

CHAPTER III EXPERIMENTAL

3.1 Preparation of Photocatalyst

3.1.1 Materials

Hydrogen tetra chloraurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) obtained from Aldrich and silver nitrate (AgNO_3) supplied by Fluka were used as precursors for gold and silver, respectively. TiO_2 (Degussa P25) used as a photocatalyst obtained from JJ-Degussa. Methanol (CH_3OH) from Lab-Scan was a solvent for dip coating preparation.

3.1.2 Preparation Procedures

3.1.2.1 Calcined TiO_2 (Degussa P25)

Pure TiO_2 catalysts used in this experiment were prepared by varying calcination temperature. TiO_2 was incipiently wetted by H_2O . After that, it was dried at 110 °C overnight and calcined at 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 900 °C and 1200 °C for 3 hr.

3.1.2.2 Metal Doped on TiO_2 (Degussa P25)

Metal doped TiO_2 (Au/TiO_2 and Ag/TiO_2) was prepared by incipient wetness impregnation. A calculated amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ or AgNO_3 was dissolved in distilled water. Then, the solution was added dropwise to incipiently wet TiO_2 particles. After that, it was dried at 110 °C overnight and calcined at 500 °C for 3 hr.

3.1.2.3 TiO_2 on #8 Stainless Steel Mesh

Stainless steel mesh was cleaned using detergent and then sonicated in water for 30 min. After that, it underwent several rinses in distilled water followed by drying. The substrate was accurately weighted prior to coating.

The next step was to dip the prepared cylindrical stainless steel mesh in the suspension of TiO_2 in methanol (1.0% w/v). The stainless

steel mesh was dipped into the suspension for 15 times and dried at 110 °C overnight.

3.2 Crystal Characterization

3.2.1 Crystal Structure

X-ray diffraction patterns of all catalysts were obtained by using a Rigaku Dmax-2200 diffractometer equipped with a graphite monochromator and a Cu tube for generation a CuK α radiation (wavelength 1.5406 Å). Sample particles were spread on a glass slide specimen holder and its diffraction angles were examined between 5-90° at a scanning rate of 2 θ of 1.5° per min with 0.02° increments. CuK α radiation of the X-ray source at $\lambda = 0.154$ nm was operated at 40 kV, 30 mA, and 1.20 kW. The digital output of the proportional X-ray detector and the goniometer angle measurements were transmitted to an online microcomputer for storing the data and the data were analyzed using PC-APD version 3.5B. The peak positions of the samples were compared with the standard files to identify crystalline phases.

X-ray diffraction is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the patterns of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

X-ray diffraction patterns were used for the crystallite size (d) estimation by line broadening measurements with the Debye-Scherrer equation:

$$d = \frac{k\lambda}{b \cos \theta} \quad (3.1)$$

where

- λ = the wave length (nm)
- k = the Debye-Scherrer constant (1.0)

- b = the full width at half maximum (FWHM) of the broadened peak
- θ = the Bragg angle of the reflection (degree)
- d = the crystallite size (nm)

3.2.2 Surface Area Measurement

The Brunauer-Emmett-Teller (BET) method was utilized to determine the surface area of the catalysts. The characterization is based on the physical adsorption of an inert gas using Autosorb-1 Gas Sorption system (Quantachrome Corporation). It operates by measuring the quantity of gases adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area of $16.2 \times 10^{-2} \text{ m}^2/\text{molecule}$ was employed as an adsorbate at a liquefied nitrogen temperature (77 K).

The catalyst amount of 0.2 g was dried and outgassed in the sample cell at 300 °C for at least 3 hr before adsorption. The specific surface area of each catalyst was evaluated from five points adsorption isotherm. The results were analyzed using Autosorb ANAGAS software Version 2.10. To ensure the accuracy of the data, the BET method was employed to measure surface area of each catalyst at least twice.

3.3 **Photocatalysis Experiment**

3.3.1 Materials

4-chlorophenol (4-CP) with 98% purity obtained from BDH was used as a model pollutant in this study. Hydroquinone obtained from Ajax and hydroxyhydroquinone from Aldrich were used for analysis of intermediate products. HPLC grade of acetonitrile (CH_3CN) and methanol (CH_3OH) purchased from Lab-Scan were used as a mobile phase for a High Pressure Liquid Chromatograph (HPLC). High purity of oxygen was obtained from Thai Industrial Gases Public, Co. Ltd.

3.3.2 Experimental Set-Up

3.3.2.1 *Batch Operation*

A 1000 cm³ reagent bottle was used as a batch reactor in the study. The UV light source, an 11-watt low-pressure mercury lamp (PHILIPS PL-S 11W TUV) with a wave length in the range of 200-280 nm, 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 mix during the experiment. The reactor was covered by an opaque PVC box to prevent the outer effects and for UV protection. The set-up of the photocatalytic batch reactor is shown in Figure 3.1.

3.3.2.2 *Continuous Operation*

Figure 3.2 shows the schematic diagram of the experimental set-up for the continuous operation. There were 4 connected CSTRs. Each reactor was 650 cm³ in volume with a water jacket to control solution temperature. A cylindrical stainless steel mesh was packed into each reactor on a support structure. A magnetic stirrer was used to mix the aqueous solution during the experiment. The UV lamp was held inside the reactor to illuminate the solution thoroughly. Before each experiment, all reactors were covered with aluminium foil for reflecting the light. Samples were drawn through a sampling valve, which was at the end of each reactor.

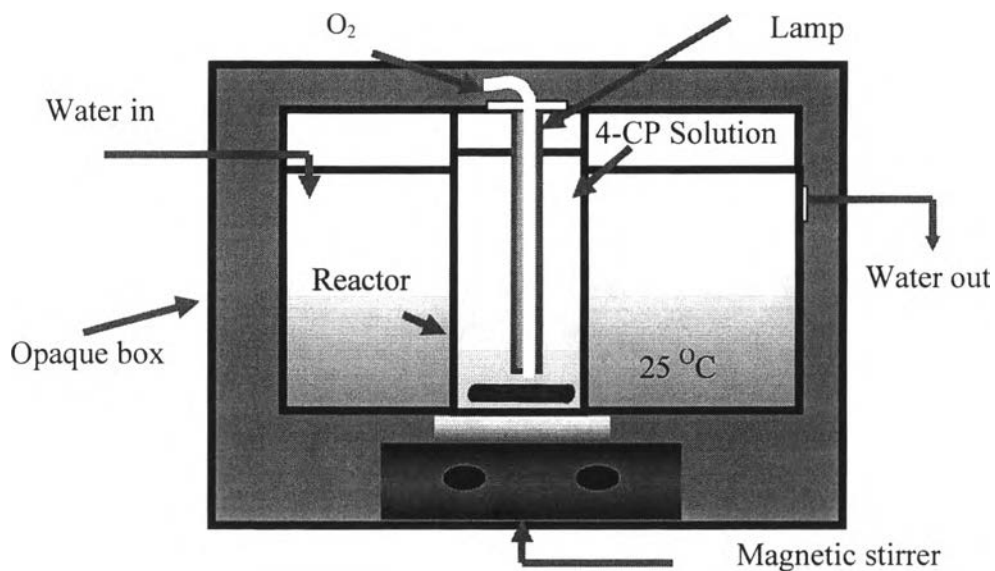


Figure 3.1 Schematic diagram of the photocatalytic reactor used in batch operation.

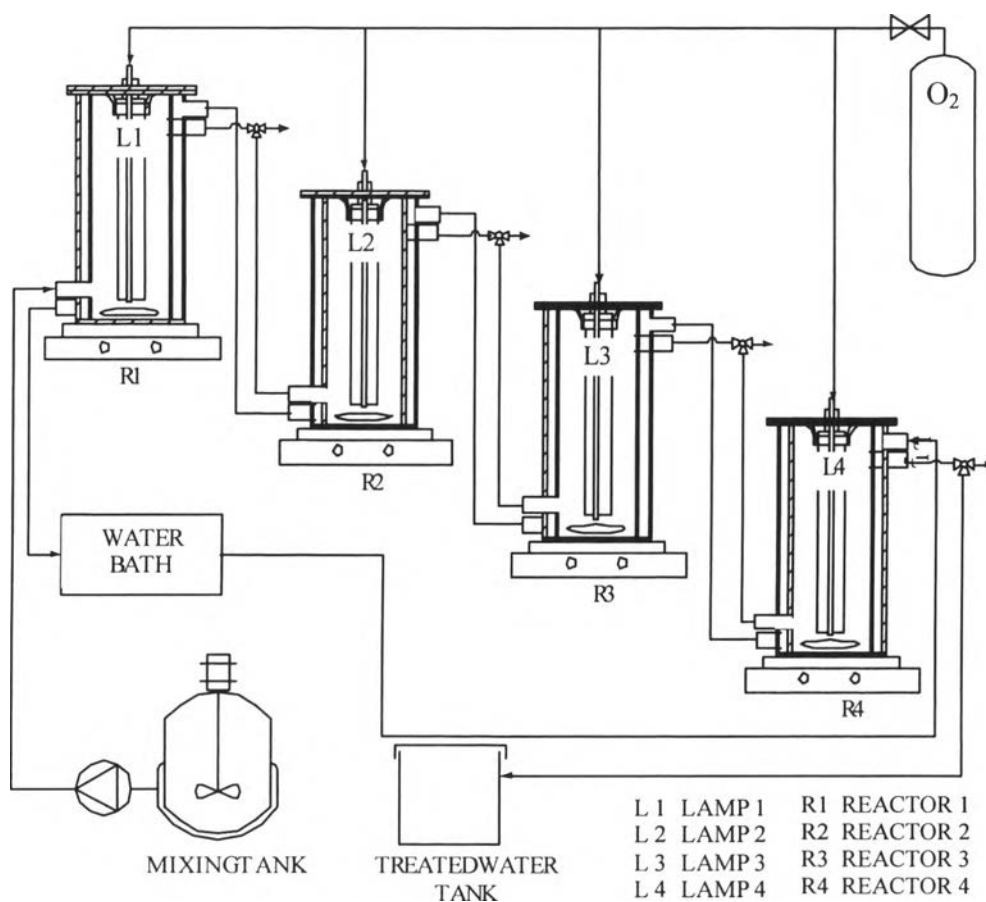


Figure 3.2 Schematic diagram of the photocatalytic reactor used in continuous operation.

3.3.3 Experimental Procedure

3.3.3.1 *Batch Operation*

450 cm³ solution containing 0.5 mM 4-CP and 0.5 g/l catalyst were added into the reactor. Before the irradiation, the solution was well stirred for 30 min to allow equilibrium adsorption of the solute on equipment with simultaneously blowing of O₂ to saturate the solution in the dark and O₂ was also continuously fed into the system during the experiment. The concentration of the substrate in the bulk solution at this point was used as the initial value. The temperature was maintained at room temperature (about 25 °C) by the thermostat bath. The experiment started when the UV lamp was turned on. During the experiment, 25 cm³ samples were taken every 20 min for 1 hr after that the samples were withdrawn every 60 min for 5 hr.

3.3.3.2 *Continuous Operation*

0.5 mM 4-CP was well stirred in the mixing tank with simultaneously blowing O₂ in the dark. Before the operation all the sampling valves were closed, and then the solution was pumped through reactor 1, 2, 3 and 4, respectively. After the reactors were filled with the solution, O₂ was introduced to saturate the solution in the reactor and waited until reaching the steady flow of the solution. The concentration of the substrate in the bulk solution at this point was used as the initial value. The experiment started when the UV lamp was turned on. After reaching the steady state, 25 cm³ samples were taken at the end of each reactor. The same procedure was repeated to increase the number of samples.

3.3.4 Analytical Methods

The collected samples were centrifuged and filtered through a nylon filter membrane (0.2- μ m pore size, 25-mm diameter) to remove all solid particles. Then, the solution samples were analyzed for their composition using a Hewlett Packard HPLC equipped with an ODS-2 spherisorb column (125-nm length, 4-nm internal diameter, and 5 μ m particle diameter) and UV detector adjusted to 270 nm for detection of 4-CP. The mobile phase was a

mixture of 40:60 volume ratio of acetonitrile to deionized water with the flow rate of 1.0 cm³/min. By comparison of the retention times with standard substances, all chemicals or intermediates produced can be identified. The concentration of any compounds can be calculated by using the calibration factor obtained from the calibration curve of a known concentration of that compound. Total organic carbon (TOC) was also determined by a Shimadzu TOC analyzer (TOC-500A).