag/TiO_2 (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
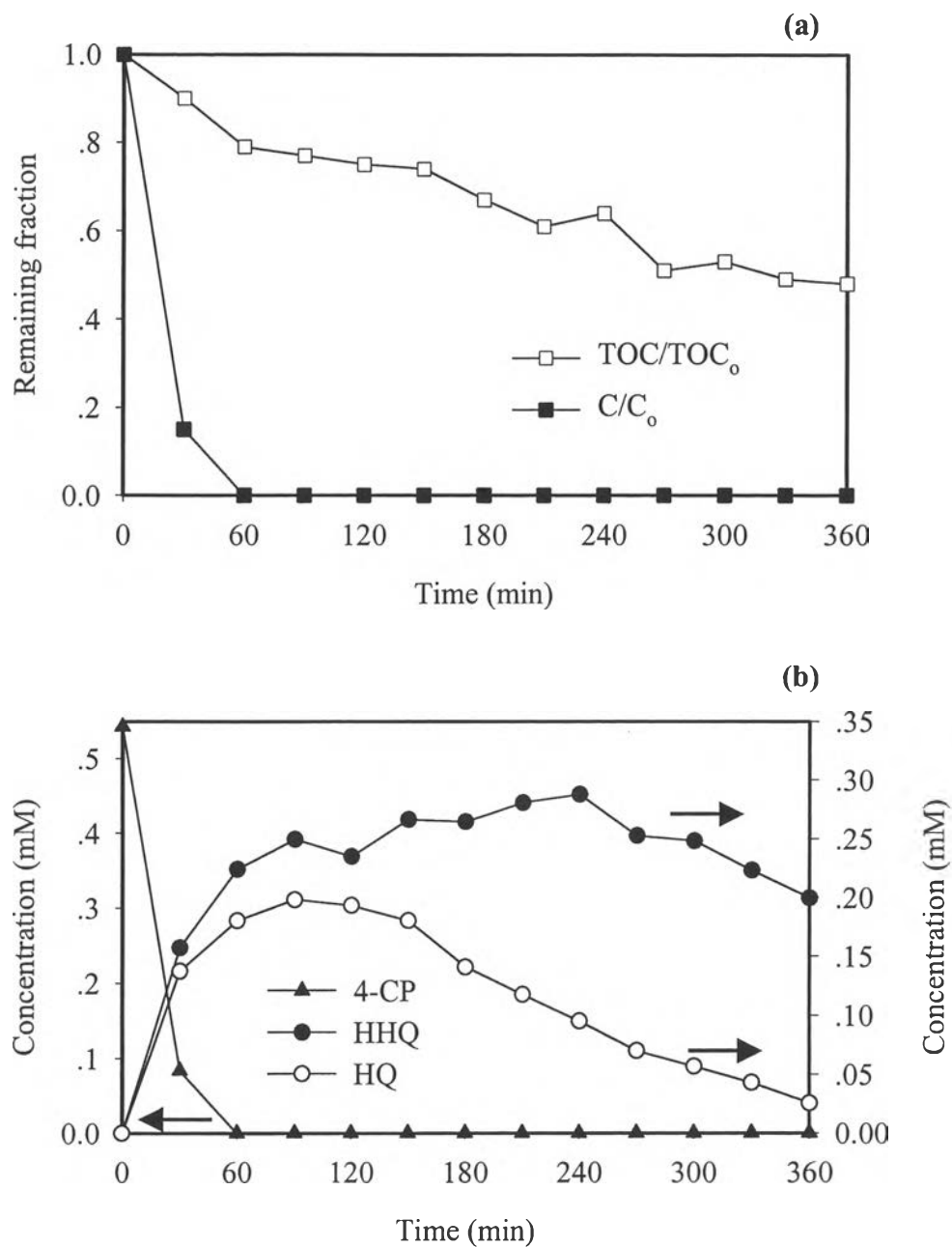
Figure 4.14 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.1% Ag/TiO$_2$ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
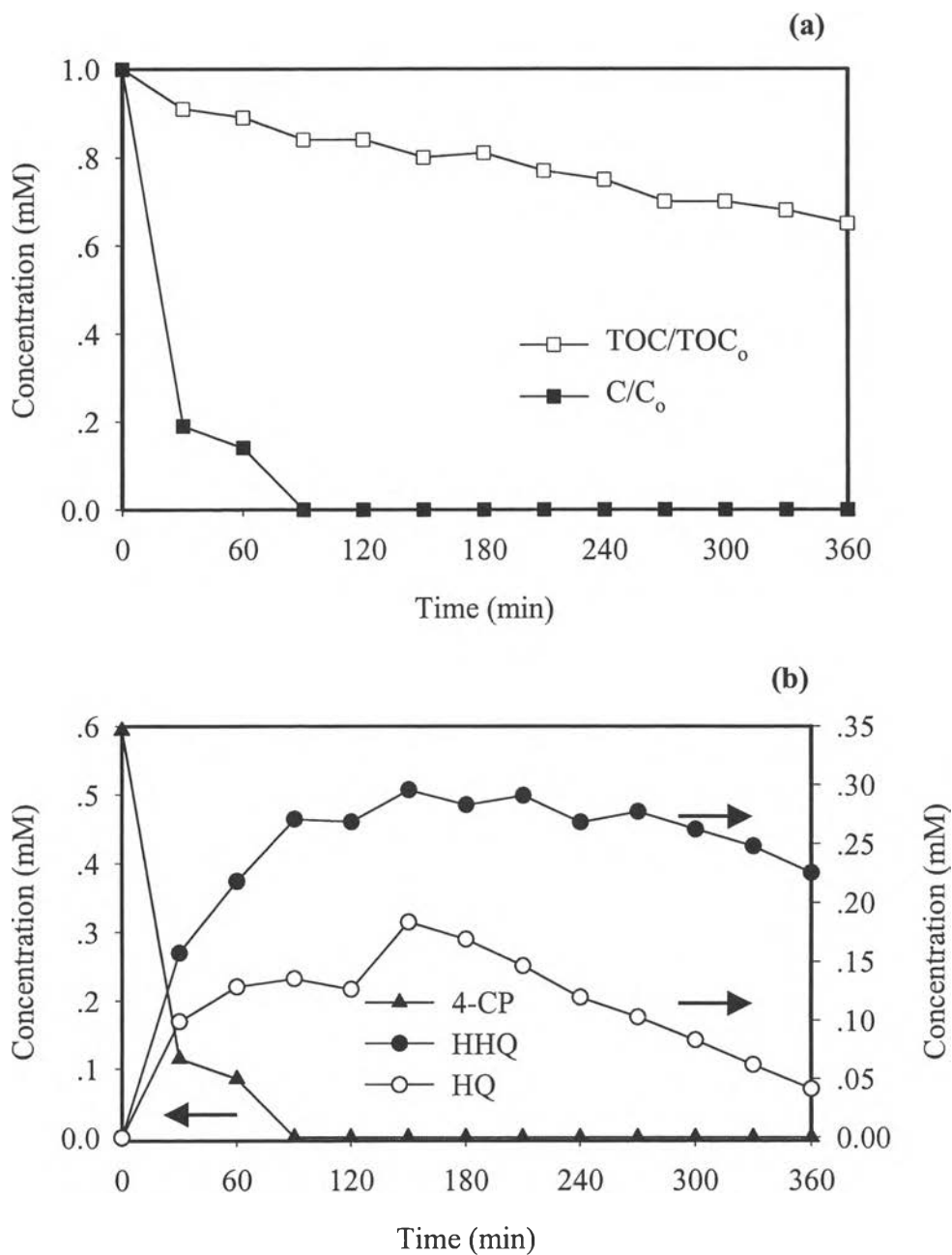
Figure 4.15 Photocatalytic degradation of 4-CP as a function of irradiation time using 1% Ag/TiO$_2$ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
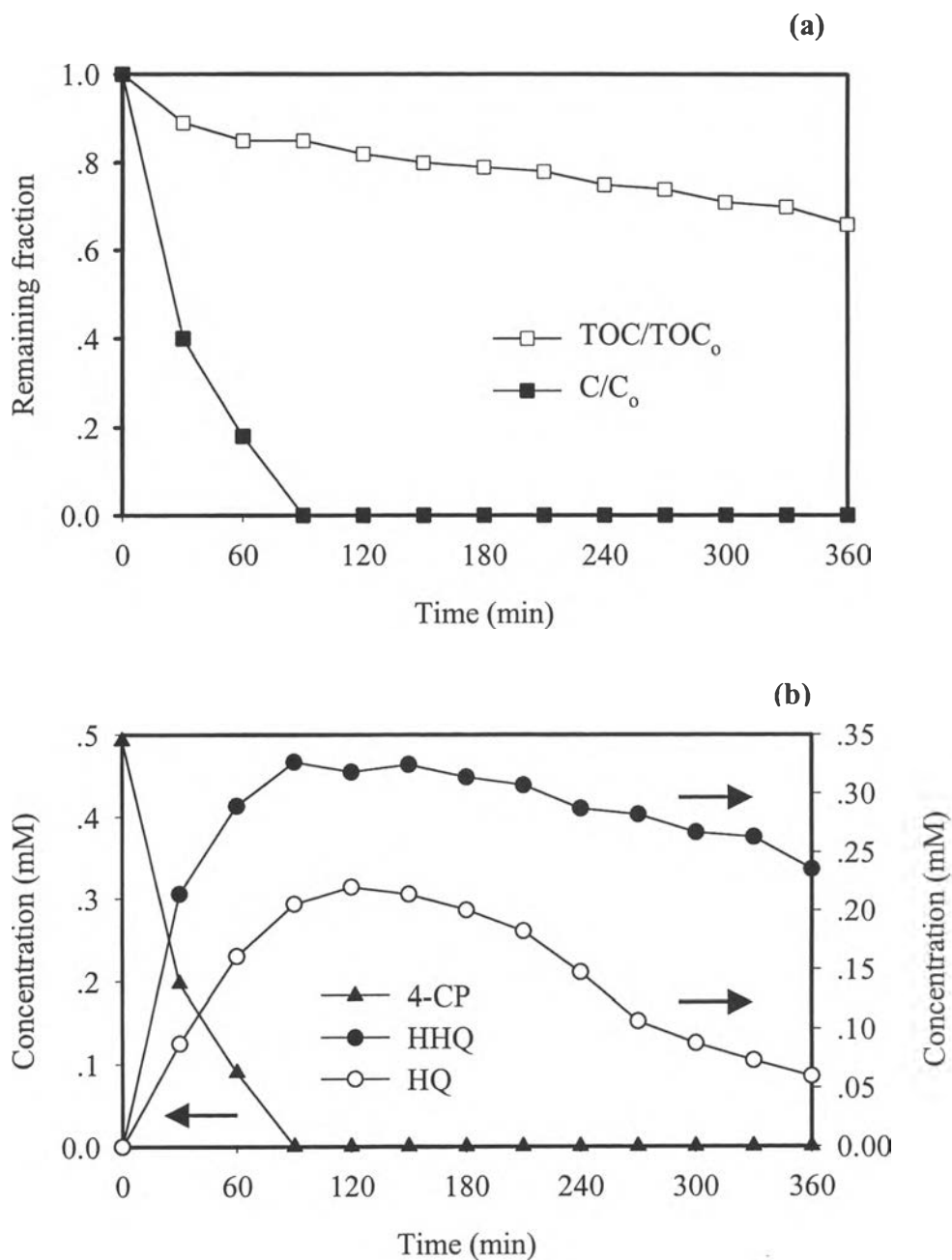
Figure 4.16 Photocatalytic degradation of 4-CP as a function of irradiation time using 1.5% Ag/TiO$_2$ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
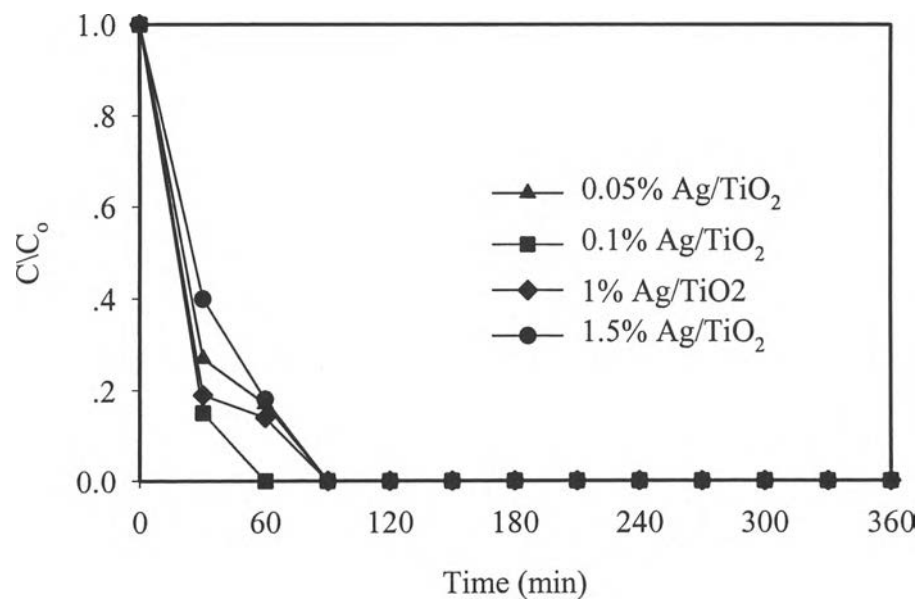
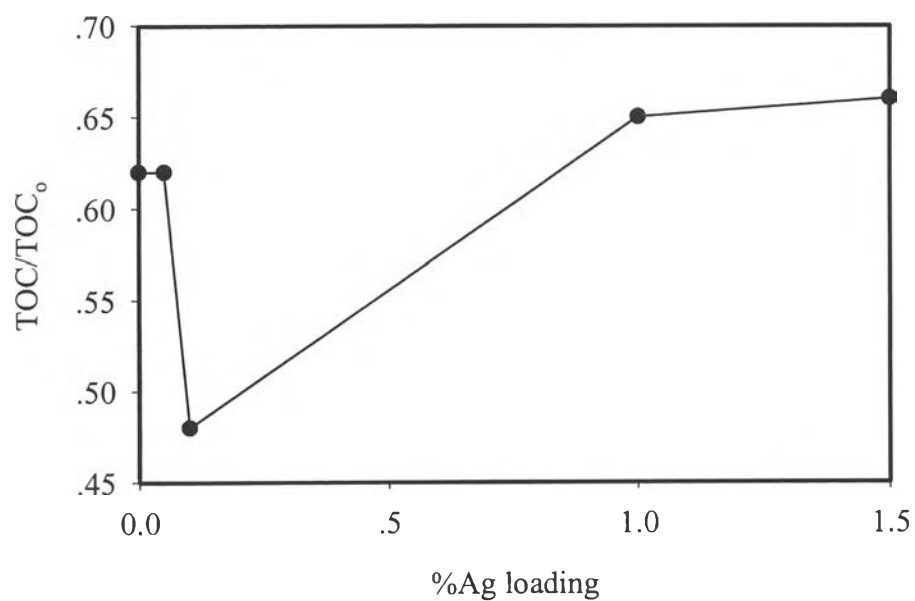**Figure 4.17** Comparison of remaining fraction of 4-CP at different %Ag loadings.

Figure 4.18 Remaining fraction of TOC at 360 minutes for different %Ag loadings in TiO_2.

formation resulting in decreasing the recombination process as well as enhancing the oxidation reaction by its oxidative property. But when the amount of Ag increases to a certain level, the photoelectron will transfer from the semiconductor to metal particles as well as the decrease of $O_2^{\bullet-}$ resulting in the increase of recombination and lowering the photocatalytic activity (Blazkova *et al.*, 1998). Another possible explanation is that Ag increases the rate of direct hole oxidation pathway leading to improving the photocatalytic activity (Ilisz and Dombi, 1999).

4.2.4 Photocatalytic Degradation of 4-CP with 0.1% Au-0.1% Ag/TiO₂

To study the effect of bimetallic catalyst on the 4-CP degradation, the optimum amounts of Au and Ag mentioned earlier were added to TiO_2 (sol-gel). Figure 4.19 shows the degradation using 0.1% Au-0.1% Ag/TiO_2. No significant improvement of the degradation with Au-Ag bimetallic/TiO_2 catalyst was observed. It is worth to note that 4-CP, HQ, and HHQ concentration profiles of the system with 0.1% Au-0.1% Ag/TiO_2 were similar to those with 0.1% Ag/TiO_2. The reason may be the similarity of the BET surface areas of these two catalysts. This result implies that the addition of Ag has stronger effect than Au resulting in the approximately the same photoctalytic activity of 0.1% Au-0.1% Ag/TiO_2 and 0.1% Ag/TiO_2. It is possible that 0.1% Au-0.1% Ag/TiO_2 shows the better TOC result than 0.1% Ag/TiO_2 as increases time more than 360 minutes. As seen in Figure 4.20, except TiO_2 (Degussa P25), 0.1% Ag/TiO_2 and 0.1% Au-0.1% Ag/TiO_2 give the highest photocatalytic activity in terms of the lowest remaining fraction of TOC at 360 minutes.

4.2.5 Effect of Mobility

In the mobilized system, photocatalytic degradation of 4-CP was carried out with TiO_2 (sol-gel) particles of 0.5 g/l suspended in 0.5 mM 4-CP solution of 450 ml solution while in the immobilized system, 100 ml 4-CP solution with 5 glass plates coated with TiO_2 (sol-gel) of 0.2865 g/l was used. Figures 4.21 shows the remaining fraction and concentration profiles of intermediate products in the immobilized systems. Table 4.3 compares the initial degradation rates of the
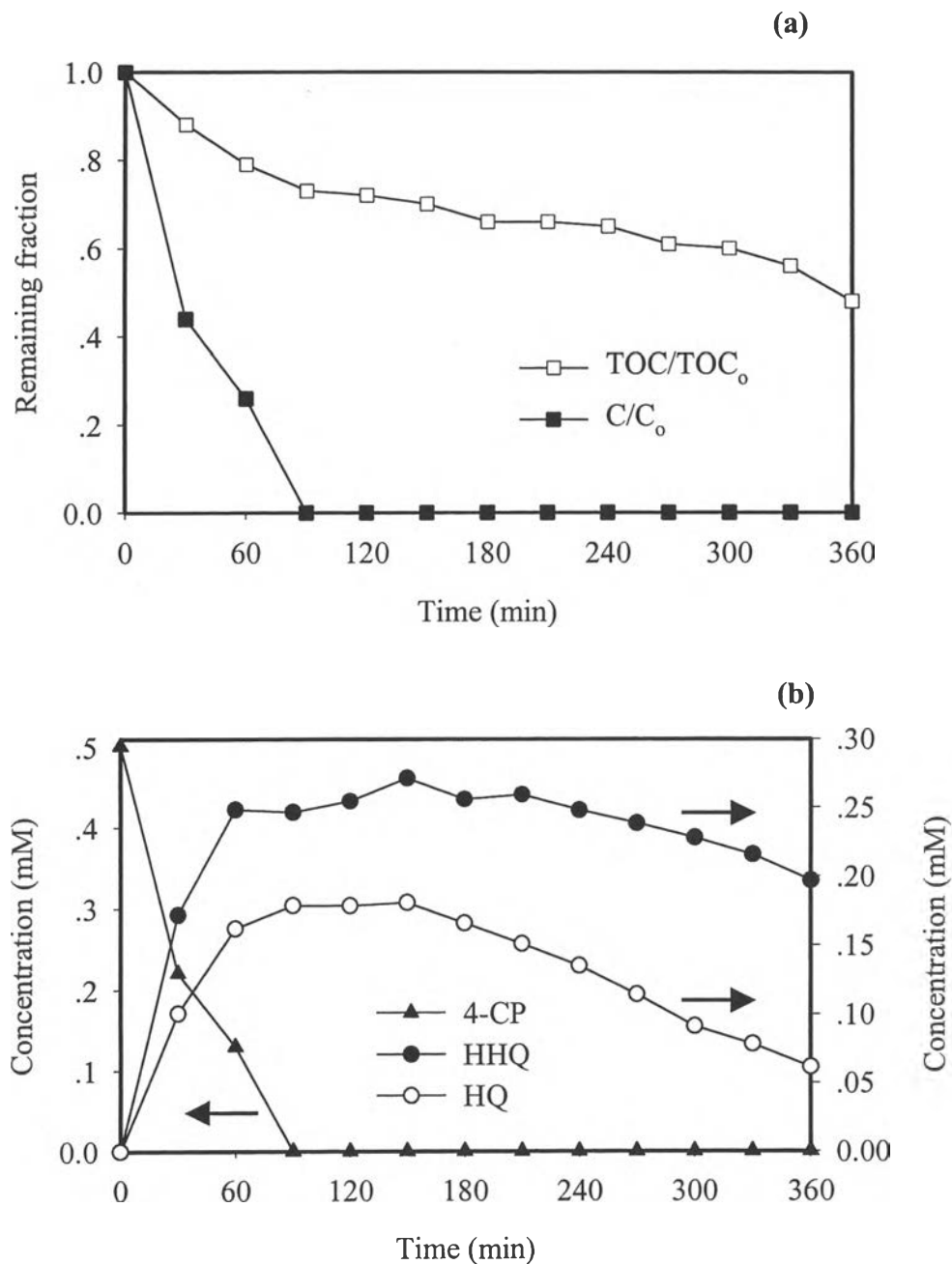
(a)

(b)

Figure 4.19 Photocatalytic degradation of 4-CP as a function of irradiation time using 0.1% Au-0.1% Ag/TiO$_2$ (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP and 298 K.
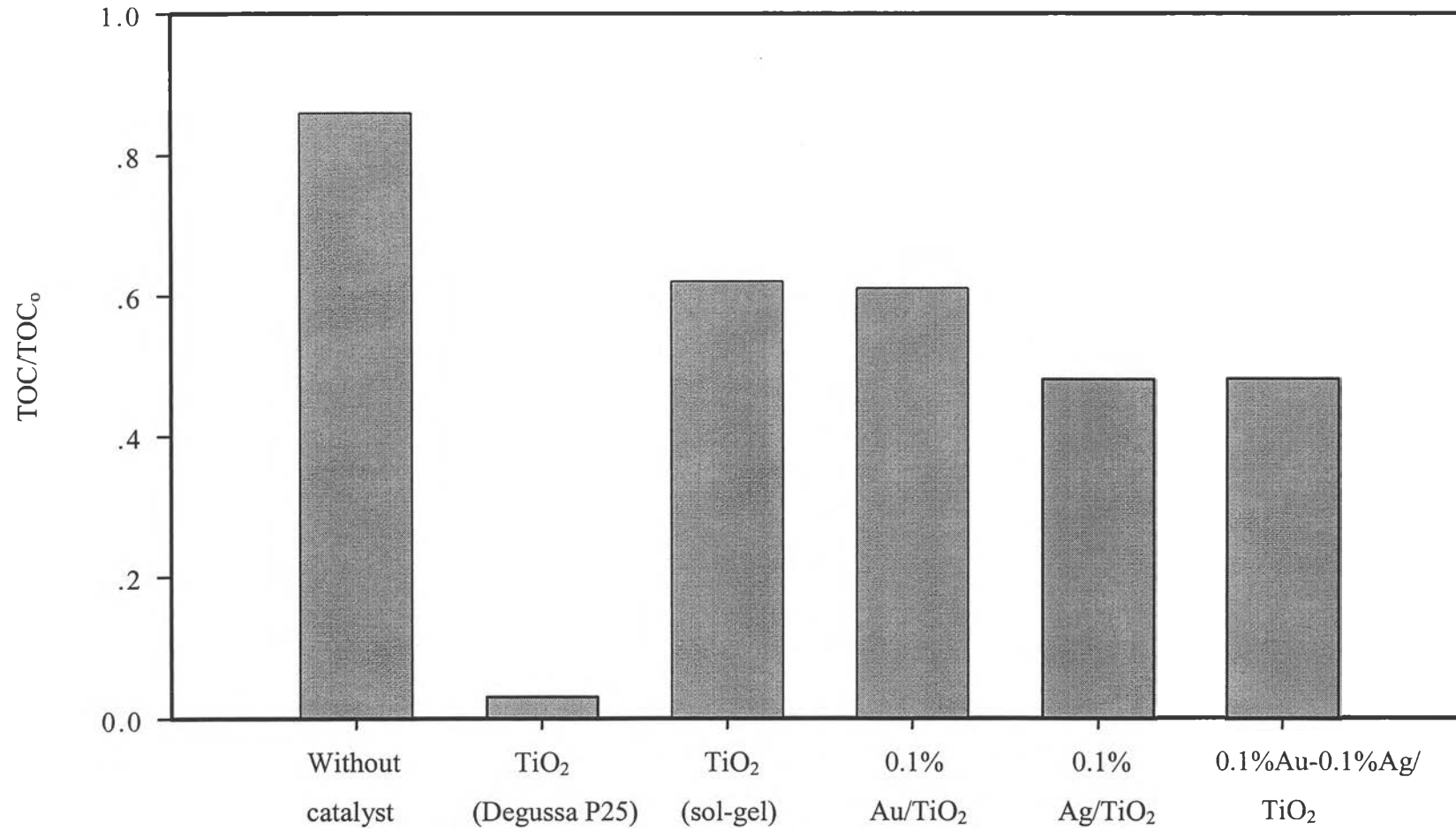
Figure4.20 Remaining fraction of TOC at 360 minutes for different catalysts in photodegradation of 4-CP.
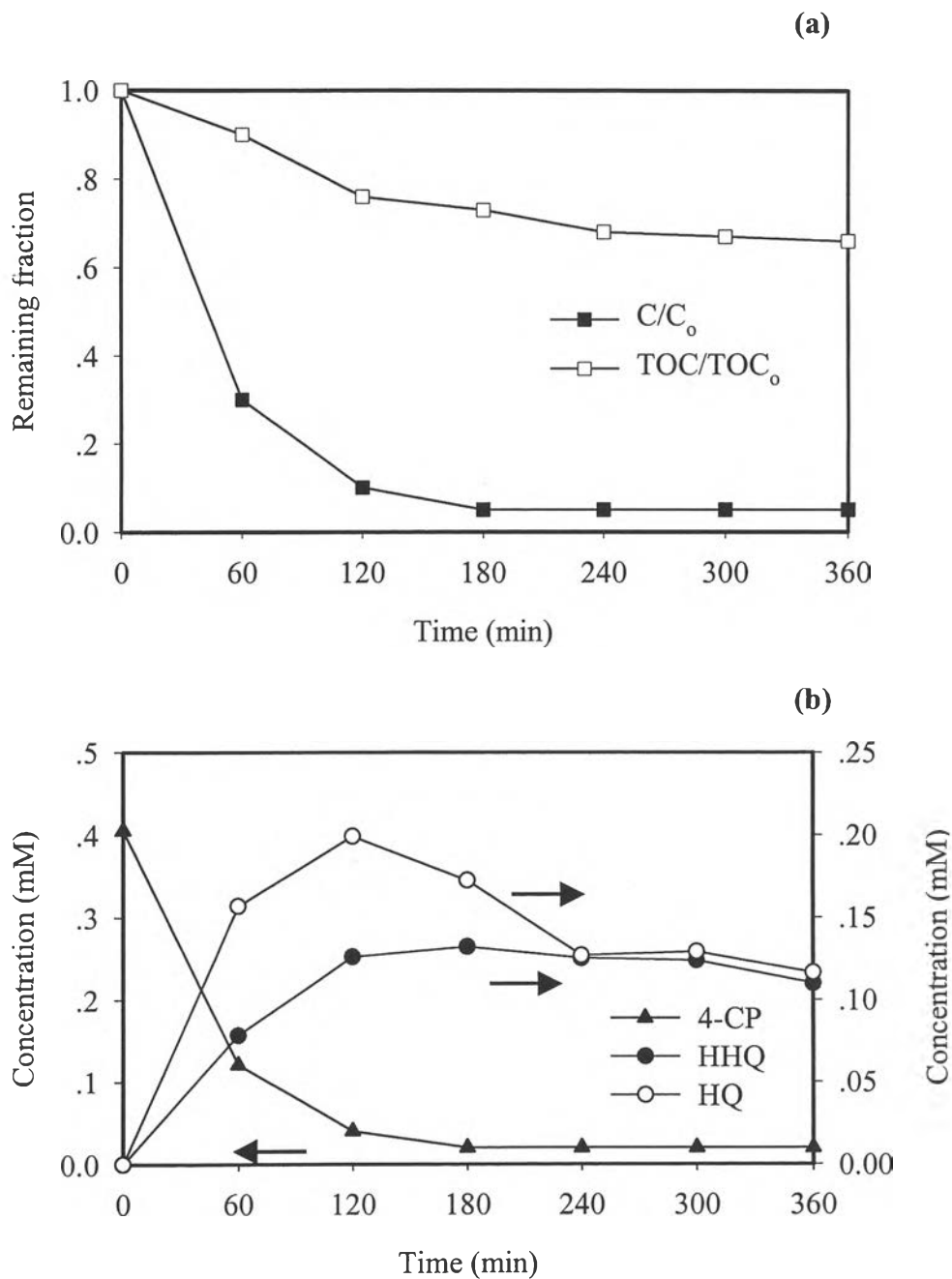
(a)

(b)

Figure 4.21 Photocatalytic degradation of 4-CP as a function of irradiation time using the immobilized TiO_2 (a) remaining fractions of 4-CP and TOC (b) concentration profiles of the intermediate products. Experimental condition: 0.2865 g/l catalyst, 0.5 mM 4-CP, 298 K.

of degradation. With the immobilized catalyst, the intermediate products increase in the first period until 240 minutes and remain constant afterwards, while they are dramatically reduced in the suspended system. It implies that the intermediate product degradation effectiveness of the immobilized TiO_2 (sol-gel) is much lower than that of the suspended system. But in case of immobilized system, no catalysts lose and easy separation from the system. In addition, the reason why mobilized system is better than immobilized system because of better homologous mixing and more surface area to be exposed to the UV for the immobilized system.

Table 4.3 Comparison of the photocatalytic degradation of 4-CP in the suspended and immobilized system

	Suspended System	Immobilized System
Catalyst loading (g/l)	0.5	0.287
Initial rate of 4-CP degradation (mole/(min.g cat.))	2.66×10^{-5}	1.65×10^{-5}
Initial rate of TOC degradation (ppm/(min.g cat.))	0.947	0.537