CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Chemicals

Reagents used in this research were analytical grade. Nanocrystalline titanium dioxide is prepwered via sol-gel hydrolysis and condensation of isopropanol (Merck) and titanium tetraisopropoxide (TTiP) (Aldrich chemicals). Analytical grade 2-chlorophenol (Merck) together with 18 MΩ deionization water was used to prepare the 2-CP solutions for the photoactivity test. Both chemicals were purchased from Merck Company, and used as received.

3.1.2 Photochemical reactor

A 1-litre photochemical batch reactor consists of outer and inner compartments. The inner part was an angular quartz vessel for a 254 nm low pressure mercury lamp of 10 watts. This inner well was jacketed to permit a water flow for the cooling purpose. The outer quartz compartment was the solution receiving well with two sampling ports. This system was well agitated by a stirrer bar. The picture of photochemical reactor is provided in Figure 3.1

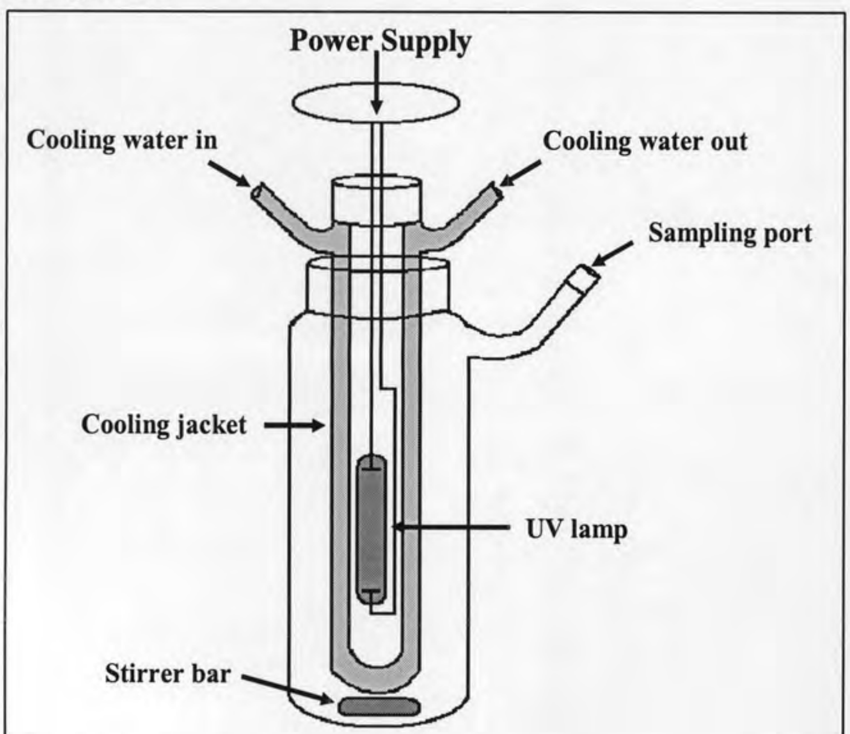

Figure 3.1 Photochemical reactor

The experiment of this research can be divided into 3 parts.

- Part I: Synthesis of TiO_2/AC composite.

  Different molar ratios of TiO_2/AC composite that were synthesized include (TiO_2: AC = 1:0, 1:10, 1:30, 1:50, 1:70, 1:100 and 0:1 and TiO_2/O_2 = 1:0) In the following experiment, the TiO_2/AC with the optimum molar ratio from the previous part was used to investigated the optimum calcination temperature in ranges of 500°C, 800°C, 1100°C, and 1300°C.

- Part II: Characterization of synthesized TiO_2/AC composite material.
- Part III: Treating of 2-CP using synthesized TiO_2/AC composite.

Part I: Synthesized of TiO_2/AC composite.

In the preparation of precursor solutions for TiO_2/AC composite, titanium (IV) tretra-isopropoxide (TTiP,$Ti[OCH(CH_3)_2]_4$, Aldrich chemicals) were used as the source material for Ti. TTiP was first diluted with isoproproxide, which were used as a solvent. DI water and activated carbon were mixed together; DI used for hydrolysis of TTiP, and then added to the TTiP-isopropanol solution. Then let the solution dry at room temperature and gel was formed as shown in Figure3.2

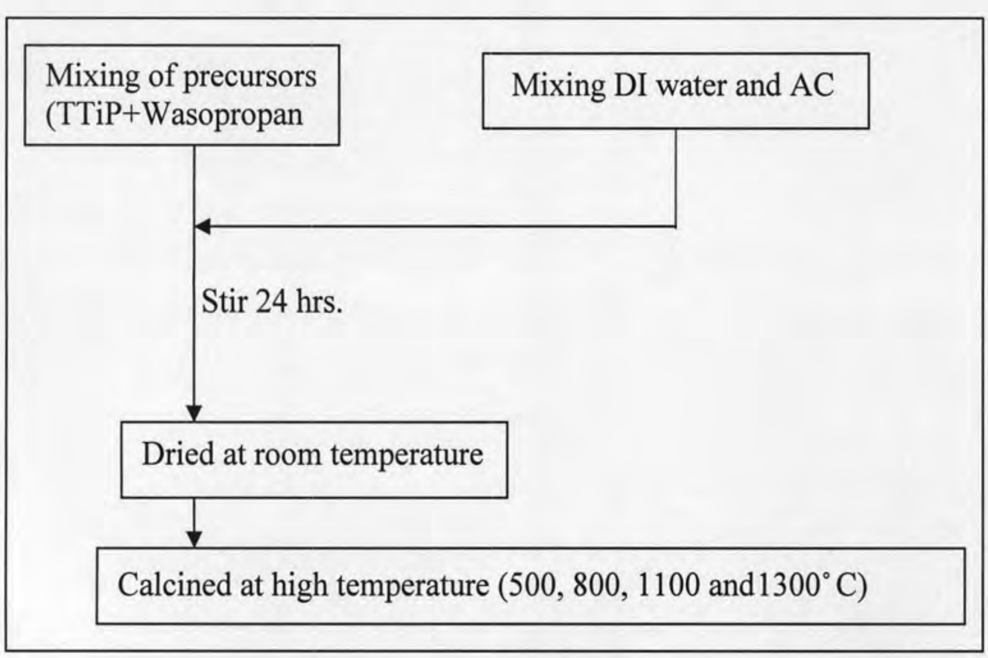

Figure 3.2 Preparation procedures for TiO_2/AC composite.

To determine the optimum condition in preparation of TiO_2/AC composite, the parameters affecting TiO_2/AC composite properties, which were the variation molar ratios of TTiP: isopropanol: DI: AC and calcinations temperature were investigated.

- Investigation of the effect of molar ratios of TiO_2/AC composite preparation.

The optimum ratio of TTiP: AC was determined by varying amount of AC at TiO_2: AC = 1:0, 1:10, 1:30, 1:50, 1:70, 1:100 and 0:1, respectively.

After mixing of all chemicals, the gel was calcined at 500° C for 30 min. In this experiment, the synthesized of TiO_2/AC composite without AC were also performed with the same experimental conditions as the controlled material.

- Investigation of the effect of different type of TiO_2 composite preparation.

The molar ratio of TiO_2/O_2 was 1:0 and synthesized was performed with the same experimental conditions.

- Investigation of the effect of calcination temperature on TiO_2/AC composite preparation.

The obtained optimum ratios of TiO_2/AC were used for preparation of TiO_2 precursor solutions. The temperature of the calcination were varied as 500°C, 800°C, 1100 °C and1300° C, respectively. In this experiment set, the syntheses of TiO_2/AC composite without AC were also performed with the same calcination temperature as the control experiment.

Part II: Characterization synthesized TiO_2/AC composite.

The prepared TiO_2/AC composite were characterized by using different techniques. The investigated characteristics of TiO_2/AC composite can be described as following:

2.1) Surface morphology of TiO_2/AC composite.

To obtain surface morphology of synthesized TiO_2/AC composite, the composite were examined by scanning electron microscopy (SEM). The differences in morphology of composite in each condition were identified.

2.2) Crystal structure of TiO_2/AC composite.

To obtain the ratio of anatase to rutile of TiO_2/AC composite obtaining from each condition, The TiO_2/AC composite were characterized by x-ray diffraction (XRD). The graphical plots of anatase to rutile ratio were illustrated as a function of studied parameters, which were molar ratios and calcinations temperatures.

Part III: Treating of 2-chlorophenol by using synthesized TiO_2/AC composite.

Wastewater containing 2-CP was synthesized corresponding to the concentrations that might be found in industrial wastewater. 2-CP solution were prepared by dissolve 2-CP (C_6H_5OCl) and distilled water.

In this part, TiO_2/AC composite derived from selected conditions in Part I were used as the photocatalysts for 2-CP removal from synthetic industrial wastewater. The reaction was carried out in a cylindrical UV photoreactor with photocatalytic activity.

- **Removal of 2-CP by adsorption process**

The studied concentration of 2-CP solution was 100, 150, 200, 250 and 300 mg/L for adsorption process. TiO_2/AC composite were placed in the synthetic 2-CP solution in the reactor with its surface coated by aluminum foil. Prior to UV illumination, 2-CP solution were equilibrating in the dark with TiO_2/AC composite surface for 90 min. to allow for the adsorption process. Then, the sample after adsorption were syringed out to analyze the concentration of 2-CP with a UV-Vis spectrophotometer. During the experiments the suspension of TiO_2/AC composite in the 2-CP solution were agitated thoroughly by a magnetic stirrer (Figure 3.3). The residual 2-CP concentrations in the aqueous solution were plotted as a function of time. The observed adsorption isotherms from each experimental condition were calculated.

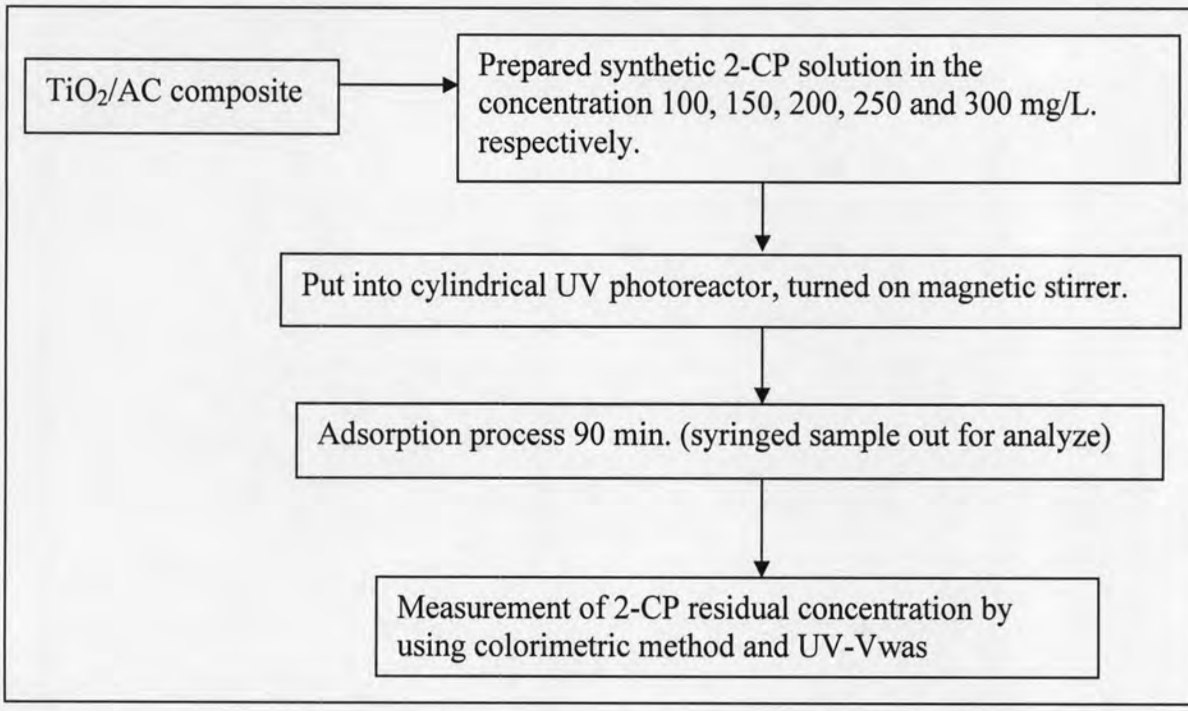

Figure 3.3 Schematic diagram for treating of 2-CP by adsorption process.

- **Removal of 2-CP by photocatalysis process**

The concentration of 2-CP solution was 300 mg/L for irradiation process. TiO_2/AC composite were placed in the synthetic 2-CP solution in the reactor with its surface coated by aluminum foil. Prior to UV illumination, 2-CP solution were equilibrating in the dark with TiO_2/AC composite surface for 90 min to allow for the adsorption process. Then, a UV lamp was turned on to illuminate the TiO_2/AC composite for 180 min. The sample after adsorption and illumination was syringed out to analyzed the concentration of 2-CP with a UV-Vis spectrophotometer. During the experiments, the suspensions of TiO_2/AC composite in the 2-CP solution were agitated thoroughly by a magnetic stirrer (Figure 3.4). The residual 2-CP concentrations in the aqueous solution were plotted as a function of time. The observed kinetic constant, k_{obs}, from each experimental condition were calculated.

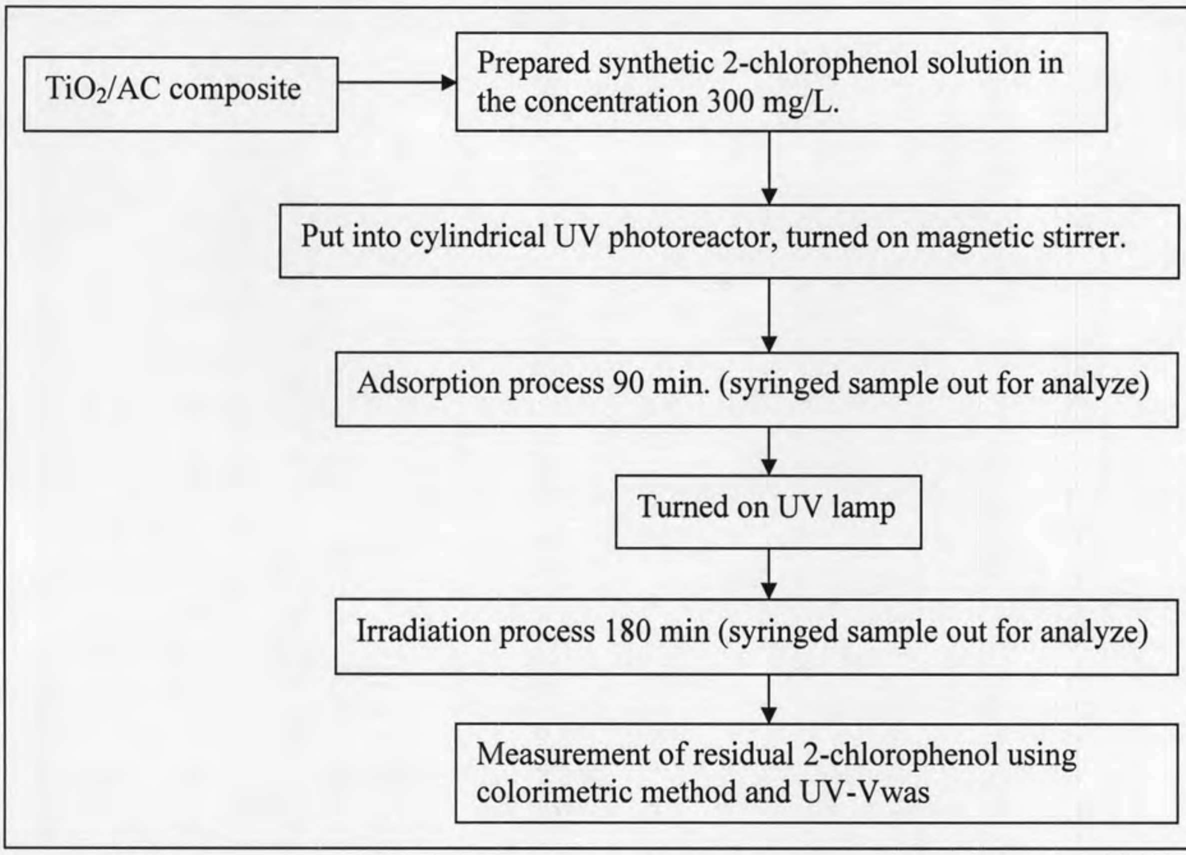

Figure 3.4 Schematic diagram for treating of 2-CP by adsorption and irradiation process.

Experimental works in this section were divided as following:

3.1) Effect of molar ratios of TiO_2 to AC on adsorption and photocatalytic activity of each ratios of TiO_2/AC composite.

In this part, TiO_2/AC composite were obtained from different molar ratios of TiO_2 to AC with 500° C calcinations temperature were used to treat 2-CP in adsorption and photocatalysis process. All types of TiO_2/AC composite were experimented as follow:

Table 3.1 Molar ratios of TiO_2: AC used in TiO_2/AC synthesis

Type of TiO_2	The molar ratio of TiO_2/AC
TiO_2/AC/N_2	1:0, 1:10, 1:33, 1:50, 1:70, 1:100, and 0:1
TiO_2/O_2	1:0
TiO_2/P-25	1:0 (commercial TiO_2)

Results from this section were reported as the plot of the observed adsorption isotherm, photocatalytic kinetic constant, k_{obs} as a function of 500 °C calcination temperature of each molar ratios of TiO_2/AC composite.

The optimum molar ratio of TiO_2/AC composite from this part was used to investigate the effect of calcination temperatures on adsorption and photocatalytic activity in next part.

3.2) Effect of calcinations temperatures on adsorption and photocatalytic activity of selected molar ratios of TiO_2/AC composite.

In this part, adsorption and photocatalytic oxidation efficiency in 2-CP removal using each molar ratios of TiO_2/AC composite in various calcination temperatures were studied. The experiments were divided as following:

Table 3.2 Investigated calcination temperatures used in TiO_2/AC synthesis

Molar ratios of TiO_2/AC composite	Calcination temperatures in synthesized TiO_2/AC composite
1:0	500°C, 800°C, 1100°C and1300°C
A*	500°C, 800°C, 1100°C and1300°C
0:1	500°C, 800°C, 1100°C and1300°C

A*: the optimum molar ratios of TiO_2/AC from 3.1

Results from this section were reported as the plot of the observed adsorption isotherm, photocatalytic kinetic constant, k_{obs} as a function of calcinations temperatures of selected molar ratios of TiO_2/AC composite.

3.3) Comparison of properties and photocatalytic ability of synthesized TiO_2/AC composite.

To compare the ability in hazardous waste removal using synthesized TiO_2/AC composite, the highest efficiency in photocatalytic removal of 2-CP using TiO_2/AC composite were compared.

In addition, other properties of three molar ratios of synthesized TiO_2/AC composite in the best condition were compared as well. The properties comparisons were described as follow:

Table 3.3 Properties analysis of selected molar ratio of TiO_2/AC composite

Three molar ratios of synthesized TiO_2/AC composite : 1:0, A*, 0:1	
Crystal properties: - Crystal structure - Surface morphology structure	**Photocatalytic properties:** - 2-CP removal efficiency - Adsorption Isotherm - Photokinetic constant, k_{obs}

3.4) Determination of mineralization of 2-CP removal in photocatalysis process.

1. Measure the intermediate that occurred during treatment by Gas Chromatography/Mass Spectrophotometer (GC/MS) of residual concentration of 2-CP in 1:0, A*, 0:1 TiO_2/AC composite.
2. Measure the Total Organic Carbon (TOC) of residual concentration of 2-CP in 1:0, A*, 0:1 TiO_2/AC composite.