CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 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 tetraisopropoxide (TTiP), Aldrich chemicals). Diethylene glycol and polyethylene glycol was purchased from Carlo erba chemical. Analytical grade K_2CrO_4 (Merck Chemicals) together with 18 MΩ 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 purchased from Merck Company, and used as received.

3.1.2 Photochemical reactor

A 1-litre photochemical batch reactor was used in all performed experiments. The photoreactor 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 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

3.2 Methodology

The experiments performed for this research can be divided into 3 main parts.

Part I – Synthesis of nanoparticles TiO_2.

Three types of nanoparticles included:

- Nanoparticle TiO_2 without any stabilizing agent
- Nanoparticle TiO_2 with DEG
- Nanoparticle TiO_2 with PEG

Part II – Characterization of synthesized nanoparticles TiO_2.

Part III - Treating of chromium (VI) using synthesized nanoparticles TiO_2.

3.2.1 Part I – Synthesis of TiO_2 nanoparticles

In the preparation of precursor solutions for nanoparticles TiO_2 without any stabilizing agent, titanium (IV) tetra-isopropoxide (or TTiP, $Ti[OCH(CH_3)_2]_4$, Aldrich chemicals) was used as the source material for Ti. TTiP was first diluted with ethanol, which was used as a solvent. HNO_3, DI water and ethanol were mixed together and used as the acidic catalyst for the hydrolysis of TTiP. The acidic solution was added drop wise to the TTiP-ethanol solution. Then let the solution dry at room temperature and gel was formed as shown in Figure 3.2.

For the synthesis of the nanoparticle TiO_2 with stabilizing agent (DEG or PEG), the stabilizing agent (DEG or PEG) was added to the mixture of the precursor solutions and vigorous stirring was continued for 1 hr prior to the drying process.

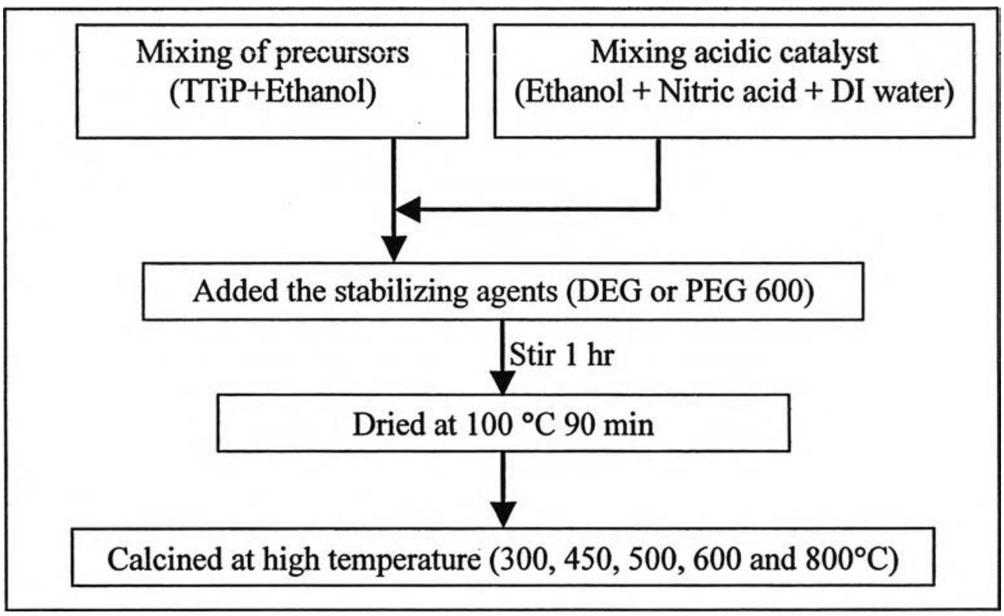

Figure 3.2 The preparation procedure for nanoparticles TiO_2

To determine the optimum condition for the preparation of the nanoparticles TiO_2, the parameters affecting nanoparticles TiO_2 properties, which were the variation molar ratio of TTiP : ethanol : HNO_3 : H_2O, calcination temperature and type of stabilizing agent, had to be investigated.

1.1 Investigation of the effect of the type of stabilizing agents (without stabilizing agent, with DEG, and with PEG)

The experiments throughout this thesis were carried out using three types of nanoparticle TiO_2. The first type was a nanoparticle using titanium (IV) tetra-isopropoxide as precursor and ethanol as solvent with water and HNO_3 as catalysts. The second type of nanoparticle, DEG was added in the synthesis method and in the third type PEG was added as stabilizing agent.

1.2 Investigation of the effect of the amount of stabilizing agents on nanoparticles TiO_2 preparation.

The optimum ratio of TTiP:ethanol:HNO_3:H_2O: stabilizing agent (DEG or PEG) was determined by varying the stabilizing agent concentration (DEG or PEG) as the first parameter at 0, 0.5, 1, 1.5 and 2.0 mol/L, respectively, with a constant TTiP:ethanol:HNO_3:H_2O ratio as 1:20:1:1.

After mixing all chemicals appeared as a clear solution, the gels were calcined at 450°C for 30 min. In this experimental set, the synthesis of nanoparticle TiO_2 without any stabilizing agents was also performed with the same experimental conditions as the control experiment.

1.3 Investigation the effect of calcination temperature on nanoparticles TiO_2 preparation.

The obtained optimum ratio of TTiP:ethanol:HNO_3:H_2O: stabilizing agent was used for preparation of TiO_2 precursor solutions. The temperatures of the calcination were varied as 300, 450, 500, 600, 700, and 800 °C, respectively. In this experiment set, the synthesis of nanoparticle TiO_2 without any stabilizing agent was also performed with the same calcination temperatures as the control experiment.

3.2.2 Part II – Characterization synthesized nanoparticles TiO_2

The prepared TiO_2 nanoparticle were characterized by using different techniques. The investigated characteristics of TiO_2 can be described as follow:

2.1 Surface morphology of nanoparticles TiO_2

To obtain surface morphology of synthesized TiO_2, the powders were examined by scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM). The differences in morphology of nanoparticle in each condition were identified.

2.2 Crystal structure of nanoparticles TiO_2

To obtain the ratio of anatase to rutile of a nanoparticles obtained from each condition, the TiO_2 nanoparticles were characterized by X-ray diffraction (XRD). The graphical plots of anatase to rutile ratio were illustrated as a function of the studied parameters, which were amount of stabilizing agent and calcinations temperatures.

2.3 Crystal size of nanoparticles TiO_2

Two ways to obtain the crystal size of nanoparticle TiO_2 in this work were: size measuring by calculating from Debye-Scherrer formula with the information from X-ray diffraction (XRD). The plots of crystal size of nanoparticle TiO_2 as a function of studied parameters (amount of stabilizing agent and calcinations temperatures) were obtained from this part.

2.4 Surface area of nanoparticles TiO_2

In this work, surface area information was identified using surface area analyzer by Brunauer, Emmett & Teller (BET) model. The surface areas from each nanoparticle TiO_2 were compared. This information was used to describe the adsorption ability of each nanoparticle in Part III of this thesis

2.5 Pore volume and pore size of nanoparticles TiO_2

Pore volume and pore size of nanoparticle TiO_2 were identified by Barrett, Joyner & Halenda (BJH) method. Information of porosity of nanoparticles together with surface area information were used to explain the adsorption behavior of each TiO_2 nanoparticle obtaining from the experimental results in Part III.

3.2.3 Part III - Treating of chromium (VI) using synthesized TiO_2 nanoparticles

Industrial wastewater

Industrial wastewater containing chromium (VI) was used in this work. Chromium (IV) solution was prepared by dissolving potassium chromate (K_2CrO_4) in distilled water. The concentration of the chromium (VI) solution was 50 mg/L. The pH of the resultant solution was adjusted to 3 with diluted H_2SO_4.

In this part, the TiO_2 nanoparticle derived from selected conditions in Part I were used as the photocatalysts for chromium (VI) removal from synthetic industrial wastewater. The reactions were carried out in a cylindrical UV photoreactor with photocatalytic activity. TiO_2 nanoparticles were placed in the synthetic chromium (VI) solution in the reactor with its surface coated by aluminum foil. Prior to UV illumination, the chromium (VI) solution was equilibrated in the dark with the TiO_2 surfaces for 60 minutes to allow for the adsorption process. Then, a UV lamp was turned on to illuminate the TiO_2 nanoparticle for 210 minutes. The samples after illumination were syringed out to analyze the concentration of chromium (VI) with a UV-Vis spectrophotometer. During the experiments, N_2 was bubbled into the system at a constant flow-rate and the suspension of TiO_2 nanoparticle in the chromium (VI) solution was agitated thoroughly by a magnetic stirrer. The residual chromium (VI) concentrations in the aqueous solution were plotted as a function of time. The observed kinetic constants, k_{obs}, from each experimental condition were also calculated.

Experimental works in this section were divided as follow:

3.1 Effect of amount of stabilizing agent on photocatalytic activity of each TiO_2 nanoparticle.

In this part, TiO_2 nanoparticle obtaining from different amounts of stabilizing agent with 450°C calcination temperature were used to treat chromium (VI) in photocatalysis process. All three types of nanoparticle TiO_2 were experimented as shown in Table 3.1:

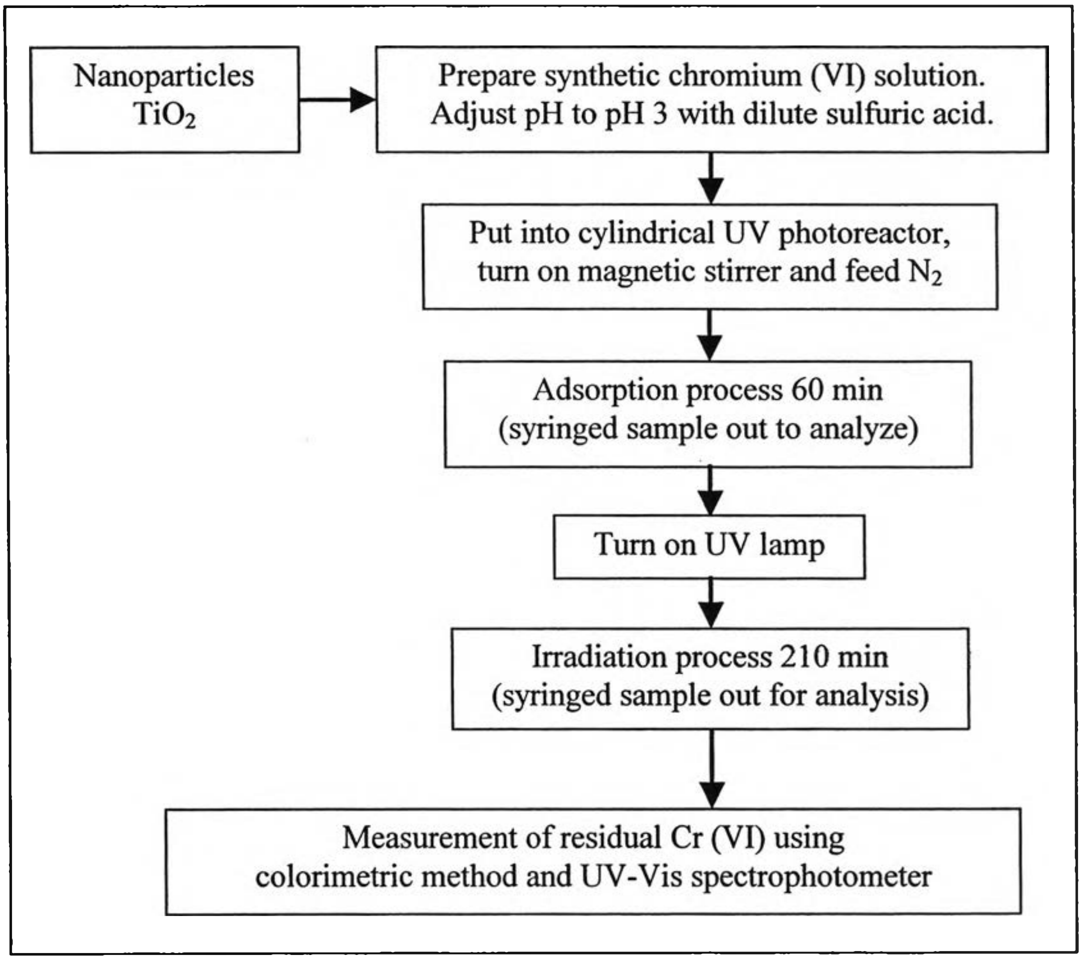

Figure 3.3 Schematic diagram for treating of chromium (VI)

Table 3.1 Experimental conditions to study effect of stabilizing agent on photocatalytic activity of nanoparticle TiO_2

Types of nanoparticle TiO_2	**Amount of stabilizing agent in synthesizing nanoparticle TiO_2**
TiO_2 without stabilizing agent	-
TiO_2 with DEG	0.5, 1, 1.5 and 2.0 mol/L
TiO_2 with PEG	0.5, 1, 1.5 and 2.0 mol/L

Results from this section were reported as the plot of the observed kinetic constant, k_{obs}, as a function of calcinations temperature of each types of TiO_2 nanoparticle.

3.2 Effect of calcination temperature on photocatalytic activity of each nanoparticle TiO_2

In this part, photocatalytic reduction efficiencies in chromium (VI) removal using each type of TiO_2 nanoparticle in various calcination temperatures were studied. The experiments were divided as shown in Table 3.2:

Table 3.2 Experimental conditions to study effect of calcination temperatures on photocatalytic activity of nanoparticle TiO_2

Types of nanoparticle TiO_2	Calcination temperatures in synthesizing nanoparticle TiO_2
TiO_2 without stabilizing agent	300, 450, 500, 600, 800°C
TiO_2 with DEG	300, 450, 500, 600, 800°C
TiO_2 with PEG	300, 450, 500, 600, 800°C

Results from this section were reported as the plot of the observed kinetic constant, k_{obs}, as a function of calcinations temperature of each types of TiO_2 nanoparticle.

3.3 Comparison of properties and photocatalytic ability of synthesized nanoparticle TiO_2.

To compare the ability in hazardous waste removal using synthesized TiO_2 nanoparticle, the highest efficiency in photocatalytic removal of chromium using TiO_2 nanoparticle with three conditions (without stabilizing agent, with DEG, and with PEG) were compared.

In addition, other properties of three types of synthesized nanoparticle TiO_2 in the best condition were compared as well. The property comparisons are described as shown in Table 3.3:

Table 3.3 Properties study to compare of properties and photocatalytic ability of synthesized nanoparticle TiO_2

<table>
<tr><td colspan="2">Types of nanoparticle TiO₂: TiO_2 without stabilizing agent,
TiO_2 with DEG
TiO_2 with PEG</td></tr>
<tr><td>Crystal property:
- Crystal structure
- Crystal size
- Surface area
- Pore volume
- Pore size</td><td>Photocatalytic property:
- Chromium (VI) removal efficiency
- Kinetic constant, k_{obs}</td></tr>
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