

# CHAPTER III

## METHODOLOGY

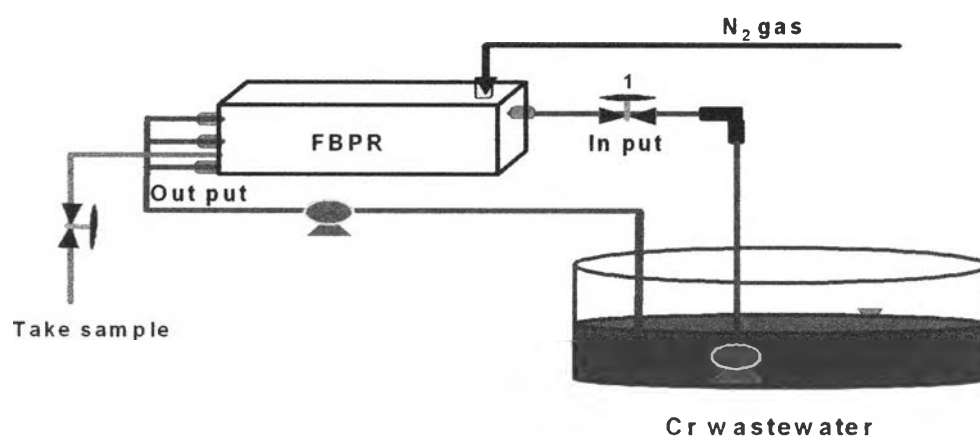


### 3.1 Designing and setting up a fixed bed photocatalytic reactor (FBPR)

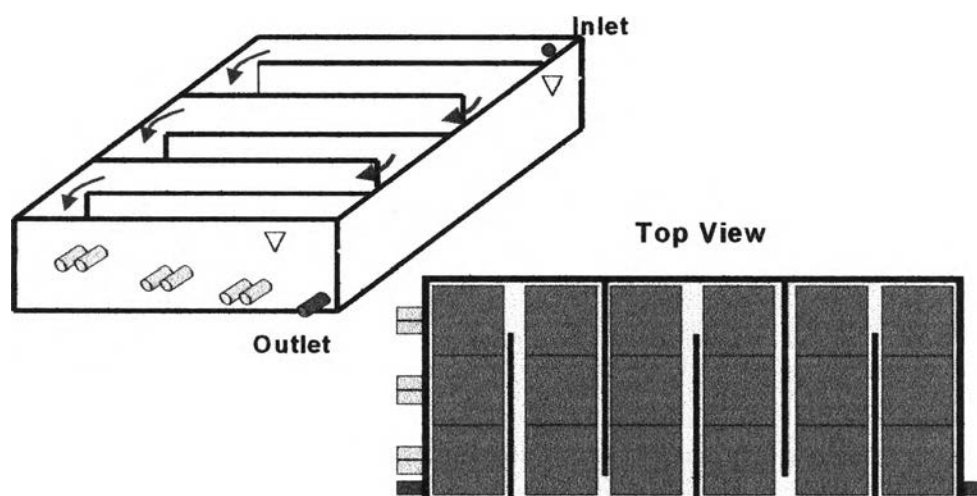
The criteria of the fixed bed photoreactor design were;

- A volume capacity of 10 liters,
- A concentration of chromium (VI) in synthetic wastewater was 25 ppm,
- A continuous mode,
- The other available equipment were;
  - a UV-lamp 60 cm long,
  - the flow rate of pump that can be adjusted was 20 - 140 ml/s.

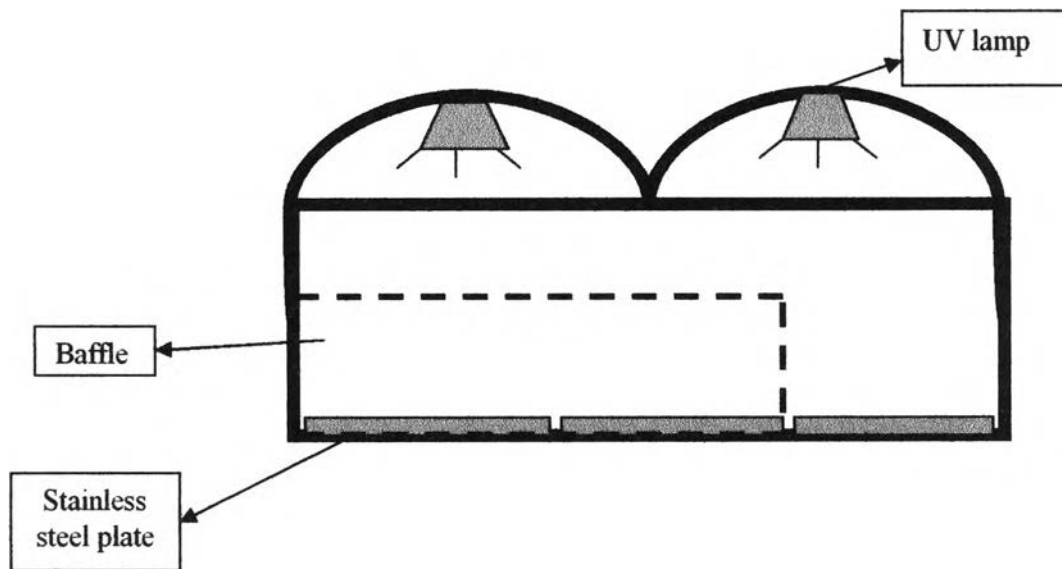
This reactor had the maximum volume capacity of about 10 liters. All baffles played a role in separating each section to give the turbulent flow and also giving much contacting time. The entire reactor was made from aluminums. Two UV lamps were used as the light sources to stimulate the photocatalytic reduction reaction. The mode of the photoreactor was set to be a continuous flow and the height of the wastewater would be held constant. The inlet flow was controlled by a pump. The height of wastewater was controlled by an outlet height. Figure 3.1 illustrated a schematic of the fixed bed photocatalytic reactor. Figure 3.2 indicated the top view of the fixed bed photocatalytic reactor. Moreover, Figure 3.3 showed the side view of the photoreactor. And Figure 3.4 demonstrated the real fixed bed photocatalytic reactor (FBPR) which was used in the photocatalytic activity tests.



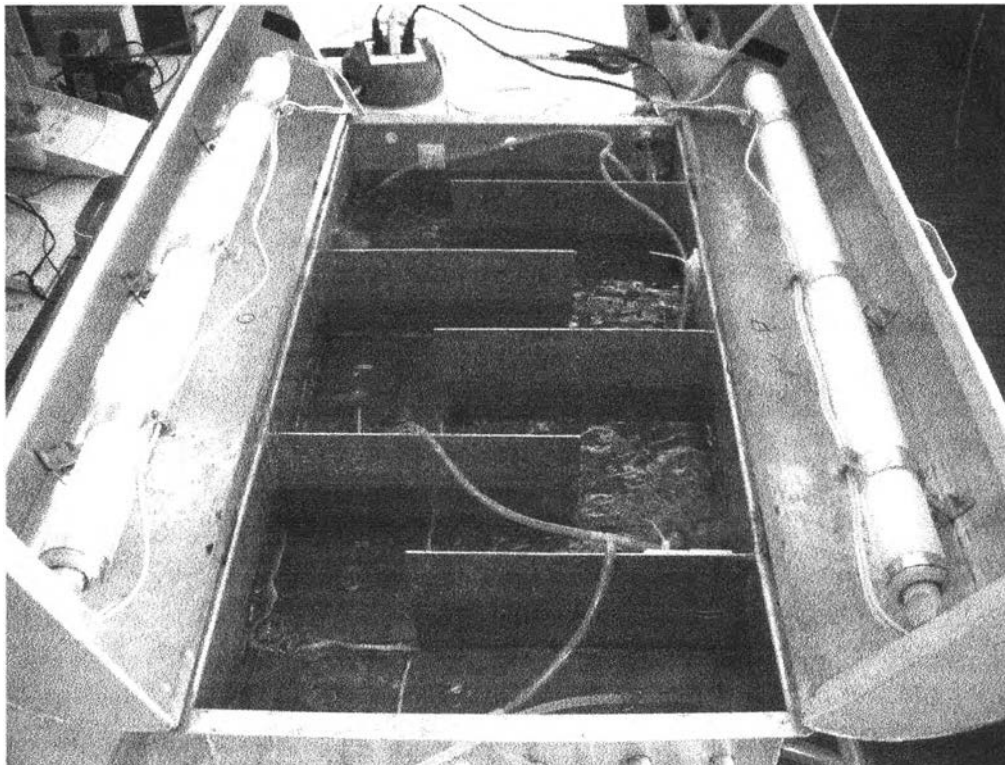
**Figure 3.1** The system of wastewater treatment with FBPR



**Figure 3.2** The top view of FBPR



**Figure 3.3 The side view of FBPR**



**Figure 3.4 The real fixed bed photocatalytic reactor (FBPR)**

### **3.2 Preparation of the TiO<sub>2</sub> thin films coated on stainless steel plates by the sol-gel dip-coating method.**

#### **3.2.1 Chemicals**

All chemicals in this study were analytical grade. The TiO<sub>2</sub> sol was prepared from titanium (IV) butoxide (Ti (OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, Aldrich Chemicals) used as a precursor and absolute ethanol supplied by Merck Chemicals used as a solvent. Acetyl acetone was obtained from Carlo Erba Chemicals used as an additive. A stock solution of hexavalent chromium was prepared by dissolving analytical grade K<sub>2</sub>CrO<sub>4</sub> (Merck Chemicals) in tap water, with H<sub>2</sub>SO<sub>4</sub> and NaOH (Merck Chemicals) used for pH adjustment.

#### **3.2.2 Preparation of stainless steel plates**

Stainless steel plates (type 316L) were cleaned by 2% HF for 5 minutes to remove the oily plate surface area. Then they were dipped in a mixed solution of water and anhydrous ethanol, and dried at room temperature (Liqiang et al., 2003). Before starting the dipping process, every plate would be weighed accurately.

#### **3.2.3 Preparation of TiO<sub>2</sub> thin films (Pongpom, 2004)**

The TiO<sub>2</sub> precursor was titanium (IV) butoxide (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, Aldrich chemicals). The solvent was ethanol. The colloidal solution of TiO<sub>2</sub> was prepared by the sol-gel method. Not only ethanol representing as a solvent, but also acetyl acetone would be added to remain as an additive which helps to increase the surface area and prevent the cracking of the layers. After that, all of the chemicals would be mixed for 1 hour. The condition of the solution was in the ratio of titanium (IV) butoxide: ethanol: HCl: acetyl acetone, i.e., 1: 30: 0.5: 1, respectively.

After mixing all of them, the dip coating process would be done within the rate of dipping at 1 mm/s. The coated plates needed time to be dried at room temperature and calcined at different temperatures for a half hour in an electric furnace.

Pongpom, S., 2004 studied the ratio of these conditions by testing with a small batch scale. She found that the ratio of titanium (IV) butoxide: ethanol: HCl: acetyl acetone, i.e., 1: 30: 0.5: 1, respectively is the best condition. The surface area which had taken from the SEM morphology was the smoothest. The best condition from her study was used to prepare nanocrystalline thin layers  $\text{TiO}_2$  which were studied in the next experimental issue.

### **3.2.4 Characterization of $\text{TiO}_2$ thin films**

The coated  $\text{TiO}_2$  thin films were characterized by using different techniques:

- The adhesive test by adhesive tape.
- The corrosive test by dipping the  $\text{TiO}_2$  thin films coated on substrates into  $\text{HNO}_3$  and NaOH within the concentrations of 1, 5 and 10 M, respectively.
- The surface morphology of  $\text{TiO}_2$  thin films was observed by a scanning electron microscopy (SEM).
- The crystalline formations of  $\text{TiO}_2$  thin films were identified by the X-ray diffraction (XRD).
- The thickness of  $\text{TiO}_2$  thin films was discerned by the field emission scanning electron microscopy (FE-SEM).

#### **3.2.4.1 Adhesive test (ASTM D 3359-95a)**

This standard adhesive test method was used to examine the adhesion of  $\text{TiO}_2$  thin films obtained on stainless steel plates. At the beginning, the adhesive tape was got stuck over the nanocrystalline films with the same tape running direction. Then the tape would be smooth by rubbing from the fingers, and removed by peeling it off rapidly. Finally, the

surface area of removal was checked comparable to the previous coating medium. The TiO<sub>2</sub> thin films could be still on stainless steel plates.

#### **3.2.4.2 Corrosive test**

The corrosion stability tests of the TiO<sub>2</sub> thin films obtained on stainless steel plates were evaluated via the aggressive conditions: 1, 5 and 10 M of HNO<sub>3</sub> and NaOH. The robust TiO<sub>2</sub> thin layers should not be removed from the mediums after immersing them into the solutions for 30 minutes.

#### **3.2.4.3 Scanning Electron Microscopy (SEM)**

The surface morphology and smoothness of TiO<sub>2</sub> thin layers were discerned by a scanning electron microscopy (SEM, JEOL JSM-5800 LV) with applied a constant acceleration voltage of 15 kV.

#### **3.2.4.4 X-ray diffraction (XRD)**

The crystalline structures of TiO<sub>2</sub> thin films were verified by an x-ray diffractometer. The x-ray diffraction patterns of TiO<sub>2</sub> anatase structure were recorded on a Philip diffractometer using Cu K  $\alpha$  radiation and a step size of 0.02° in the range of 2 $\theta$  at 20-70°. The step time was 1 second which was adequate for a good obtainable signal-to-noise ratio in the reflections of two comparable studied TiO<sub>2</sub> nanocrystalline phases, i.e. anatase phase (101) (at 2 $\theta$   $\approx$  25.3°) and rutile phase (110) (at 2 $\theta$   $\approx$  27.35°).

X-ray diffraction is a widely technique used to resolve the dissimilar structures and phases in some specimen, dependable upon their characteristics diffraction behavior under x-ray illumination of an admitted wavelength. For instance, different phases will give the different diffractions at the specific incident angles. XRD patterns can also be calculated a relatively quantitative analysis by measuring the intensity of the diffraction lines. In order to comparable the different samples at the same phase, the higher intensity would provide the higher quantity.

The x-ray diffraction patterns were estimated the crystalline size by measuring the line broadening in the Debye-Scherrer equation (Horikoshi et al., 2001; Roquerol et al., 1998):

$$L = K\lambda / \beta \cos \theta$$

Where,

L	=	the crystalline size (nm)
K	=	the Debye-Scherrer constant (usually taken as 0.89)
$\lambda$	=	the wavelength of the x-ray radiation (Cu K $\alpha$ = 0.15418)
$\beta$	=	the line width at half-maximum height of the broadened peak
$\theta$	=	the half diffraction angle of the centroid of the peak (degree)

#### 3.2.4.5 Field-Emission Scanning Electron Microscopy (FE-SEM)

The thickness was evaluated by a field emission scanning electron microscopy (FE-SEM, JEOL model JSM-634 OF) with the acceleration voltage of 5.0 kV.

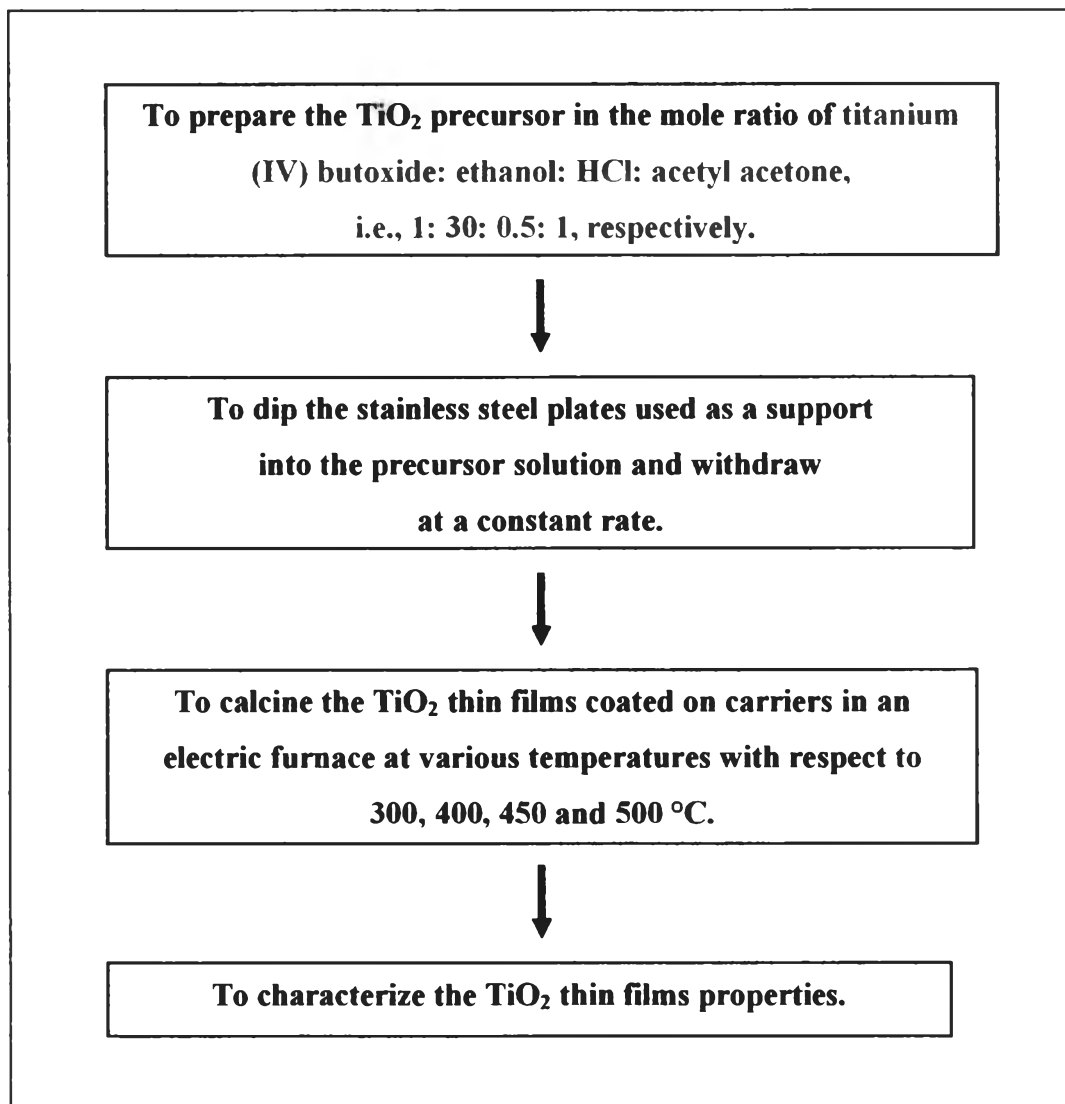
The principle of this operation is a field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage.

#### 3.2.4.6 Experimental conditions

The studied parameters which affected the synthesis conditions of TiO<sub>2</sub> thin film were;

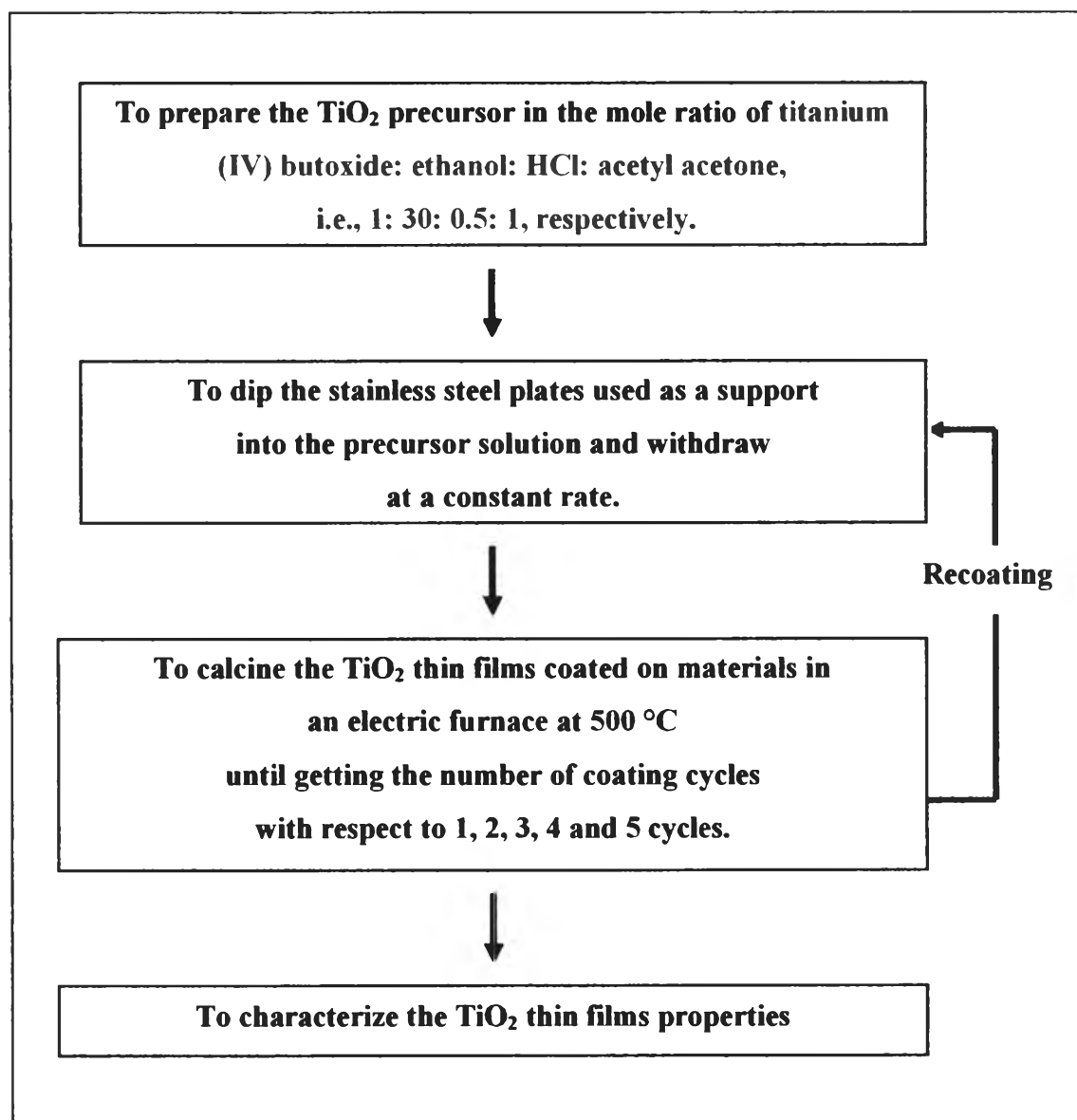
- The calcination temperatures were varied at 300, 400, 450, and 500 °C.
- The number of coating cycles which were 1, 2, 3, 4 and 5 cycles.

Figure 3.5 and Figure 3.6 provided the experimental charts of preparing the thin films  $\text{TiO}_2$  using in these tests.



**Figure 3.5 The experimental chart for preparing the  $\text{TiO}_2$  thin films coated on stainless steel plates at different temperatures**





**Figure 3.6** The experimental chart for preparing the TiO<sub>2</sub> thin films coated on stainless steel plates at different coating cycles

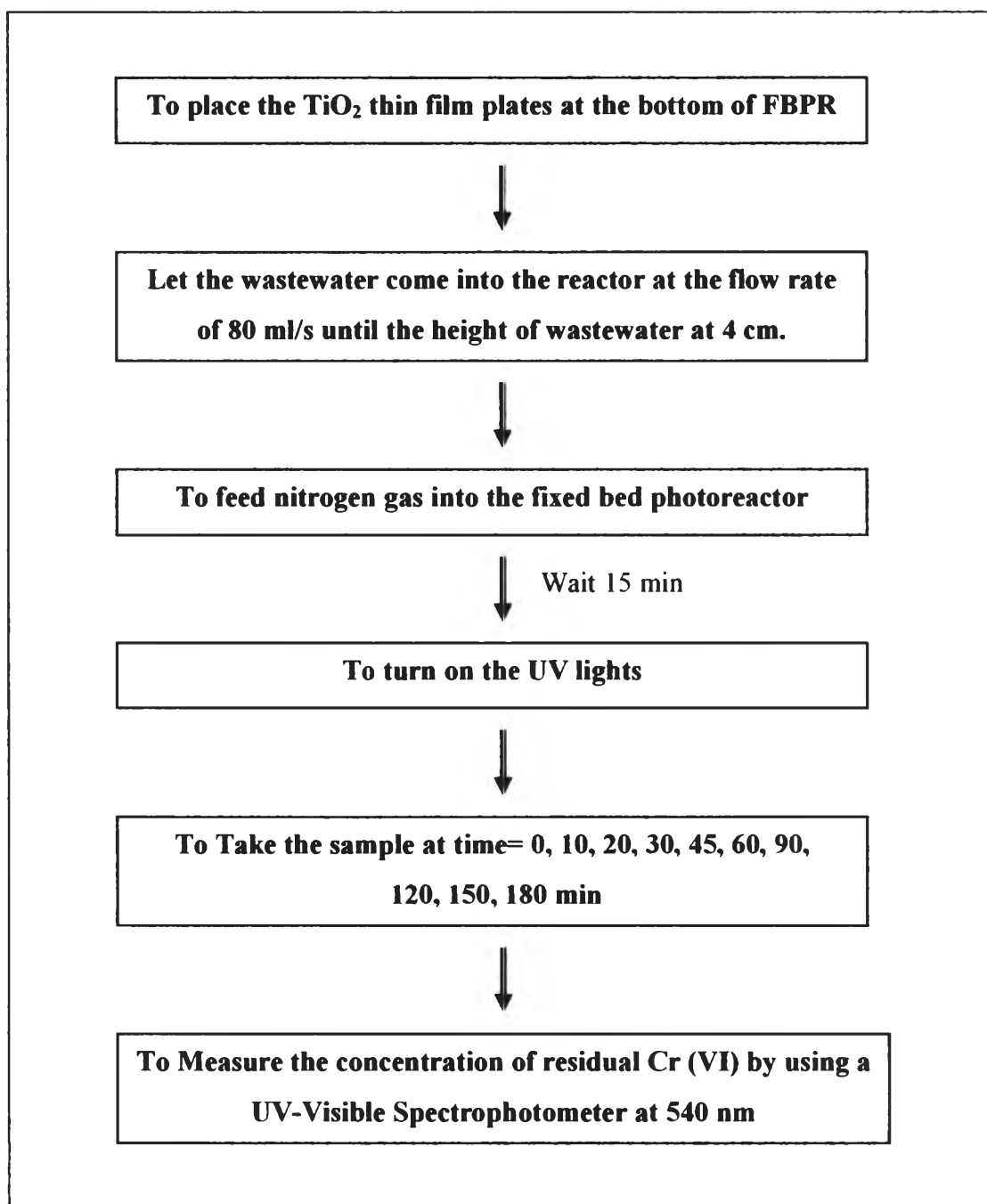
### **3.3 Finding the optimum synthesis TiO<sub>2</sub> thin film conditions using the designed fixed bed photocatalytic reactor (FBPR)**

#### **3.3.1 The syntheses of chromium (VI) wastewater**

Synthetic chromium (IV) wastewater was prepared by dissolving potassium chromate (K<sub>2</sub>CrO<sub>4</sub>) in tap water. The concentration of the chromium (VI) is 25 ppm due to the concentration corresponding to the industrial wastewater. The pH of the resultant solution would be adjusted to 3 by H<sub>2</sub>SO<sub>4</sub>.

#### **3.3.2 The experiment of the photocatalytic activities using the designed fixed bed photoreactor**

The coating TiO<sub>2</sub> plates were placed at the bottom of the reactor. Then the wastewater would be let into the reactor, and 15 minutes would be allotted for complete adsorption on the surface before the illumination (Kajivichyanukul and Watcharenwong, 2000), while nitrogen gas was fed into each section of the reactor. After that, two UV lights were turned on and the sample was taken at time equal to 0, 10, 20, 30, 45, 60, 90, 120, 150 and 180 minutes. Then the remained chromium concentration in the wastewater was measured by using a UV-Visible spectrophotometer (Jasco V-530). Additionally, the chart of this procedure was shown in Figure 3.7.



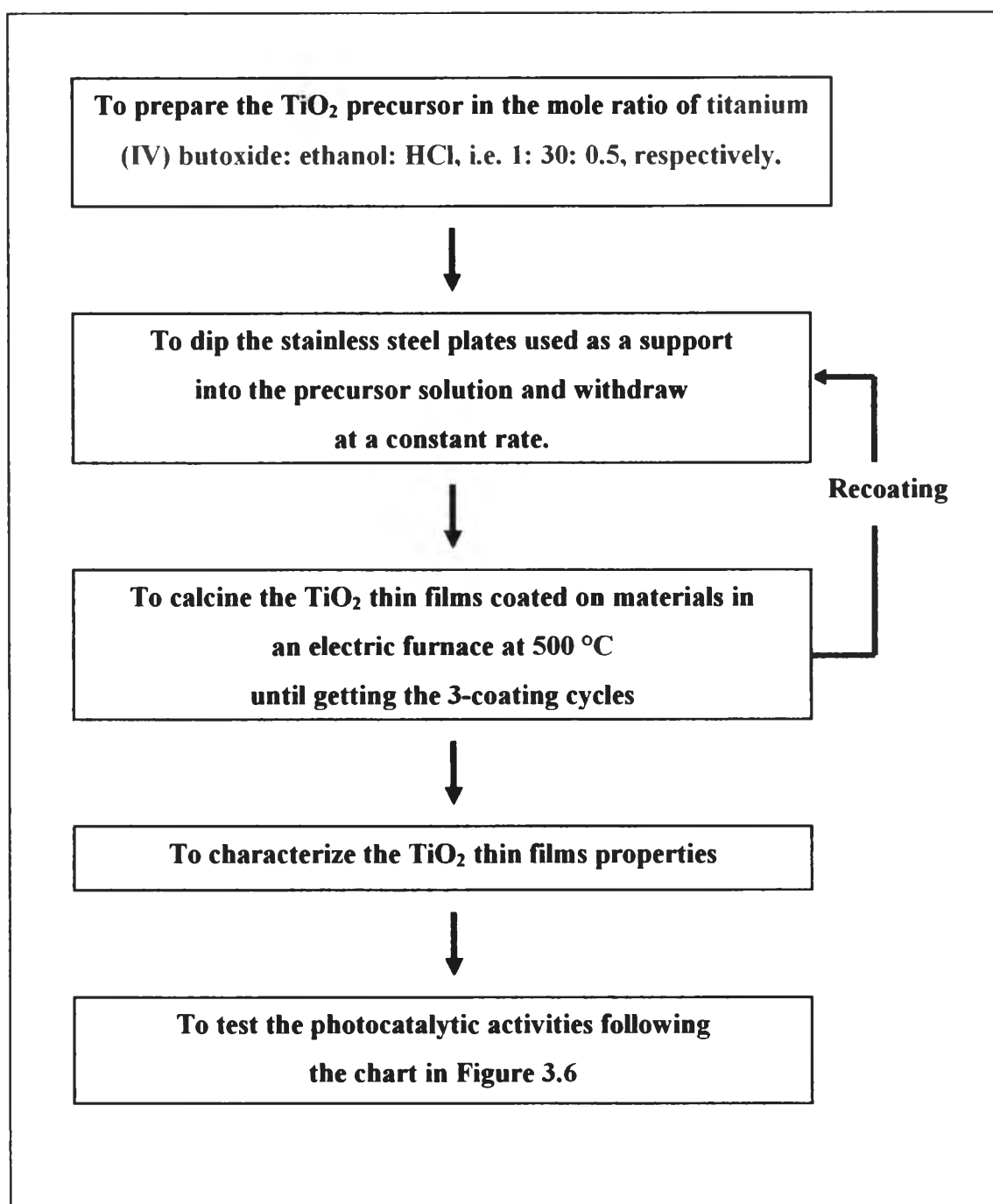
**Figure 3.7 The chart of the experiment of the photocatalytic activities using the fixed bed photocatalytic reactor (FBPR)**

Experimental conditions that were studied as follows:

***3.3.2.1 The test of photocatalysis of chromium (VI) using TiO<sub>2</sub> thin films coated on stainless steel plates with and without acetyl acetone.***

In this test, the photocatalytic activities were investigated the efficiency of the thin film TiO<sub>2</sub> prepared from the different TiO<sub>2</sub> sol with and without adding acetyl acetone. All parameters which were fixed in this test were the wavelength at 380 nm, the surface area, the initial concentration of Cr (VI) and; of course, all operating parameters were stand at the same conditions in all the experiments.

While, the independent parameters were the coating TiO<sub>2</sub> prepared with and without acetyl acetone. It is of value to note that acetyl acetone helped to increase the size of pores onto the surface morphology. However, the dependent parameters were the efficiency of the photocatalytic reduction depending on the case of the coating thin film TiO<sub>2</sub> due to their characteristics. Figure 3.8 showed the experimental chart of this test.



**Figure 3.8** The chart of the test of photocatalysis of chromium (VI) using TiO<sub>2</sub> thin films coated on stainless steel plates with and without acetyl acetone

### ***3.3.2.2 The test of photocatalysis of chromium (VI) using TiO<sub>2</sub> thin films with different calcination temperatures (300, 400, 450 and 500 °C),***

In order to this experiment, the heat-treated temperatures were varied from 300 °C to 500 °C due to the amount of the anatase structure. And the best condition from the previous part was taken to use in this part; obviously, the TiO<sub>2</sub> sol with acetyl acetone was readily used. This mole ratio was used is titanium (IV) butoxide: ethanol: HCl: acetyl acetone, i.e., 1: 30: 0.5: 1, respectively. The chart of this experiment was indicated in Figure 3.5. However, the varied parameters were the thin film TiO<sub>2</sub> coated on stainless steel plates calcined at different heat treatment with respect to 300, 400, 450 and 500 °C. And also the dependent parameters were the efficiency of the photocatalytic reduction. Besides, the fixed parameters were the wavelength at 380 nm, the surface area, the initial concentration of Cr (VI) and all operating parameters were still the same conditions in all the experiments.

### ***3.3.2.3 The test of photocatalysis of chromium (VI) using TiO<sub>2</sub> thin films with various coating cycles (1, 2, 3, 4 and 5 cycles)***

In this test, the stainless steel plates were coated corresponding to the best conditions from two previous issues, it was consist of the TiO<sub>2</sub> sol with adding acetyl acetone and then all coating plates were calcined at 500 °C. At the temperature over 500 °C, the stainless steel plate would become FeO (Ferrous oxide) placed on the surface. Moreover, the independent parameters were the number of dip coating cycles (1, 2, 3, 4 and 5 cycles) due to their thickness. On the one side, the dependent parameters were the efficiency of the photocatalysis. Moreover, the fixed parameters were the wavelength at 380 nm, the surface area, the initial concentration of Cr (VI) and all operating parameters were still the same conditions in all the experiments. Figure 3.6 represented the chart of this experiment.

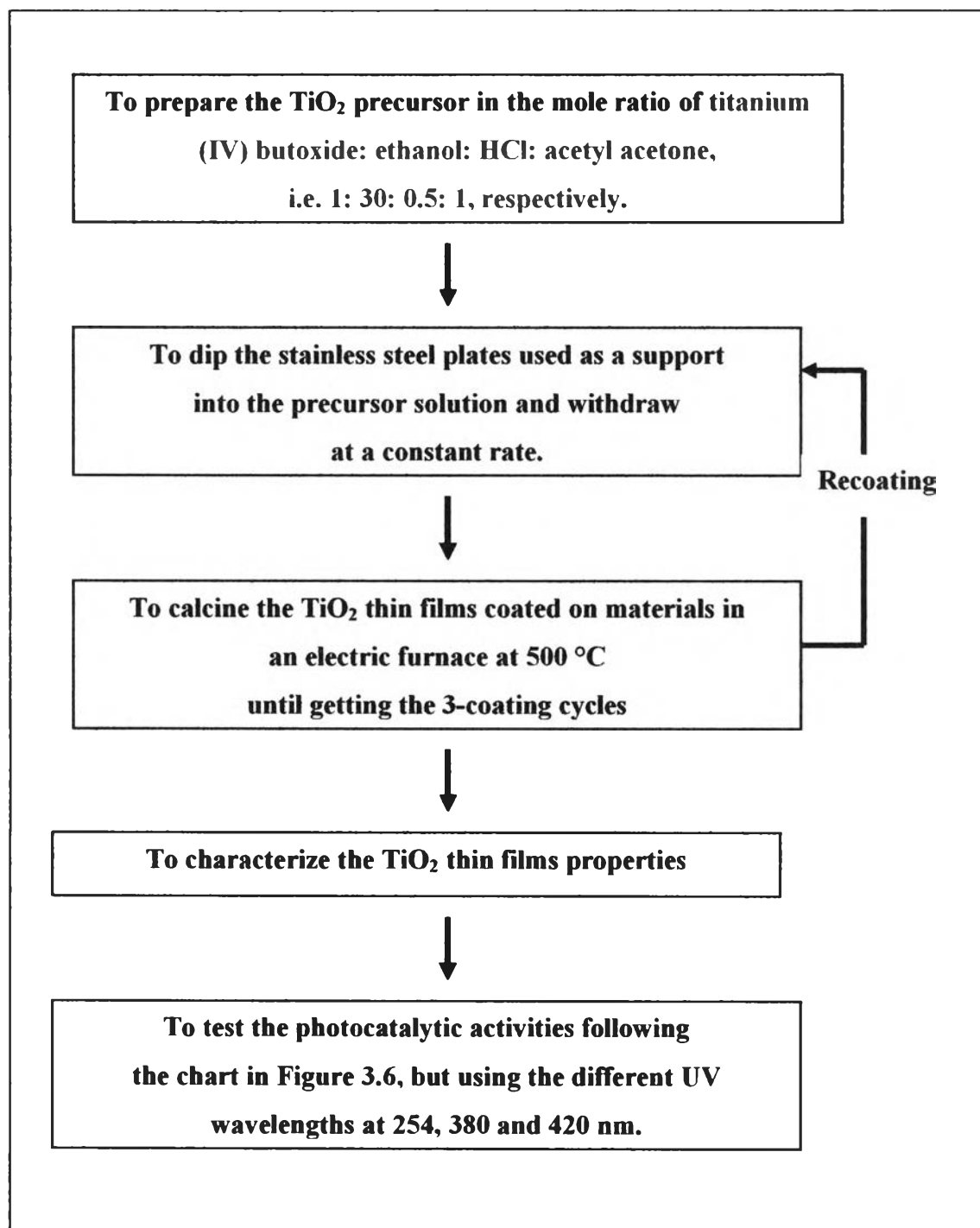
### **3.3.2.4 The test of photocatalysis of chromium (VI) using TiO<sub>2</sub> thin films with ultraviolet light wavelengths at 254, 380 and 420 nm.**

In this experiment, the different wavelengths were determined due to their energy. As known that the UV wavelength at 254 nm, which is in the range of UVC, gives the energy nearly the band gap energy of TiO<sub>2</sub>. Meanwhile, the UV wavelength at 380 nm, which is in the range of UVA, gives the energy equals to the band gap energy of TiO<sub>2</sub>. However, the UV wavelength at 420 nm, which is in the range of visible light, gives the less energy than the band gap energy. The independent parameters were the different wavelengths of UV and visible light regions with respect to 254, 380 and 420 nm. Accordingly, the dependent parameters were the efficiency of photocatalysis in which all illuminations. The fixed parameters were the thin film TiO<sub>2</sub> derived from the best conditions from the previous study, which were the thin film TiO<sub>2</sub> with adding acetyl acetone, then calcining at 500 °C for 30 minutes with 3-coating cycles, the surface area, the initial concentration of Cr (VI) and all operating parameters were still the same conditions in all the experiments. Figure 3.9 manifested the chart of this experiment.

### **3.3.3 Colorimetric Method (standard method, 1998)**

This method was used to find the remained chromium (VI) in the synthetic wastewater by following these steps;

- Take the sample 5 ml,
- Add H<sub>3</sub>PO<sub>4</sub> 0.25 ml,
- Adjust pH to 1 by 0.2 N H<sub>2</sub>SO<sub>4</sub> ,
- Dilute with distilled water into a volumetric flask 100 ml
- Add diphenylcarbazide 2 ml into the flask,
- Wait 5 minutes to get a complete color,
- Measure the absorbance by a UV-Visible spectrophotometer



**Figure 3.9** The chart of the test of photocatalysis of chromium (VI) using TiO<sub>2</sub> thin films with ultraviolet light wavelengths at 254, 380 and 420 nm