CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Materials used in this study were chemicals and reagents which were of analytical grade and used as received from the suppliers.

- Titanium (diisoproproxide) bis (2, 4-pentanedionate) 75 wt% in 2-propanol (TIAA), 99% purity (Acros Organics)
- Titanium dioxide (anatase) powder, 99.8% purity (Sigma Aldrich)
- Tin (IV) chloride (Fluka)
- Phenol (Merck)
- Guaiacol (Sigma Aldrich)
- Syringol ((Sigma Aldrich)
- Polyvinyl pyrrolidone (PVP) ($M_n = 1\ 300\ 000$) (Sigma Aldrich)
- Acetic acid (Merck)
- Isopropanol (Merck)
- Ethanol, 100% purity (BDH)
- Methanol, HPLC grade (BDH)
- Milli-Q water

3.2 Method for preparing tin doped titanium dioxide

Based on the previous study conducted by Nuansing et al. (2006), polymer source was prepared by using a ratio of 4.5 g PVP to 75 ml ethanol. To obtain a solution of metal source, 14.85 g of TIAA was dissolved in the solution of 30 ml acetic acid and 30 ml ethanol. The solution was then mixed with the prepared PVP/ethanol solution. The mixture was vigorously stirred at room temperature to get the homogeneous polymer solution until the dense gel was obtained and then dried in an oven at 100°C for 24 hours. The dried precursor was calcined in air at 500 - 900°C for 3 hours in the Muffle Furnace. The calcined TiO_2 were ground and passed through the sieve mesh no.230 (ϕ = 63 μm) (Figure 3-1). Nanocrystalline materials were characterized by TG/DTA, XRD, BET, SEM.

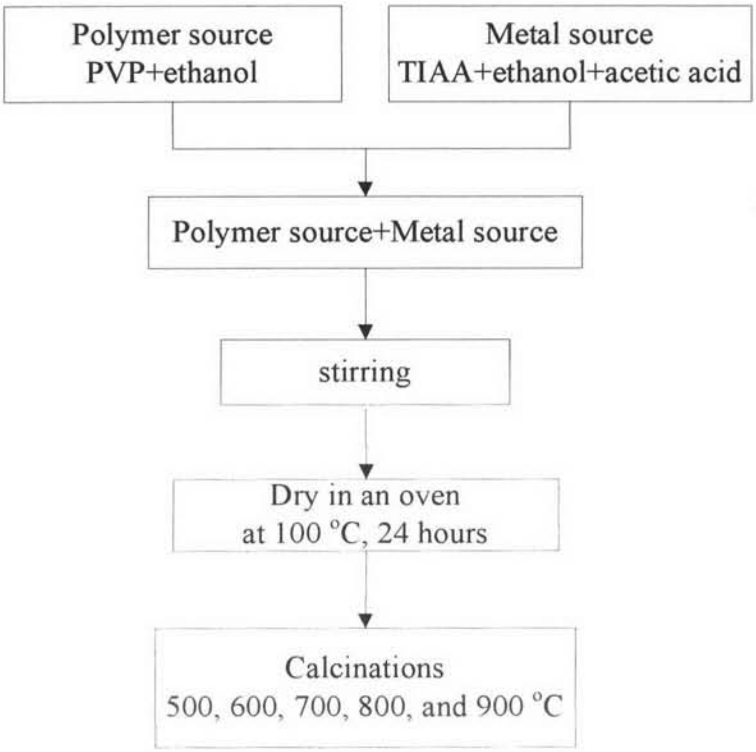


Figure 3-1 Diagram for preparation of TiO_2 nanocrystalline photocatalyst

3.3 Method for preparing tin-doped titanium dioxide (Sn-doped TiO_2)

To determine the optimum ratio of titanium dioxide and tin oxide by using the different ratio of Titanium (Ti):Tin(Sn) at 1, 2 and 3 % Sn by mole of Ti. Tin was added in the step of preparing metal solution. The dried precursor was calcined in air at the optimum temperature for 3 hours in the Muffle Furnace. The calcined TiO_2 were ground and passed through the sieve mesh no.230 (ϕ = 63 μm) (Figure3-2). Then the prepared materials were characterized by XRD, BET, and SEM

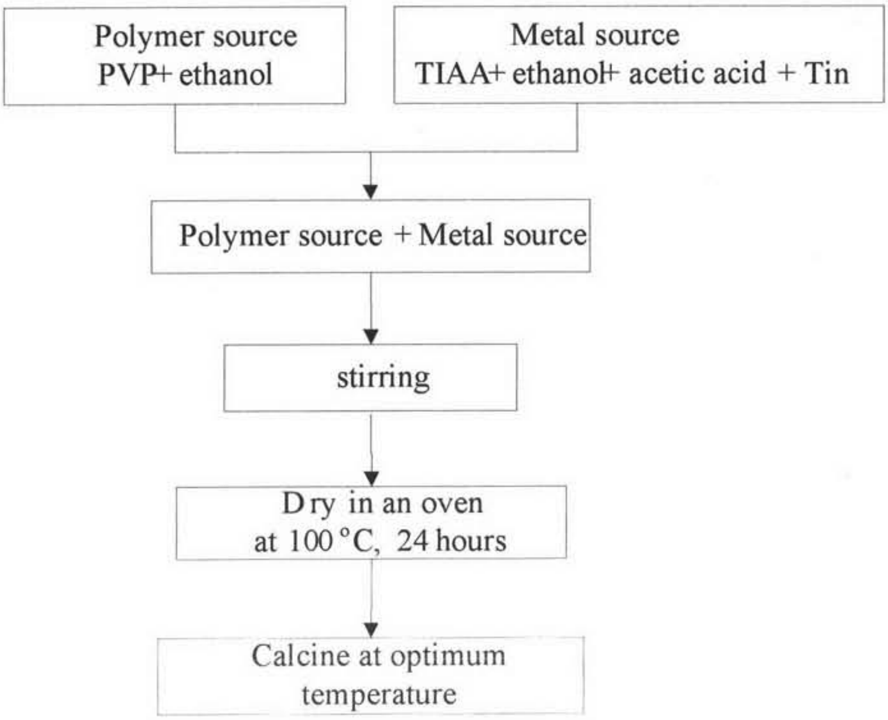
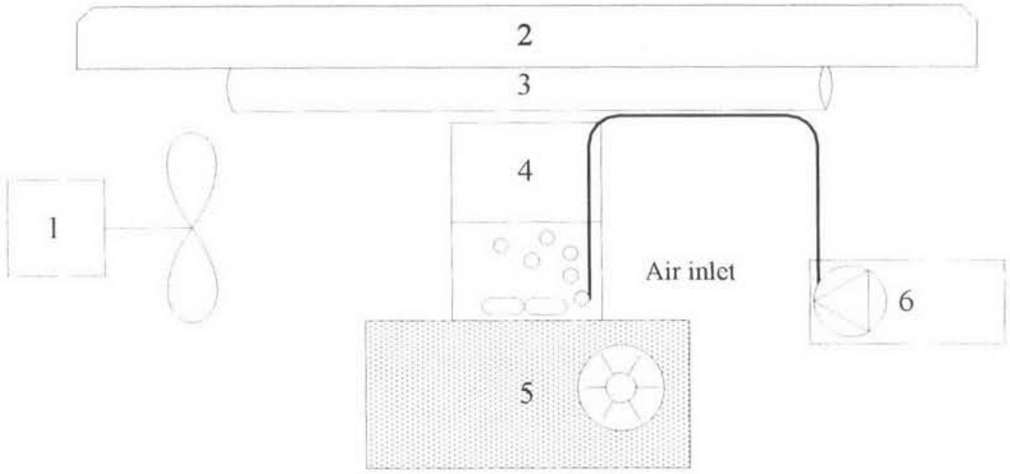


Figure 3.2 Diagram for preparation of Sn-doped TiO_2 photocatalyst.

3.4 Testing for photocatalytic performance

Testing for photocatalytic performance was implemented to all experimental investigations including optimum temperature, optimum ratio, intermediate production, kinetic study and real wastewater testing. The experiments setting up for photocatalytic reaction (Figure 3-3) were performed in a Pyrex vessel. The parallel experiments were carried out for the synthesized TiO_2 and commercial TiO_2 in order to compare the degradation performance. For each experiment, 200 ml of the designated concentration of phenolic compound solution (i.e. 10 ppm for optimum temperature and ratio and 100 ppm for intermediates study) suspended with 0.4 g of the synthesized or commercial TiO_2 with an initial pH at 7. The mixture was maintained as a suspension by magnetic stirring. The ambient air was circulated by an electric fan to control at the ambient temperature. Aeration was provided through an aquarium aerator. Prior to irradiation, the suspension was left for 1 hour in the dark in order to achieve the maximum adsorption of the phenol onto the semiconductors surface (Bekkouche et al. 2004). The suspended solution was then illuminated by two Philips TLD 15W/05 lamps (intensity 8,400 $\mu W/cm^2$, Ultraviolet Intensity Meter J-

221 BLAK-RAY), emitting ultraviolet radiation with a maximum radiation peak at 375 nm. The distance between the liquid surface and light source was about 15 cm. Sample of 2 ml was withdrawn at the regular intervals of time and filtered to separate TiO_2 from liquid by nylon filter pore size 0.45μm. The withdrawn samples were then analyzed for type of intermediates and concentration of phenolic compounds by liquid chromatography and gas chromatography. For the intermediate study and real wastewater testing, all sample was taken 50 ml and then extracted to by liquid liquid extraction. Fifty-mL of each sample was done by extracting the liquid samples for three times with 10 mL of dichloromethane in separation funnel. The organic fraction of the samples was evaporated and then redissolved in 1 mL of isopropanol before analyzing by GC techniquue. The percent recovery of this extraction technique was 95%.



1 Cooling fan
2 Aluminium foil shield
3 2-Lamps of Philip TLD 15W/05
4 Pyrex vessel
5 Magnetic stirrer
6 Aerator

Figure 3-3 Diagram of experiment setup for photocatalytic reaction.

3.5 Characterization Techniques

3.5.1 Thermogravimetric-differential thermal analysis (TG-DTA)

Thermogravimetric-differential thermal analysis (TG-DTA) (Perkin-Elmer, USA) with a heating rate of 10°C/min in static air up to 1000°C was employed to determine the temperature for possible decomposition and crystallization of the dried gel. The determined temperature also indicated the complete burning of sol gel precursor.

3.5.2 X-Ray Diffraction (XRD) Analysis

The synthesized TiO_2 nanoparticles were characterized for phase transformation (anatase to rutile), grain size calculation, fraction ratio of anatase and rutile by using X-ray diffraction (XRD) on a Bruker AXS (D8 ADVANCE) diffractometer at 40 kV, 40 mA (Cu $K\alpha$=1.5406 Å). The step size was 0.02 degree/step and step time was 0.2 sec/step. The working range was $2\theta = 20–80$. The strongest peaks of TiO_2 corresponding to anatase (101) and rutile (110) were selected to evaluate the crystallite size according to Equation (3.1) is commonly known as the Scherer's equation (Suryanarayana and Norton, 1998).

$$L = \frac{k\lambda}{\beta\cos\theta} \qquad \text{.....................}\mathbf{(3\text{-}1)}$$

where L is the length of the crystal in the direction of the d spacing, k is a constant of 0.9, λ is the wavelength of the x-ray used (1.5406 Å), β is the full width at half-maximum (FWHM) of the selected peak and θ is the Bragg's angle of diffraction for the peak. The mass fraction of content phase anatase and rutile in the samples was calculated from intensities of XRD spectra according to the Spurr's equation as shown in the Equation (3-2) (Spurr and Myers, 1957).

$$F_R = \frac{1}{1+1.26\left[I_A(101)/I_R(110)\right]} \qquad \text{.....................}\mathbf{(3\text{-}2)}$$

where F_R is the percentage content of rutile at each temperature, $I_A(101)$ and $I_R(110)$ are the integral (101) intensities of anatase and (110) of rutile, respectively.

3.5.3 BET method for Specific Surface Area Measurement

Specific surface areas of the TiO_2 were obtained by using the standard BET method on a Micromeritics ASAP 2010 sorption analyzer with common adsorbate, N_2, at -196 °C. Prior to the measurement, samples were pretreated with heat at 105 °C overnight to remove moisture.

3.5.4 Scanning Electron Microscopy (SEM)

SEM was used for determination of morphology, agglomeration, and dispersion of crystal. Powder samples were scattered on an adhesive carbon tape which was attached on a aluminum holder. The sample was then coated with gold by sputtering and then transferred into the sample chamber of the microscope (LEO SEM 1450VP).

3.6 Aanalytical Techniques

3.6.1 Liquid Chromatography

Liquid chromatography is the technique used for measuring organic compounds including phenolic compounds. Sample of 2 ml was withdrawn at the regular intervals of time and filtered to separate TiO_2 from liquid by nylon filter pore size 0.45μm. The phenol concentration was determined by means of high performance liquid chromatography (HPLC). The HPLC separations were carried out at ambient temperature on a system consisting of a LC-10AD pump (Shimadzu, Japan) equipped with a SPD-10A UV/VIS spectrophotometer detector (Shimadzu, Japan). Samples were injected in a sample loop of 20μl and detection wavelength was 270 nm. Phenol was chromatographed on a Shimp-pack CLC-ODS (150mm×6.0mm i.d., 5 μm) and eluted by methanol/water (3:7, v/v), flow rate 1 ml/min.

3.6.1 Gas Chromatography with Flame Ionization Detector

Concentrations of phenolic compounds were measured by gas chromatography (GC) with flame ionization detector (FID). Prior to GC/FID analysis, the samples were extracted by means of conventional method liquid-liquid extraction by 50 ml of sample was extracted three times with 10 ml of dichromethane then the extracted sample was removed dichromethane by evaporator and then make up volume to 2 ml with isopropanol. The GC-FID (Perkin Elmer) equipped with a DB-624 capillary column (30 m×0.32 mm) (J&W Scientific). Temperature conditions were programmed as follows: The column oven was initially set at 100 °C for 5 min, and then programmed to 230 at a 5 °C/min rate, and it was held for 5 min at the final temperature.

3.6.3 Gas Chromatography Mass spectrometry

GC/MS analysis was provided to identify intermediates from photocatalytic degradation. The samples were extracted by liquid-liquid extraction , 100 ml of sample was extracted three times with 10 ml of dichromethane then the extracted sample was removed dichromethane by evaporator and then make up volume to 2 ml with isopropanol. A Shimadzu GC-17A QP-5050 GC/MS system equipped with a fused silica capillary column (SPB-608, Supelco) 30m×0.25 mm, 0.25 μm. The injection was operating in the splitless mode. Helium (>99.999% purity) was used as the carrier gas. The column oven was initially set at 80 °C for 5 min, then programmed to 160 at a 5 °C/min rate, where it was held for 5 min and finally to 280 °C at a 10 °C/min rate, where it was held for 5 min. The ionization mode was electron impact (70eV) and data was collected in the full scan mode (m/z 40-350).