

CHAPTER III

METHODOLOGY

3.1 Chemicals

The reagents used in this research were analytical grade. Nanocrystalline titanium dioxide was prepared via sol-gel hydrolysis and condensation of ethanol solutions (Merck Chemicals) of titanium(IV) butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, Aldrich chemicals). Acetylacetone was purchased from Carlo erba chemical. Analytical grade K_2CrO_4 (Merck Chemicals) together with 18 M Ω deionization water was used to prepare the Cr(VI) solutions for photoactivity test. The pH of the solution was adjusted to the desired value by adding NaOH or H_2SO_4 . Both chemicals were prepared from Merck Company, and used as received.

3.2 Preparation of TiO_2 thin films on glass plate for Cr(VI) photoreduction.

3.2.1 Preparation of TiO_2 precursor solutions

In the preparation of precursor solutions for TiO_2 films, titanium (IV) butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, 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 were mixed together and used as the acidic catalyst for the hydrolysis of titanium(IV) butoxide. The acidic solution was added dropwise 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 was continued for 1 hr. In this preparation, the resultant solutions were yellow and transparent.

3.2.2 Preparation of TiO₂ thin films

TiO₂ thin films were deposited on the substrates by sol-gel dip-coating techniques. Soda-lime glass plates (75 mm x 25 mm x 1.5 mm) were used as the substrates for the thin films. Before being coated, the substrates were cleaned with piranha solution (Wei *et al.*, 2003) at 70°C for 15 minutes and rinsed with distilled water. In order to avoid the deposition of TiO₂ thin films, the other side of these substrates was covered by adhesive tape. The substrates were dipped into the precursor solutions and withdrawn at a constant speed of 6 cm/min. Finally, the glass substrates coated with gel film were calcined at 500°C for 30 min in air using an electric furnace. The samples were put directly into a furnace, which was maintained at a given temperature.

3.2.3 Experimental procedure

The studied parameters included the variation mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetonone, calcination temperatures and coating cycles, were investigated to determine role of each parameters and their effects on thin film properties. Details of each experimental step are as follow:

Part I Investigation of the optimum ratio of titanium(IV) butoxide : ethanol : HCl : acetylacetonone.

The optimum ratio of titanium(IV) butoxide : ethanol : HCl : acetylacetonone were determined by varying the ethanol concentration as the first parameter at 10, 20, 30, 40, 50 and 60 mol/l, respectively. After the most suitable ethanol concentration was derived, HCl concentrations were varied as the second parameter at the values of 0, 0.5, 1 and 2 mol/l respectively. Finally, acetylacetonone concentrations were varied at the values of 0, 1, 2 and 3 mol/l respectively, to investigate the optimum ratio of titanium(IV) butoxide : ethanol : HCl : acetylacetonone. In this investigation, the coated substrates were calcined at 500°C for 30 min.

Part 2 Investigation the effect of calcination temperature on TiO₂ thin films preparation.

The obtained optimum ratio of titanium(IV) butoxide : ethanol : HCl : acetylacetone were employed for preparation of TiO₂ precursor solutions in this step. The temperatures of the calcinations were varied as 300, 400, 500 and 600°C, respectively.

Part 3 Investigation of the effect of coating cycles on TiO₂ thin films preparation.

The fixed mole ratio of titanium(IV) butoxide : ethanol : HCl : acetylacetone and calcinations temperature in the previous parts were used to investigate the effect of the coating cycles. The preparation process was respectively repeated from 1 to 3 and 5 for multiple coatings.

3.2.4 Characterization of TiO₂ thin films

All obtained TiO₂ thin films from each step were characterized by various techniques, as described below:

- Weighing method to measure quantities of TiO₂ attached on substrate.
- Adhesive test to determine the adherence property of the films. This method was done by adhesive tape (ASTM D3359-95a).
- Corrosive test to measure the corrosion resistant of the films. This method was done by dipping the coated substrates into HNO₃ and NaOH with concentrations of 1, 5 and 10 M, respectively.
- Scanning Electron Microscopy (SEM) for analysis of surface morphology and smoothness of thin film.
- X-ray diffraction (XRD) for analysis of crystal structures of TiO₂ thin films.

3.2.4.1 Weighing by scale

The results obtained from this method are the preliminary information for the evidence of TiO₂ attachment on substrate. The substrates before and after coating were weighed by the four-digit balance.

3.2.4.2 Adhesive test (ASTM D3359-95a)

In order to substantiate the adhesion of the films, adhesive tape was pasted over the film with the tape running in the same direction as the smaller angles. Then, the tape was smooth into place by finger and removed by pulling it off rapidly. After that, the area for removal of coating from the substrate or previous coating was inspected. The TiO₂ film should not peel off from substrate.

3.2.4.3 Corrosive test

The corrosion stability of the film was assessed under aggressive condition; 1M, 5, and 10M of HNO₃ and NaOH. A good film should not remove from the substrates after dipping it into the solution for 5 min.

3.2.4.4 Scanning Electron Microscopy (SEM)

Surface morphology and smoothness of thin film were observed by Scanning Electron Microscopy (JSM-5410 LV, Japan) with a constant accelerating voltage of 15 kV.

3.2.4.5 X-ray diffraction (XRD)

The crystal structures of TiO₂ thin films were identified by X-ray diffraction (XRD). X-ray diffraction patterns of the samples were recorded on a Philip diffractometer using Cu K α radiation and a step size of 0.02° in the range 20-70°. The step time was 1 second, adequate to obtain a good signal-to-noise ratio in the mean

reflections of the two studied TiO₂ crystalline phases, (101) anatase (2θ ~ 25.3°) and (110) rutile (2θ ~ 27.35°).

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

$$L = K\lambda / \beta \cos\theta \quad (3.1)$$

Where;

L	=	the crystallite size (nm)
K	=	the Debye-Scherrer constant (usually taken as 0.89)
λ	=	the wavelength of the X-ray radiation (Cu K α = 0.15418 nm)
β	=	the line width at half-maximum height of the broadened peak
θ	=	the half diffraction angle of the centroid of the peak (degree)

3.3 Investigation of Cr(VI) photoreduction using lab-made TiO₂ thin films prepared under various conditions.

3.3.1 Synthesis wastewater

Synthetic wastewater containing Cr(VI) with the concentration corresponding to the industrial wastewater was prepared for photocatalysis process using obtained TiO₂ thin films. Cr(VI) solution was prepared by dissolving potassium chromate (K₂CrO₄) in distilled water. The concentration of the Cr(VI) solution is 25 ppm. The pH of the solution was adjusted to 3 with diluted H₂SO₄.

3.3.2 Photochemical reactor

The photoreduction of Cr(VI) were performed in a 1.2 liter double-jacketed quartz reactor; the volume of reaction mixture was 1.1 liter. The photoreactor includes of two compartments consisting of outer and inner compartments. The outer compartment contains the treated wastewater and the chemical reagents with 2 sampling ports. The inner one is an angular vessel (30 mm. ID) for 10 watts low

pressure mercury lamp with a major emission at 254 nm. This inner well is jacketed to permit a water flow for cooling purpose. The cooling water is provided for the inner part to prevent excessive heating of the reaction. The picture of photoreactor is shown in Figure 3.1

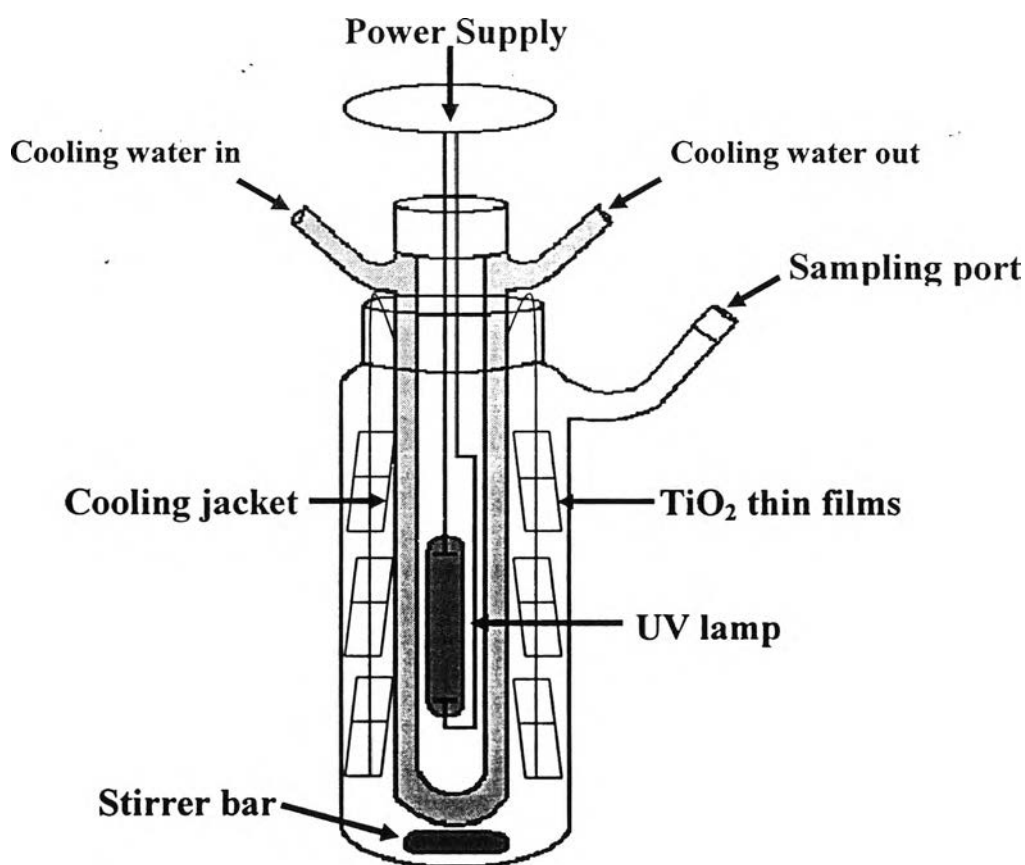


Figure 3.1 Sketch of photochemical reactor.

3.3.3 Experimental procedure

In this part, six glass plates of TiO_2 thin films derived from the selected conditions in 3.2 were used as the photocatalysts for Cr(VI) removal from synthetic industrial wastewater. The reaction was carried out in a cylindrical UV photoreactor with photocatalytic activity. TiO_2 thin films were placed in the synthetic Cr(VI) solution in the reactor. The surface of reactor was coated by aluminum foil. Prior to UV illumination, the Cr(VI) solution was equilibrated in the dark with the TiO_2 surfaces for 10 min to allow all chemicals entering the equilibrium condition. Then,

the UV lamp was turned on to illuminate the TiO₂ thin films for 180 min. At appropriate time intervals, 0, 5, 10, 15, 30, 60, 90, 120, 150 and 180 min respectively, the samples were syringed out from the photoreactor for analysis. The solutions were analyzed for the remaining concentrations of Cr(VI) by the UV-Vis spectrophotometer. During the experiments, the Cr(VI) solution was agitated thoroughly by a magnetic stirrer.

3.3.4 Analytical measurement

The remaining concentrations of Cr(VI) were analyzed by a colorimetric method. The UV-Visible spectra for Cr(VI) measurement were recorded on a Hewlett-Packard model diode array spectrometer. The analytical conditions according to *Standard Methods* (1989) were set as follows:

- Use 0.2N H₂SO₄ and a pH meter to adjust the sample to pH 1.0 ± 0.3.
- Transfer the sample to a 100-ml volumetric flask, dilute to 100 ml and mix.
- Add 2.0 ml diphenylcarbazide solution to each sample using an automatic pipet.
- Allow 5 min for full color development.
- Measure the absorbance at 540 nm, using a 1-cm absorption cell.

3.4 Experimental chart

The experimental charts are provided in Figure 3.2 and Figure 3.3

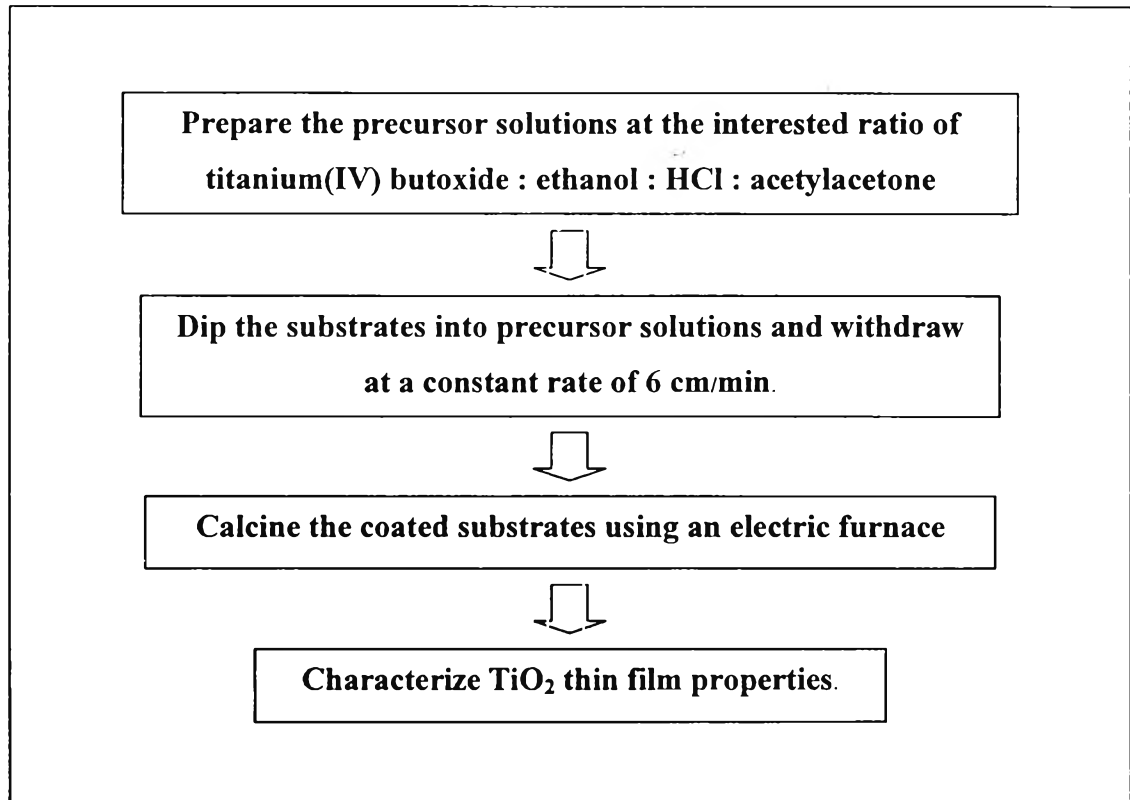


Figure 3.2 Experimental chart of TiO₂ thin film preparation.

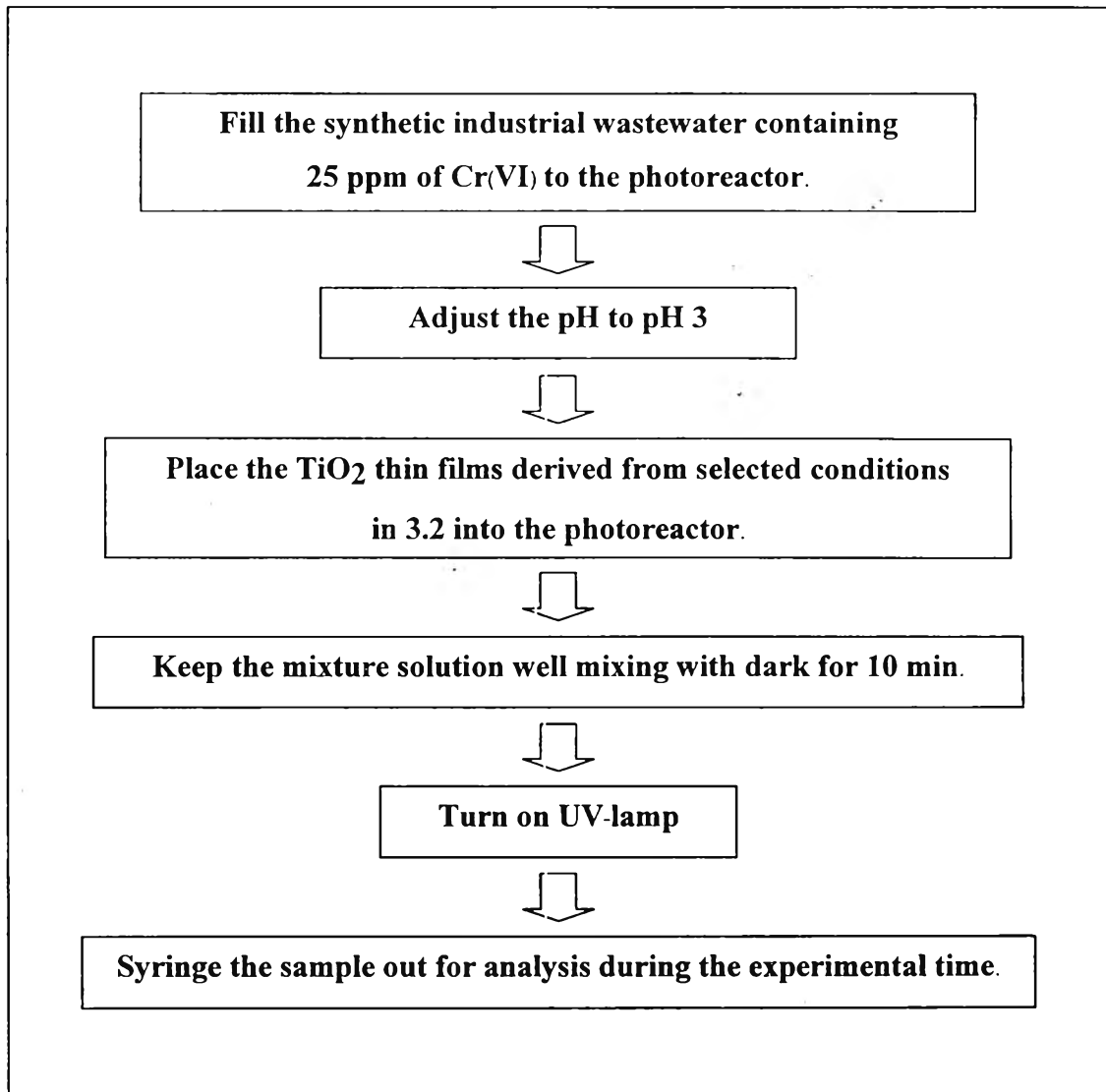


Figure 3.3 Experimental chart of photocatalytic reduction of Cr(VI).