

## Chapter 2

### Methods of study

#### 2.1 Materials

- 2.1.1 Ammonium hydroxide (Ammonia solution) 28.0-30.0%,  $\text{NH}_4\text{OH}$ ; A.R., code no. 9721-03, J.T. Baker, U.S.A.
- 2.1.2 Acetic acid,  $\text{CH}_3\text{COOH}$ , A.R., code no. 2789, LAB-SCAN, Ltd., Ireland.
- 2.1.3 Aluminium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , A.R., code no. 417427, Carlo Erba, France.
- 2.1.4 Boric anhydride,  $\text{B}_2\text{O}_3$ , A.R., code no. 389 883/1 43799, Fluka, Switzerland.
- 2.1.5 Hydrochloric acid,  $\text{HCl}$ , A.R., code no. 9535-03, J.T. Baker, U.S.A.
- 2.1.6 Nitric acid 69.0-70.0%,  $\text{HNO}_3$ ; A.R. code no. 9601-04, J.T. Baker, U.S.A.
- 2.1.7 Orthophosphoric acid 85%(%w/v),  $\text{H}_3\text{PO}_4$ ; A.R. code no. 7664-38-2, Carlo Erba, France.
- 2.1.8 Silver nitrate,  $\text{AgNO}_3$ , A.R. code no. 102333J, BDH, England.
- 2.1.9 Sulfuric acid,  $\text{H}_2\text{SO}_4$ , A.R. code no. 9681-03, J.T. Baker, U.S.A.
- 2.1.10 Titanium dioxide P25, code no. D-60287, Degussa AG, Frankfurt, Germany.
- 2.1.11 Titanium tetrachloride,  $\text{TiCl}_4$ , A.R. code no. 488407, Carlo Erba, France.
- 2.1.12 Filter papers No.42, Cat No. 1442 125; Qualitative, Whatman, England.
- 2.1.13 Universal indicator; Full range pH 1-14, Whatman, England.
- 2.1.14 Methylene blue,  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$ ; redox indicator, Riedel de Haen, Germany.

#### 2.2 Instruments

##### 2.2.1 Chemistry Department, PSU

1. Analytical balances; AE 200S, SNR M10802, Mettler Toledo A.G., Switzerland.
2. Centrifuge; EBA 20, Hettich, Germany.
3. Fourier-transformed infrared spectrophotometer, FT-IR, EQUINOX55, Bruker, Germany.

4. Magnetic stirrer, Jenway 1000, JENWAY, UK.
5. Oven, National, Heinicke Company, U.S.A.
6. UV-Visible spectrophotometer, UV-VIS, UV-2401, Shimadzu, Japan.
7. UV-Visible spectrophotometer; SPECORD S100, Analytik Jena GmbH, Germany.
8. Wooden compartment (0.5m × 0.5m × 0.5m) with two tubes of 20 watts blacklight F20T12-BLB, CE, U.S.A.

#### 2.2.2 Scientific Equipment Center, PSU

1. Differential thermal analyzer, DTA, DTA7, Perkin Elmer, U.S.A.
2. Scanning electron microscope, SEM, JEOL JSM-5800LV, Japan.
3. Thermogravimetric analyzer, TGA, TGA7, Perkin Elmer, U.S.A.
4. Transmission electron microscope, TEM, JEOL JEM-2010.
5. Wavelength dispersive x-ray fluorescence spectrometer, WDXRF, PW2400, Philips, Netherlands.
6. X-ray diffractometer, XRD, PHILIPS X'Pert MPD, Netherlands.

#### 2.2.3 Chemical Engineering Department, PSU

1. Surface area / pore size study, SA 3100, Coulter, U.S.A.

### 2.3 Methods

The work can be divided into 2 parts; (1) preparation and characterization of undoped titanium dioxide and trivalent (Al, B)-doped titanium dioxide by sol-gel method, and (2) studies of photocatalytic property by decolorizing methylene blue under UV source (blacklight 20 watts). The products were then characterized by various techniques such as XRD, BET, FT-IR, TGA, SEM, TEM, XRF, and diffused reflectance UV-VIS. These techniques were used to study in the first part while UV-VIS technique was used in the second part.

### 2.3.1 Preparation of undoped TiO<sub>2</sub> and trivalent (Al, B)-doped TiO<sub>2</sub>

#### 2.3.1.1 Synthesis of undoped TiO<sub>2</sub>

Titanium tetrachloride (TiCl<sub>4</sub>) was used as a main starting material without any further purification. Titanium tetrachloride solution was prepared by dissolving 20 mL of TiCl<sub>4</sub> in 100 mL cold-distilled water. This solution was then mixed with 2 mL concentrated HCl which acted as hydrolysis catalyst in a 3-neck round bottom flask, and then was refluxed and maintained at 95°C in a temperature controlled bath under vigorous stirring for 13 h to carry out hydrolysis and condensation reaction. The mixed solution was slowly treated with concentrated NH<sub>4</sub>OH until the pH value was 7. The reaction was maintained for 13 h with continuous stirring. The experimental procedure was schematically shown in Fig 1. Through the hydrolysis and condensation reactions, the sol-gel transition took place gradually. Subsequently, the white precipitate formed and was separated from the solution by using vacuum-filtered and repeatedly washed with distilled water until free of chloride ion (using 0.1 M AgNO<sub>3</sub> solution). The powder was then dried at 105°C for 24 h and ground to fine powder and denoted as **undoped TiO<sub>2</sub>**.

#### 2.3.1.2 Synthesis of trivalent (Al, B)-doped TiO<sub>2</sub>

##### 2.3.1.2.1 Synthesis of Al-doped TiO<sub>2</sub>

The appropriate amount of aluminium sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O) which dissolved in distilled water was added into titanium tetrachloride solution which prepared by dissolving 20 mL of TiCl<sub>4</sub> in cold-distilled water in a 3-neck round bottom flask. Conc. HCl 2 mL was added into this reaction and then refluxed and maintained at 95°C under vigorous stirring for 13 h. Then the sol was treated with NH<sub>4</sub>OH solution, and maintained for 13 h with continuous stirring to give the gel precursor. The precipitate was separated from solution by filtration and repeatedly washed with distilled water until free of chloride ion. The products were dried at 105°C for 24 h and ground to fine powder and denoted as **Al-doped TiO<sub>2</sub>**. In the case of Al-doped TiO<sub>2</sub> samples many parameters were investigated such as the amount of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O and distilled water, types of acid, and calcined temperature.

#### 2.3.1.2.2 Synthesis of B-doped TiO<sub>2</sub>

For the B<sub>2</sub>O<sub>3</sub> doped titanium dioxide samples extensive variation of parameters were studied: B<sub>2</sub>O<sub>3</sub> content (0.5 wt%, 1.0 wt%, 2.0 wt%, 3.0 wt%, 4.0 wt%, 5.0 wt%, 10.0 wt%), type of acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, H<sub>3</sub>PO<sub>4</sub>), amount of distilled water (100 mL, 150 mL, 200 mL), and different calcined temperatures (400°C, 500°C, 600°C, 700°C, 800°C) were prepared by sol-gel process. The appropriate amount of B<sub>2</sub>O<sub>3</sub> was dissolved in hot distilled water, and then added into titanium tetrachloride solution in the 3-neck round bottom flask. 2 mL of acid was added and then the mixed solution was refluxed at 95°C under vigorous stirring for 13 h. The sol was then treated with NH<sub>4</sub>OH solution, and maintained for 13 h with continuous stirring to give the gel precursor. The precipitate was separated from solution by filtration and repeatedly washed with distilled water until free of chloride ion. The product was dried at 105°C for 24 h and ground to fine powder and denoted as **wt%\_B doped TiO<sub>2</sub>**, **acid\_B doped TiO<sub>2</sub>**, **water\_ B doped TiO<sub>2</sub>**, **calcined\_ B doped TiO<sub>2</sub>**.

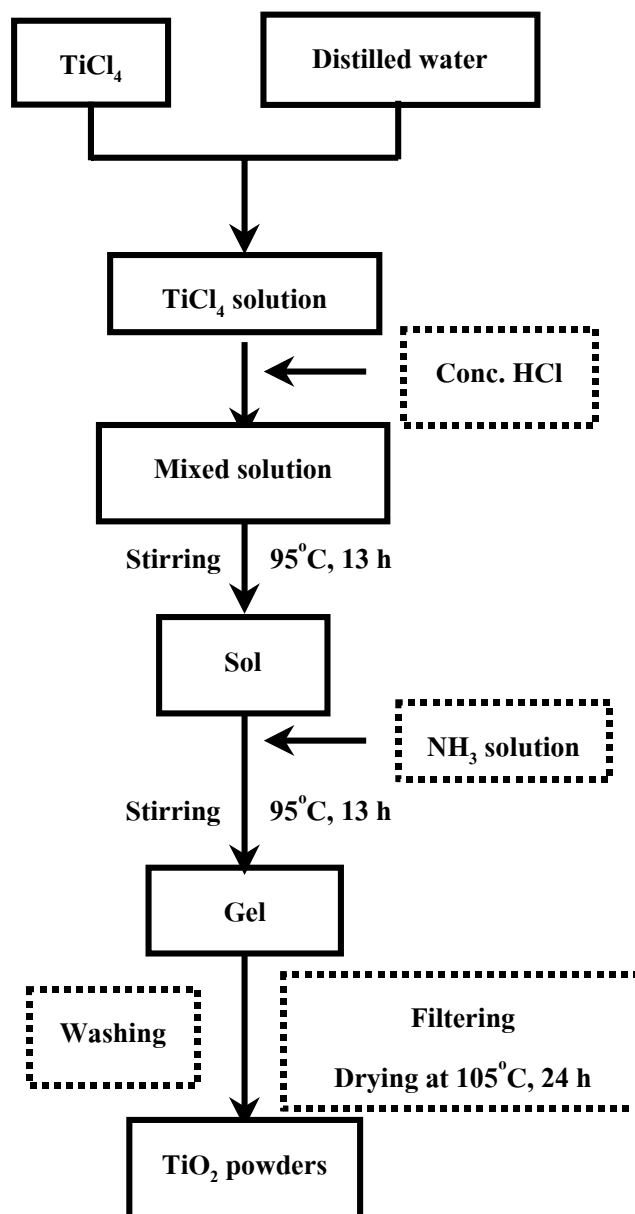


Figure 15 Flow chart of the preparation of undoped  $\text{TiO}_2$  powder by sol-gel method

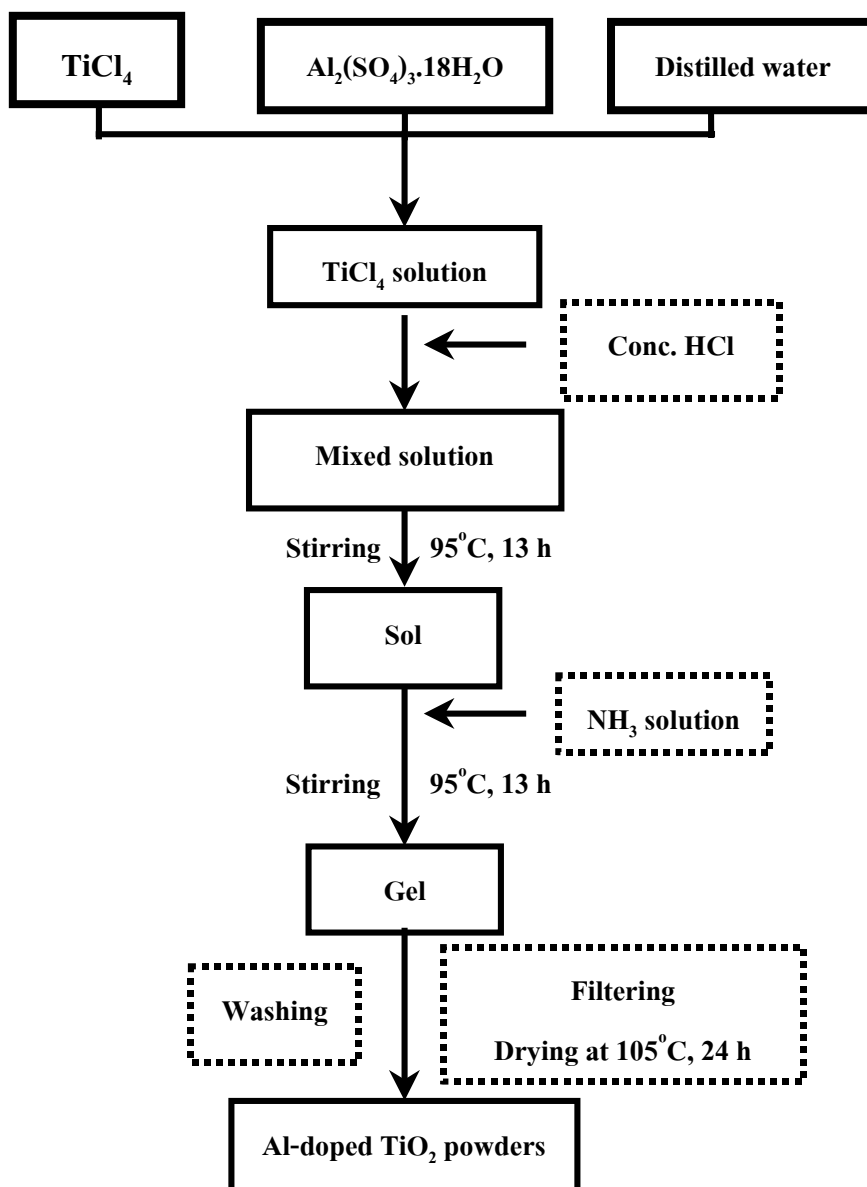


Figure 16 Flow chart of the preparation of Al-doped TiO<sub>2</sub> powder by sol-gel method

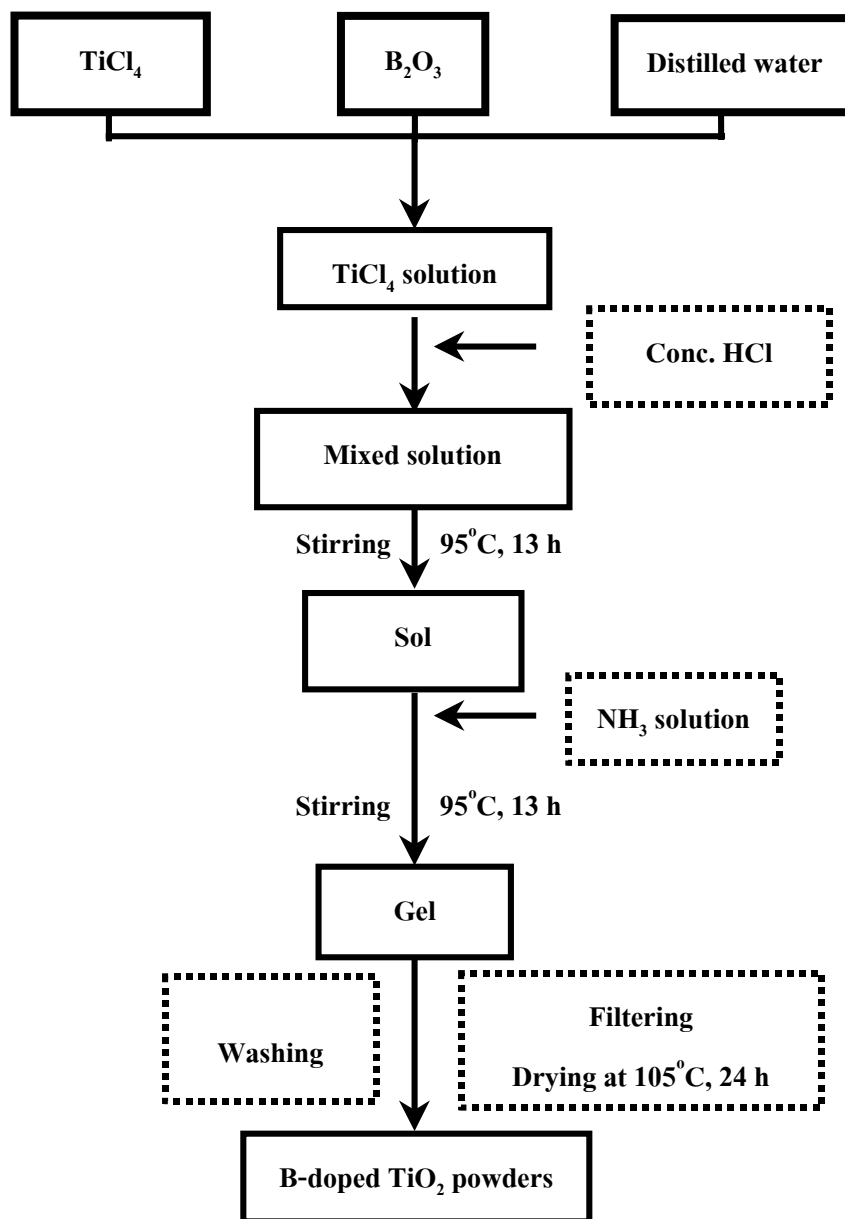


Figure 17 Flow chart of the preparation of B-doped TiO<sub>2</sub> powder by sol-gel method

## 2.3.2 Characterization of undoped TiO<sub>2</sub> and trivalent (Al, B)-doped TiO<sub>2</sub>

### 2.3.2.1 X-ray powder diffractometry (XRD)

The XRD technique was used to study crystalline phase identification and to estimate the crystallite size of each phase by using Scherer formula;

$$L = \kappa\lambda / (\beta\cos\theta) \quad \text{.....(12)}$$

where L is the crystallite size

$\lambda$  is the wavelength of the X-ray radiation (CuK $\alpha$  = 0.15406 nm)

$\kappa$  is a constant usually taken as 0.89

$\beta$  is the line width at half maximum height

$\theta$  is the diffracting angle

The XRD spectra of undoped TiO<sub>2</sub> and trivalent (Al, B)-doped TiO<sub>2</sub> samples were acquired at the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla using X-ray diffractometer, XRD, PHILIPS X'Pert MPD.

### 2.3.2.2 Surface area / Pore size

The specific surface area and pore size were determined using the BET method (Coulter, model SA3100, U.S.A.) by N<sub>2</sub> chemisorption. All data were acquired by the Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla.

### 2.3.2.3 Fourier-transformed infrared spectrophotometry (FT-IR)

The functional groups were checked by FT-IR in diffused reflectance mode at 4000 – 400 cm<sup>-1</sup> with KBr as blank (EQUINOX 55, BRUKER, Germany).

### 2.3.2.4 Thermogravimetric analysis (TGA)

This technique was done to determine mass change with temperature in the range 100 – 1,200°C under nitrogen atmosphere with heating rate of 10°C/min (TGA7, Perkin Elmer, U.S.A.). All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla.



#### 2.3.2.5 Differential thermal analysis (DTA)

DTA was used to determine the temperatures of phase changes in the temperature range of 100 – 1,200°C under nitrogen atmosphere with heating rate of 10°C/min (DTA7, Perkin Elmer, U.S.A.). All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla.

#### 2.3.2.6 Scanning electron microscopy (SEM)

The external morphology of the samples were observed on a SEM: JEOL JSM-5800LV scanning electron microscope (SEM) using high vacuum mode with secondary electron image conditions and electron micrograph technique. All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla.

#### 2.3.2.7 Transmission electron microscopy (TEM)

The morphology of materials on an atomic scale with resolution larger than 2 Å was acquired by TEM (TEM: JEOL JSM 2010) using high voltage condition about 200 kV and electron micrograph technique. All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla.

#### 2.3.2.8 Ultraviolet–visible spectrophotometry (UV–VIS)

UV-VIS diffused reflectance studies were performed on a UV-VIS absorption spectrophotometer (UV – 2401) at the scan range 200 – 800 nm with a 2.0 nm slit width and BaSO<sub>4</sub> as reference to establish the absorption edge, band gap energy, and the type of band-to-band transition of titanium dioxide.

#### 2.3.2.9 Wavelength dispersive x-ray fluorescence spectrometry (WDXRF)

X-ray fluorescence spectrometry technique was used to determine the metal ion which locating on the surface of samples using WDXRF, PW2400, Philips, Netherlands. All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla.

### 2.3.3 Photocatalytic activities of methylene blue (MB) by undoped TiO<sub>2</sub> and trivalent (Al, B)-doped TiO<sub>2</sub>

#### 2.3.3.1 Preparation of calibration standard solutions

In this work, the concentration of standard methylene blue solutions were  $1.0 \times 10^{-4}$  M to  $1.0 \times 10^{-7}$  M. In order to construct reliable standard calibration curve of methylene blue, the working concentrations were divided into three ranges :  $1.0 \times 10^{-4}$  M to  $1.0 \times 10^{-5}$  M,  $1.0 \times 10^{-5}$  M to  $1.0 \times 10^{-6}$  M, and  $1.0 \times 10^{-6}$  M to  $1.0 \times 10^{-7}$  M.

#### 2.3.3.2 The experiments for photocatalytic degradation of methylene blue by undoped

TiO<sub>2</sub> and trivalent ion (Al, B)-doped TiO<sub>2</sub> comparing with commercial P25-TiO<sub>2</sub>.

In the photocatalysis studies, 0.15 g of each TiO<sub>2</sub> sample was placed in an Erlenmeyer flask which contained measured volume of MB solution (75 mL of  $2.5 \times 10^{-5}$  M MB solution). The mixture was then stirred for 1 h in the dark to reach the adsorption equilibrium in tightly closed wooden compartment (0.5 m×0.5 m×0.5 m) to avoid interference from ambient light. Then began to irradiate under UV-light (blacklight 20 watts F20T12-BLB, CE, U.S.A.) and magnetically stirred at 500 rpm for 1.5, 3.0, 4.5 and 6.0 hours. The blacklight tube was attached in a fixed position inside the top side of the compartment. The second tube was attached to the side wall of the compartment. After irradiation the mixture was centrifuged and the clear solution was measured for the change of absorbance at wavelength 614 nm and 656 nm using SPECORD S100 spectrophotometer. The concentration of MB solution after each experiment was determined quantitatively through the calibration graph constructed from standard solution of MB at various concentrations.