CHAPTER III

METHODOLOGY

3.1 Design and setting up Rotating Disc Photocatalytic Reactor (RDPR)

3.1.1 Primary design criteria of RDPR

This work focused on the innovation and evaluation of the TiO_2 Rotating Disc Photocatalytic Reactor (RDPR) for the treatment of chromium (VI) in solution. A analytical grade TiO_2 was used as the immobilized photocatalyst on the rotating disc. For designing of this reactor, firstly set the goal to innovate the prototype model which proved that the mixing in the RDPR was close to that of an ideal CSTR. This reactor had the tubular flow-through photoreactor type. The minimum volume capacity of this reactor was 5 liters. The minimum ability of this RDPR for removal chromium (VI) was 25 ppm or chromium loading as 125 mg Cr^{6+}.

The reactor was designed with the important components including:

- The material for reactor body and rotating discs plate,

- Pump specification or head requirement,

- Motor specification or power requirement,

- The appropriate intensity of ultraviolet lamps,

- Amount of catalyst discs plate (amount of TiO_2 coating surface area),

- The roof of reactor,

- The appropriate positions of each discs plate and

- N_2 consumption.

3.2 Preparation of TiO_2 thin films on stainless steel discs for chromium (VI) photoreduction.

3.2.1 Chemicals

All chemicals and reagents in this study were analytical grade. Titanium dioxide was prepared via Titanium (IV) butoxide ($Ti(OC_4H_9)_4$ obtained from Aldrich and absolute ethanol supplied by Merck were used as a Ti-precursor and a solvent, respectively. Acetylacetone from Carlo erba chemical were used as organic additives. Chromium (VI) prepared by potassium chromate or K_2CrO_4 (Merck Chemicals) used to perform the synthetic wastewater of this work. Moreover, the desired pH of the solution was adjusted with NaOH or H_2SO_4 which purchased from Merck Company, and used as received.

3.2.2 Preparation of stainless steel Disc

Stainless steel discs plate (type of 316L) would be washed via 2% of hydrofluoric acid (HF) for 5 minutes, and then dipped in a mixed solution of water and anhydrous ethanol, and dried at room temperature (Liqiang et al., 2003). Before use, the disc rinsed with distilled water and each disc would be weighed and covered with adhesive tape in order to measure the amount of TiO_2 that would be coated on one side.

3.2.3 Preparation of TiO_2 precursor solutions

In the preparation of precursor solutions for TiO_2 thin films, titanium (IV) butoxide ($Ti(OC_4H_9)_4$, Aldrich chemicals) was used as the source material for Titanium. Titanium (IV) butoxide was first diluted with ethanol, which was used as a solvent. HCl and ethanol will be mixed together and used as the acidic catalyst for the hydrolysis of titanium (IV) butoxide. The acidic solution was added drop wise to the titanium (IV) butoxide-ethanol solution under vigorous stirring at room temperature.

After that, acetylacetone was added to the mixture of precursor solutions and vigorous stirring were continued for 1 hour. In this preparation, the resultant solutions were yellow and transparent. The condition which this research interesting was in the ratio of titanium (IV) butoxide: ethanol: HCl: acetylacetone of 1: 30: 0.5: 1.

3.2.4 Preparation of TiO_2 thin films

TiO_2 thin films were deposited on the substrates by sol-gel dip-coating techniques. Stainless steel discs plate (diameter of 12 cm and perforate small hole with diameter of 1.27 cm) was used as the substrates for the thin films. The coating carried out by dipping the cleaned stainless steel discs into the precursor solutions and then withdrawing them at a constant speed. Then, the stainless steel discs coated with gel film were calcite at 500°C and 3 times coating cycles in an electric furnace.

3.2.5 Characterization of TiO_2 thin films

The prepared TiO_2 thin films would be characterized by using different techniques could be described as follow:

- Adhesive test by adhesive tape.
- Acid – alkali test by dipping the coated substrates into HNO_3 and NaOH with concentrations of 1, 5 and 10 M, respectively.
- Surface morphology of TiO_2 thin films were observed by scanning electron microscopy (SEM).
- Crystallinity of TiO_2 thin films were identified by X-ray diffraction, XRD.

3.3 Investigation the effect parameters of chromium (VI) photoreduction using lab scale RDPR.

The experiment was divided into 5 parts as follows: effect of initial pH of wastewater, effect of wastewater flow rate (Q_w), effect of rotating disc speed (V_r), effect of TiO_2 coating surface area of catalyst and effect of initial concentration of chromium (VI) in the synthesis wastewater in the operating of RDPR.

Experiment Procedure.

TiO_2 thin films discs plate derived from Part 2 were placed in RDPR that contained with the synthetic chromium (VI) solution. Before the ultraviolet lamps illumination, the chromium (VI) solution would be equilibrated in the dark system with the TiO_2 thin films disc surfaces for 15 min to allowed for the adsorption process. Then, the ultraviolet lamps were turned on to illuminate the TiO_2 thin films discs with a variation of times for each concentration. The concentrations of chromium (VI) after illumination were analyzed with a UV-Visible spectrophotometer. During the experiments, N_2 was bubbled into the system at a constant flow rate. In this part, the investigation the operating parameters of chromium (VI) photoreduction using RDPR were separated to be 6 steps:

3.3.1 Synthesis chromium wastewater

Chromium wastewater containing chromium (VI) was synthesized corresponding to the concentrations that might found in real wastewater. Chromium (VI) solutions were prepared by dissolving potassium chromate (K_2CrO_4) in water. The pH of the resultant solution adjusted with diluted H_2SO_4 or NaOH.

3.3.2 Investigation the effect of initial pH of wastewater.

In this part, the experiment were investigated by varying the pH value in the range of acid (pH 3), neutral (pH 7) and basic (pH 11). After assembled TiO_2 thin film disc plates to reactor and adjusted all operating parameters finished. The synthesis wastewater follow the desired pH values with 25 ppm of chromium (VI) were synthesized. The analysis of chromium (VI) removed were proceed via sampling the sample during the experimental times. All steps are shown in Figure 3.1

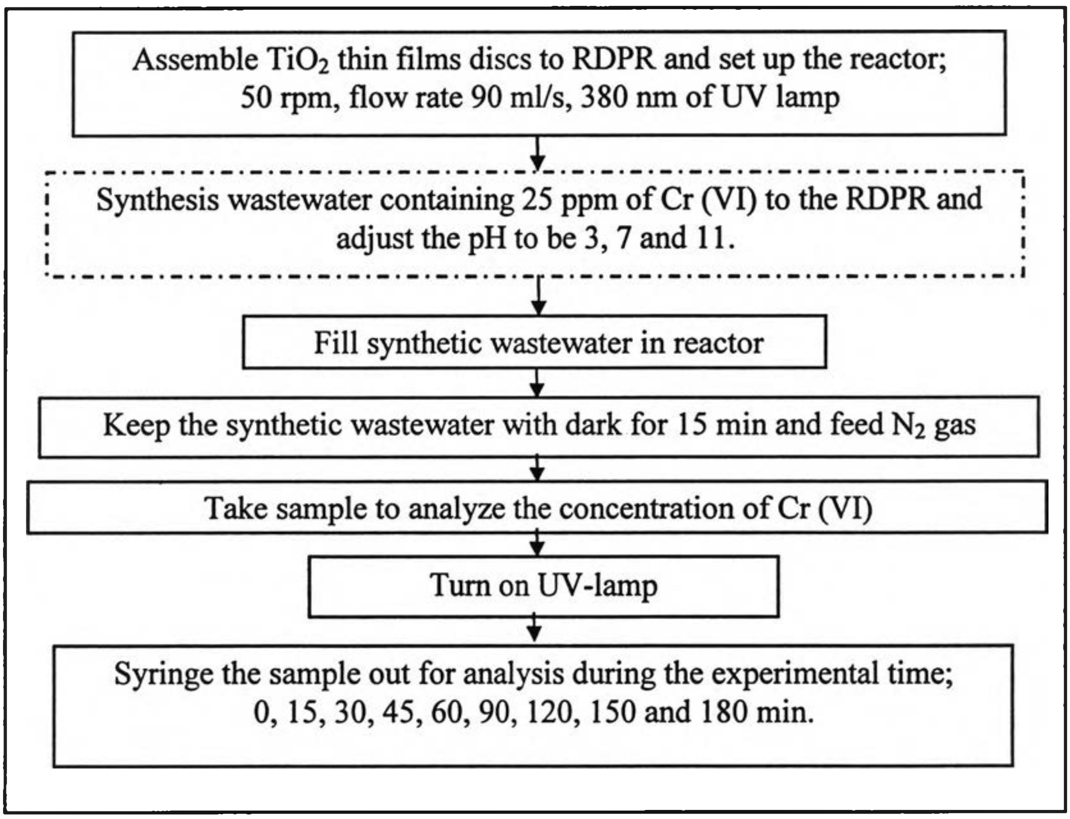

Figure 3.1 Experimental chart for the study of effect of initial pH of wastewater.

3.3.3 Investigation the effect of flow rate of wastewater.

To study the effect of wastewater flow rate, the experimental started with assemble TiO_2 thin films discs to RDPR and fixed other operating parameters (initial pH of wastewater, rotating speed discs, amount of TiO_2 coating surface area and initial concentration of wastewater). The wastewater flow rate was varied in the range of 20, 40, 60, 80 and 90 ml/s. After that, proceed the photoreaction process and sampling the samples for analysis the concentration of chromium (VI) on the time. All steps are provided in Figure 3.2

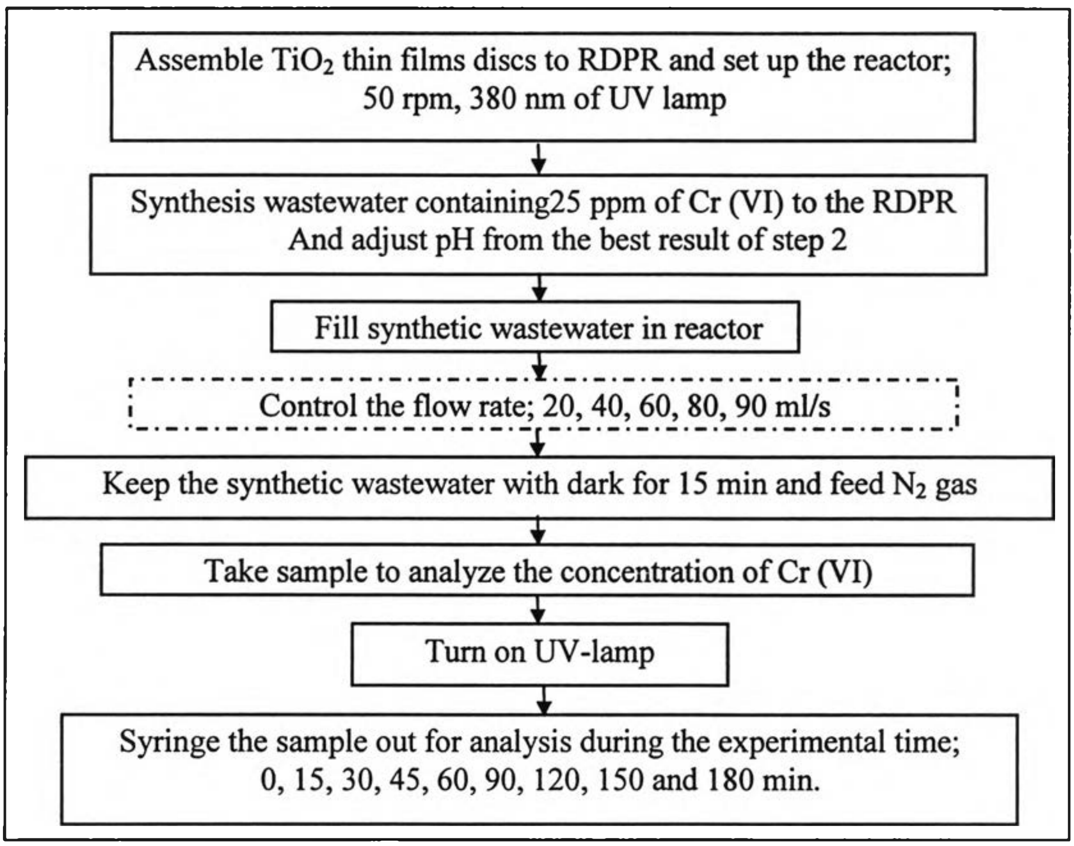

Figure 3.2 Experimental chart for the study of effect of flow rate of wastewater.

3.3.4 Investigation the effect of the rotating disc speed.

In this part, the rotation disc speed were vary as 10, 50, 100, 150 and 200 rpm. The initial pH of wastewater and the optimum wastewater flow rate were controled from the results of part 3.3.2 and 3.3.4. The experimental chart is provided in Figure 3.3

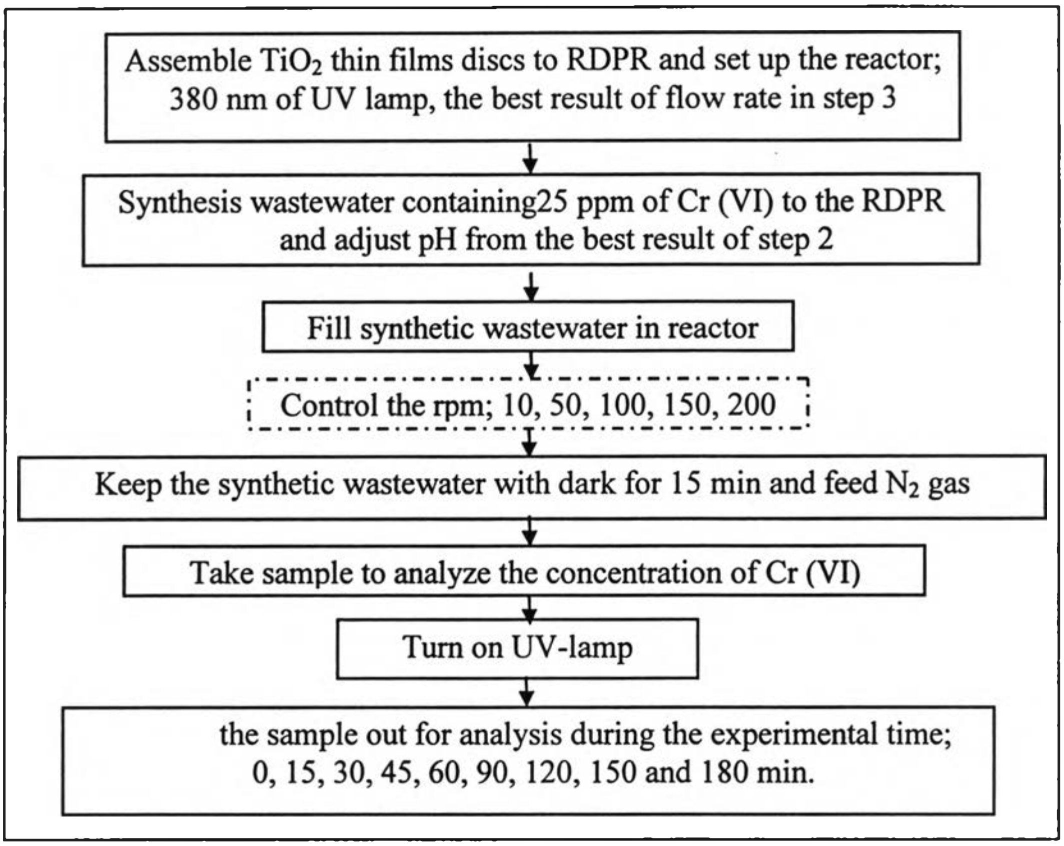

Figure 3.3 Experimental chart for the study of effect of rotating disc speed.

3.3.5 Investigation the effect of the TiO_2 coating surface area

The variations of TiO_2 coating area proceeded by vary amount of rotating discs plate in the reactor. In this part, TiO_2 coating surface areas were varied as 0.1170, 0.1754, 0.234, 0.263 and 0.2924 cm^2. The operations of this experimental part are followed from the result of previous parts. Chromium (VI) removal efficiency was investigated via sampling the solution during the experimental times. All steps are shown in Figure 3.4.

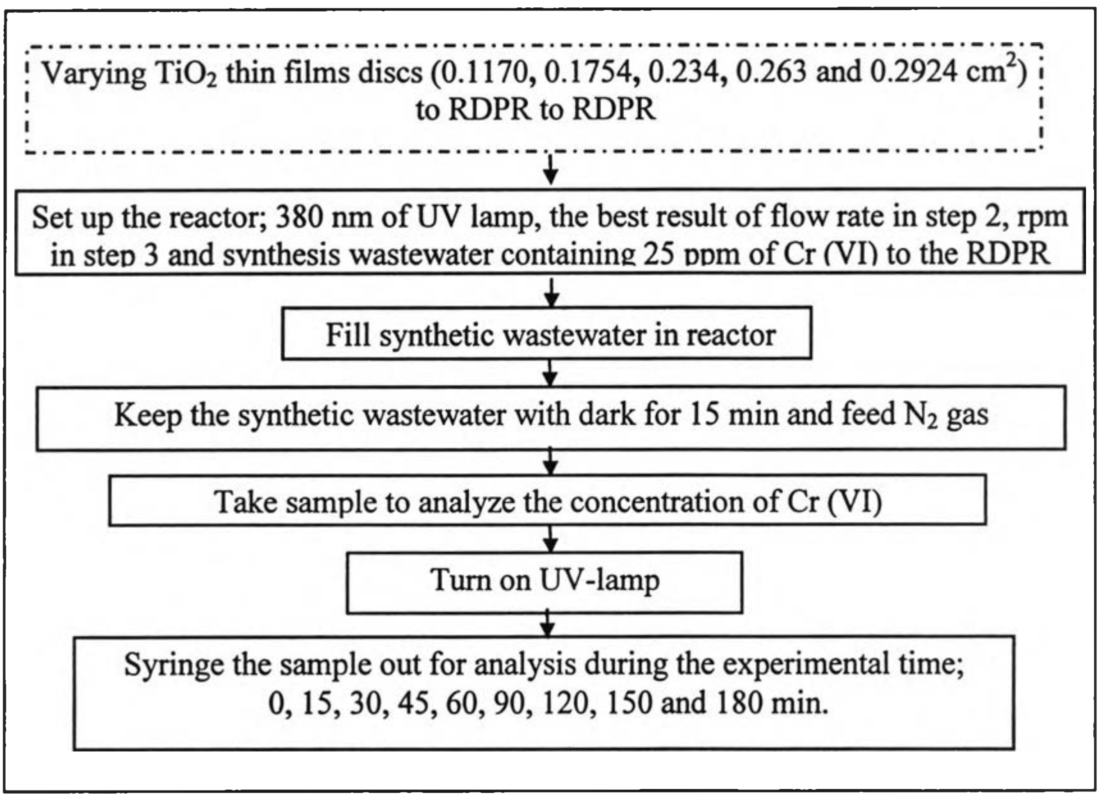

Figure 3.4 Experimental chart for the study of effect of active surface area of catalyst.

3.3.6 Investigation the effect of Initial concentration of wastewater.

The experimental was started by preparation the desired initial concentration of chromium (VI) including 25, 40, 50, 80, 100, 150, 250, 300 and 500 ppm. The operations of the reactor are proceeded follow the results of previous parts. The experimental chart is provided in Figure 3.5.

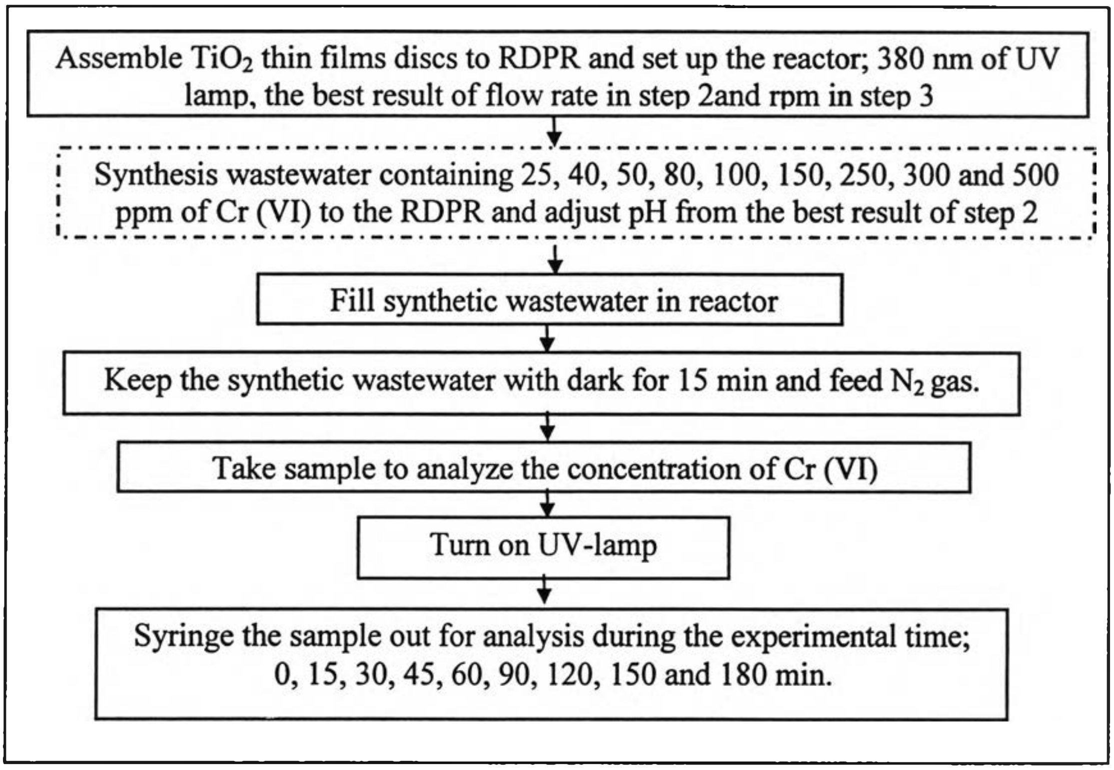

Figure 3.5 Experimental chart for the study of effect of initial concentration of wastewater.

3.3.7 Analytical method

The concentration of chromium (VI) that sampling out during experimental times was analyzed by UV/Vis spectrophotometer (JASCO V-530) at 540 nm. Diphenylcarbazide was used as the color reagent for colorimetric method to measure the concentration of chromium (VI).