Chapter 2
Methods of Study

2.1 Materials

2.1.1 Titanium dioxide; Degussa P25, code no. D-60287, Degussa AG, Frankfurt, Germany.

2.1.2 Titanium dioxide; Anatase, code no. 488257, Carlo Erba, Milano, Italy.

2.1.3 Latex; 60% HA, Chana Latex Co. Ltd, Songkhla, Thailand.

2.1.4 Methylene blue; $C_{16}H_{18}N_3SCl$, redox indicator, Riedel de Haen, Germany.

2.1.5 Hydrochloric acid; HCl, A.R., code no. 9535-03, J.T. Baker, U.S.A.

2.1.6 Sodium hydroxide; NaOH, A.R., BDH, England.

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. Magnetic stirrer; Jenway 1000, JENWAY,UK.
4. pH meter; Hanna instruments, 8519, U.S.A.
5. UV-Visible spectrophotometer; SPECORD S100, Analytik Jena GmbH, Germany.
6. Photoreactor compartment (0.9m × 0.9m × 0.9m) with five tubes of 20 watts Blacklight; F20T12-BLB, GE, U.S.A.
7. Petri dish; 3.5 inch and 4 inch diameter, Pyrex, Germany.

2.2.2 Scientific Equipment Center, PSU

1. Scanning electron microscope, SEM, JEOL JSM-5800LV, Japan.
2. X-ray diffractometer, XRD, PHILIPS X'Pert MPD, Netherlands.

2.3 Methods

The work can be divided into 2 parts; (1) preparation and characterization of Immo-TiO_2 thin films on the rubber substrate by direct mixing of commercial TiO_2 powders (Anatase; Carlo Erba, Italy, and Degussa P25; Degussa AG, Germany) with latex (60% HA) and distilled water, and (2) studies of the photocatalytic degradation of Immo-TiO_2 thin films by decolorizing methylene blue (MB) dye in aqueous solutions under UV light irradiation. The surface morphology and cross section of all Immo-TiO_2 thin films were observed by using scanning electron microscopy (SEM) technique while the X-ray diffractometer (XRD) was used to identify crystalline phases and confirms structures of some Immo-TiO_2 thin film samples. The effect of various parameters such as the amount of distilled water, the amount of latex and the amount of commercial TiO_2 powders were studied to optimize the preparation of Immo-TiO_2 thin films for maximum photocatalytic degradation of MB under UV light irradiation, and comparing with original commercial TiO_2 powders. Furthermore, the effect of pH, initial concentration of MB, and intensity of UV light were studied on the photocatalytic degradation of MB under UV light irradiation for direct application in the water purification.

2.3.1 Preparation of Immo-TiO_2 films

2.3.1.1 Synthesis of Immo-TiO_2 anatase films

The Immo-TiO_2 anatase film was prepared by mixing 0.1 g of commercial TiO_2 anatase powder (Carlo Erba) in 1 ml distilled water and stirred for 3 min after which 5 ml latex (60% HA) was added and then stirred for another 5 min. The mixture was poured into a petri dish (3.5 inch diameter) and dried at room temperature for 15 h. Afterwards, the Immo-TiO_2 anatase was taken out from petri dish, reversed and dried at room temperature about 2 h. The variation of parameters such as the amount of distilled water (1 ml, 2 ml, 3 ml, 4 ml, and 5 ml), the amount of latex (3 ml, 5 ml, 7 ml, and 9 ml), and the amount of commercial TiO_2 anatase powder (0.05 g, 0.1 g, 0.2 g, and 0.3 g) were studied to optimize the preparation of the Immo-TiO_2 anatase film for maximum photocatalytic degradation of MB dye in aqueous solution under UV light irradiation.

2.3.1.2 Synthesis of Immo-TiO_2 Degussa P25 films

The Immo-TiO_2 Degussa P25 film was prepared using almost the same method as the Immo-TiO_2 anatase films, but using commercial TiO_2 Degussa P25 powder (Degussa P25 AG) as a starting material. The variation of parameters such as amount of distilled water (1 ml, 3 ml, 5 ml, 6 ml, and 7 ml), amount of latex (3 ml, 5 ml, 7 ml, and 9 ml), and amount of commercial TiO_2 Degussa P25 powder (0.05 g, 0.1 g, 0.2 g, and 0.3 g) were carried out similarly.

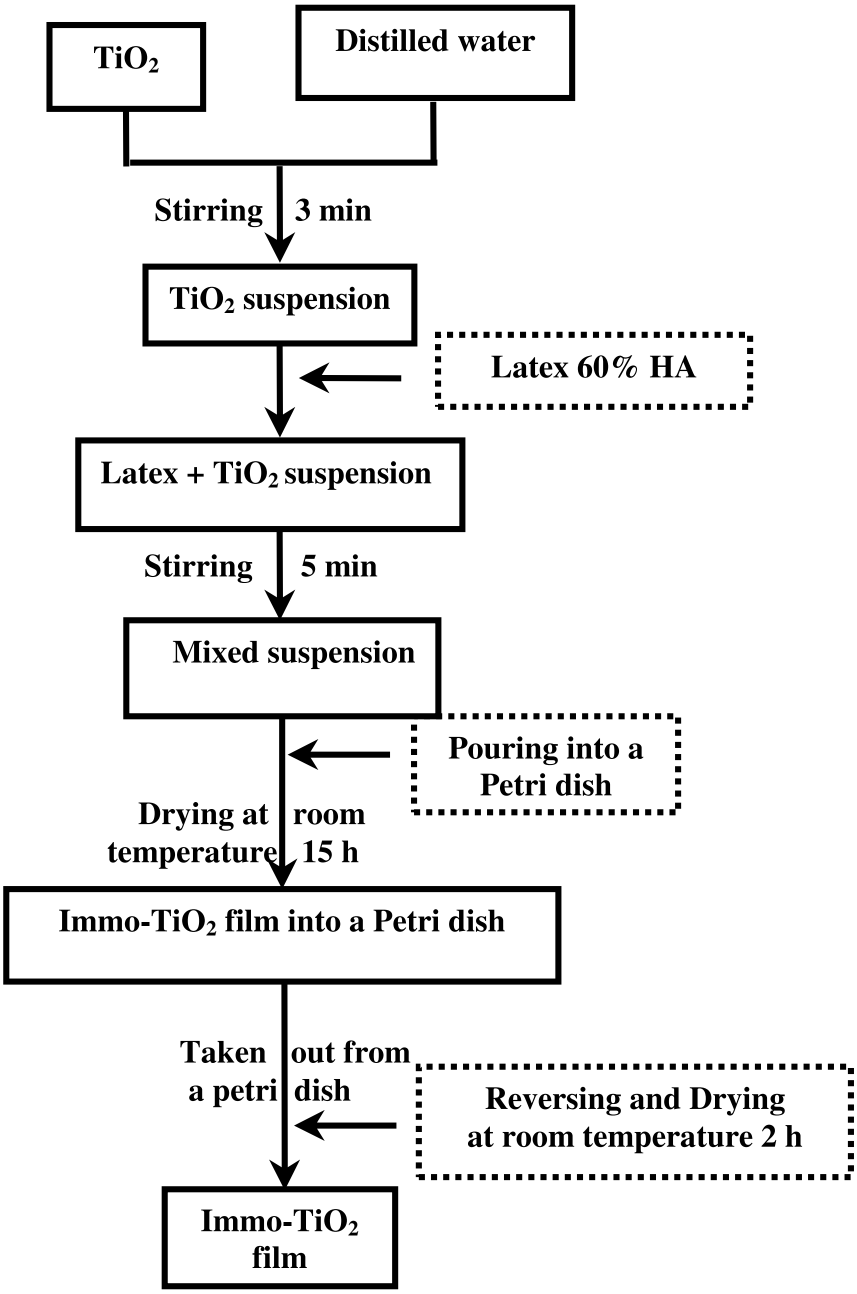

Figure 9 Flow chart of the preparation of Immo-TiO_2 films

2.3.2 Characterization of Immo-TiO_2 films

2.3.2.1 Scanning electron microscopy (SEM)

The surface morphology and cross section of all samples were observed on a SEM: JEOL JSM-5800LV scanning electron microscopy (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, Thailand.

2.3.2.2 X-ray powder diffractometer (XRD)

The XRD technique was used to study crystalline phase identification and confirms structure of Immo-TiO_2 films. The XRD spectra of the Immo-TiO_2 anatase film, Immo-TiO_2 Degussa P25 film, commercial TiO_2 anatase powder (Carlo Erba, Italy), commercial TiO_2 Degussa P25 powder (Degussa AG, Germany), and the pristine rubber substrate. All data were acquired at the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkhla, Thailand, by using X-ray diffractometer, XRD, PHILIPS X'Pert MPD.

2.3.3 Photocatalytic degradation of methylene blue (MB) by Immo-TiO_2 films

2.3.3.1 Construction of calibration graph from MB standard solution

In this work, the concentration of standard methylene blue solutions were 2.5×10^{-6} M to 3.0×10^{-5} M. In order to construct reliable standard calibration graph of methylene blue, the working concentrations were divided into five points : 2.5×10^{-6} M, 5.0×10^{-6} M, 1.0×10^{-5} M, 2.0×10^{-5} M and 3.0×10^{-5} M.

2.3.3.2 The experiments for photocatalytic degradation of methylene blue (MB) by Immo-TiO_2 thin films comparing with the original TiO_2 powders.

In the photocatalytic studies, the Immo-TiO_2 thin film was settled into a petri dish (4 inch diameter) containing 60 ml of MB aqueous solution (2.5×10^{-5}M). The solution was then stirred for 1 h in the dark to reach the adsorption equilibrium in tightly closed photoreactor compartment (0.9m X 0.9m X 0.9m) to avoid interference from ambient light. Then the irradiation began under UV-light (5 tubes of blacklight, 20 watts each, F20T12-BLB, GE, U.S.A.) and magnetically stirred at 400 rpm. The blacklight tubes were attached at fixed positions inside with one tube at the top wall and one each at four side walls of the compartment. At given irradiation time intervals (every 1 h), 4 ml of MB solution samples were collected. The degradation of MB solutions was analyzed from the changes in absorbance of the absorption maximum at 665 nm using UV-Vis spectrophotometer Specord S100, Analytik Jena, Germany. The concentration of MB solution was determined quantitatively through the calibration graph (constructed in 2.3.3.1). The optimization for preparing Immo-TiO_2 anatase film and Immo-TiO_2 Degussa P25 film on the maximum photocatalytic degradation of MB in aqueous solution under UV light irradiation were compared with original TiO_2 powders; commercial TiO_2 anatase (Carlo Erba) and Degussa P25 (Degussa AG).

In the studies of the original TiO_2 powders; commercial TiO_2 anatase (Carlo Erba) and Degussa P25 (Degussa AG), for photocatalytic activities the same set up was employed as above, but using 0.1 g TiO_2 powder, instead of the films, as a catalyst and the solution must be centrifuged before analysis.

2.3.3.3 The experiments for the effect of various parameters such as initial concentration of MB, pH, and intensity of UV light

The effect of various initial MB dye concentrations were investigated in the range of 1.0×10^{-5} M to 3.0×10^{-5} M. The pH of MB dye solutions were studied in the range of 3 to 9 by adding dilute aqueous solution of HCl and NaOH. The effect of intensity of UV light was studied by varying the amount of blacklight tubes (1, 3, and 5 tubes).