

## CHAPTER III EXPERIMENTAL



### 3.1 Photocatalyst Preparation by Sol-gel Method

#### 3.1.1 Materials

Hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6(\text{H}_2\text{O})$ ) supplied by Aldrich, tetraethylorthotitanate ( $(\text{C}_2\text{H}_5\text{O})_4\text{Ti}$ ) or TEOT and tetraethylorthosilicate ( $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ ) or TEOS, supplied by Fluka, were used as a precursor for platinum, titania ( $\text{TiO}_2$ ) and silica ( $\text{SiO}_2$ ), respectively. The hydrolysis of TEOT and TEOS was achieved with hydrochloric acid (37%), ethanol (99.7%) from BDH and deionized water. Nitric acid (65%) supplied by Lab-Scan was used to determine actual platinum loadings. The activity of the photocatalysts prepared by the sol-gel method was compared with commercially available titania, Degussa P25.

#### 3.1.2 Preparation Procedures

Photocatalysts in this experiment were prepared by the same method as described by Jung and Park (1999). For the preparation of  $\text{TiO}_2$ , the mole ratio of TEOT to water, hydrochloric acid and ethanol was 1:100:0.2:1. TEOT was added into the premixed solution, which contained water, hydrochloric acid and ethanol at room temperature. This solution was mixed for 24 hours to obtain a titania sol and ethanol was then evaporated at 75-80 °C for 5 hours by a rotary evaporator. After the ethanol evaporation, the solution was dried in an oven at 100 °C for 24 hours and then undergone the calcination step between 400-700 °C for 5 hours. For the preparation of  $\text{TiO}_2$ - $\text{SiO}_2$ , the mole ratio of total precursor (TEOT+TEOS) to water, hydrochloric acid and ethanol was 1:156:0.2:1. TEOS was added in the premixed solution to pre-hydrolyze before TEOT was added because the hydrolysis rate of TEOS

is much slower than that of TEOT. The other steps were prepared by the same procedures used for the  $\text{TiO}_2$  preparation. The mole fraction of silicon was varied from 0.1 to 0.5. The optimum mole fraction was selected to prepare  $\text{Pt/TiO}_2\text{-SiO}_2$ .

For the  $\text{Pt/TiO}_2$  and  $\text{Pt/TiO}_2\text{-SiO}_2$  preparation, the calculated amount of hexachloroplatinic acid was dissolved in the premixed solution. Then,  $\text{Pt/TiO}_2$  and  $\text{Pt/TiO}_2\text{-SiO}_2$  were prepared by the same method as those of  $\text{TiO}_2$  and  $\text{TiO}_2\text{-SiO}_2$ , respectively. The amount of Pt in  $\text{TiO}_2$  was varied from 0.2-2.0 mol %. Then, the optimum mole percent of Pt was used to prepare  $\text{Pt/TiO}_2\text{-SiO}_2$ .

### 3.1.3 Catalyst Characterizations

Crystal forms of the prepared photocatalysts were determined with a Rigaku X-ray diffractometer. The crystallite sizes of the catalysts were calculated by the Scherrer equation. BET surface area, pore size and pore volumes were determined by a Quantachrom surface area analyzer (Autosorb 1). A Bruker FTIR spectroscope was used to confirm the Ti-O-Si bond and to check whether silica was dispersed into titania for  $\text{TiO}_2\text{-SiO}_2$ . A Joel scanning electron microscope (JSM-5200) was used to study the surface of the catalysts. A Varian atomic absorption spectrophotometer (SpectrAA-300) was used to obtain the actual amount of Pt in  $\text{Pt/TiO}_2$  and  $\text{Pt/TiO}_2\text{-SiO}_2$ .

## 3.2 Photocatalytic Study

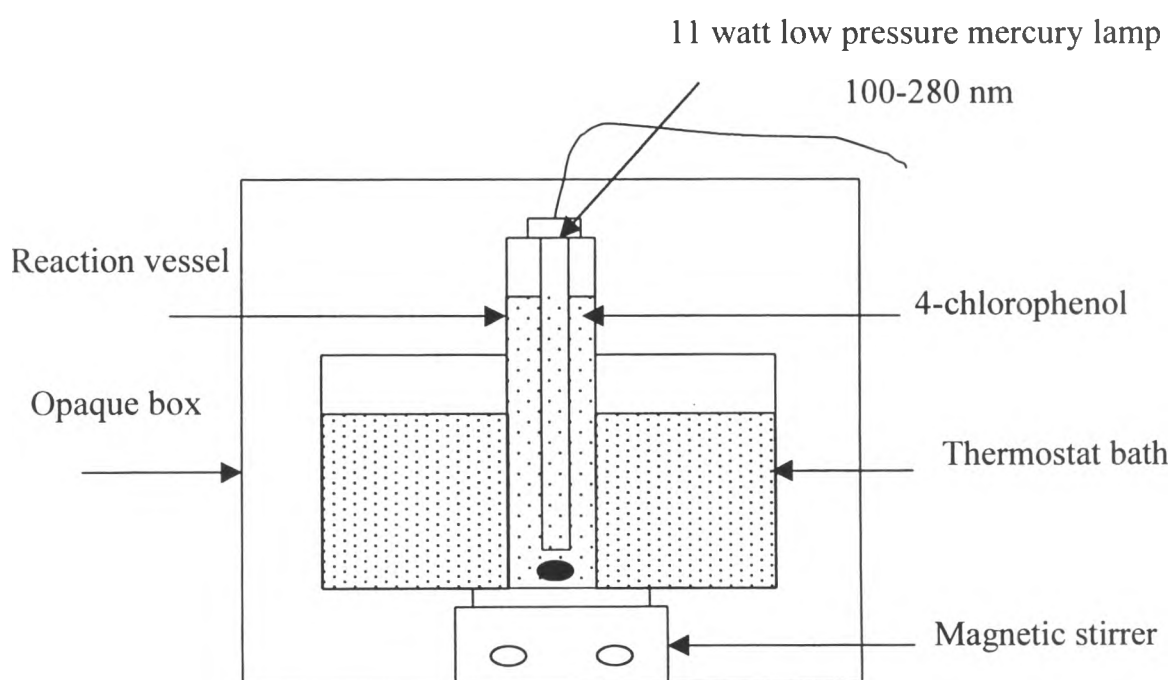
### 3.2.1 Materials

4-chlorophenol ( $\text{C}_6\text{H}_5\text{OCl}$ ) or 4-CP (98%) obtained from BDH was used as a model pollutant in this study. pH was varied using nitric acid (65%), supplied by Lab-Scan, and potassium hydroxide, supplied by Scharlau. Acetonitrile ( $\text{CH}_3\text{CN}$ ), HPLC grade from Scharlau was used as a mobile phase

for High Performance Liquid Chromatography analysis. Deionized water was used as the solvent for all experiments.

### 3.2.2 Experimental Setup

A 1000- ml laboratory bottle was used as a batch reactor for this study. The UV light source was an 11-watt low-pressure mercury lamp with a wavelength in the range of 100-280 nm. This wavelength range gives high energy enough to activate molecules of the photocatalysts. The UV lamp was dipped into the bottle in order to illuminate throughout the solution. A thermostat bath and magnetic stirrer were used to control the temperature and continuous mixing during the experiment. The reactor was covered by an opaque PVC box to prevent the outer effects and for UV protection. The setup of the photocatalytic reactor is shown in Figure 3.1.



**Figure 3.1** Schematic of the photocatalytic reactor used in this experiment

### 3.2.3 Experimental Procedure

For the irradiation experiment, 900 ml of the solution containing the desired concentration of 4-chlorophenol and a catalyst were added into the reactor. Before the irradiation, the solution was stirred well for 1 hour to allow the equilibrium adsorption of the system. Temperature was maintained at room temperature (about 25 °C) by the thermostat bath in conjunction with a cooling/heating unit. The experiment started when the UV lamp was turned on. A sample was taken every 30 minutes for 6 hours during the irradiation to measure the concentration of 4-chlorophenol and total organic carbon (TOC).

### 3.2.4 Analytical Methods

Before analysis, solution samples must be filtered with a nylon filter membrane (0.2- $\mu\text{m}$  pore size, 25-mm diameter) to remove all solid particles. 4-chlorophenol concentration was determined by a Hewlett Packard HPLC equipped with an UV detector adjusted to 270 nm for the detection of 4-chlorophenol and the ODS-2 spherisorb column (125-mm length, 4-mm internal diameter and 5  $\mu\text{m}$  particle diameter). The mobile phase was a mixture of 30 to 70 volume ratio of acetonitrile to deionized water with the flow rate of 0.3 ml/min. TOC was determined by a Shimadzu TOC analyzer (TOC-5000A).

## 3.3 Adsorption of 4-Chlorophenol on Photocatalysts

Adsorption experiments of 4-chlorophenol on different photocatalysts were carried out to determine the adsorption capacity of the photocatalysts used. In the experiments, 20-ml of different 4-chlorophenol concentration, 0.5, 1.0 and 2.0 mM were used. Each sample contained approximately 1.5 g/l of a dispersed catalyst. The suspension of the photocatalyst in the solution was stirred well in the shaking water bath (25°C) for 2 days to reach the

equilibrium. Then, the photocatalyst in the solution was removed by centrifugation and filtrated by a nylon filter membrane (0.2- $\mu\text{m}$  pore size, 25-mm diameter). The concentration of 4-chlorophenol was determined by the TOC analyzer. The adsorption constant ( $K_{\text{ad}}$ ) was calculated using the Langmuir adsorption isotherm given by

$$C_s/S_{\text{ad}} = (C_s/S_{\text{ad}}^{\text{max}}) + (1/K_{\text{ad}}S_{\text{ad}}^{\text{max}}) \quad (3.1)$$

where  $C_s$  is the solution phase concentration of 4-chlorophenol (mM),  $S_{\text{ad}}$  is the amount of 4-chlorophenol adsorbed on the catalyst (mmol/g),  $K_{\text{ad}}$  is the adsorption constant, and  $S_{\text{ad}}^{\text{max}}$  is its maximum value. From the experiment, the concentration before and after the equilibrium adsorption was available from the TOC analysis.  $S_{\text{ad}}$  can be determined by subtracting  $C_s$  from the initial concentration of 4-chlorophenol and divided by the amount of catalyst used (g/l). The term of  $C_s/S_{\text{ad}}$  is plotted as a function of  $C_s$  to obtain a linear relationship.  $S_{\text{ad}}^{\text{max}}$  and  $K_{\text{ad}}$  were determined from the slope ( $1/S_{\text{ad}}^{\text{max}}$ ) and intercept ( $1/K_{\text{ad}}S_{\text{ad}}^{\text{max}}$ ), respectively. After obtaining these values, the adsorption capacities of the photocatalysts were compared. The higher values of  $K_{\text{ad}}$  indicate higher adsorption capacity (Torimoto *et al.*, 1996). In this study, the adsorption of 4-chlorophenol on  $\text{TiO}_2$  and  $\text{TiO}_2\text{-SiO}_2$  were studied.