CHAPTER IV

EXPERIMENTAL

This chapter consists of four main sections. Section 4.1 introduces the three of photoreactor systems that were employed in this study. Preparation of TiO_2 powder is described in Section 4.2. Several characterization techniques for catalysts are discussed in Section 4.3. Finally, details on photocatalytic degradation of two different dyes are described in Section 4.4.

4.1 Photoreactor Systems

In this study, the photocatalytic degradation performances of the three reactor systems, namely, airlift reactor, bubble column and stirred tank reactor, were investigated.

4.1.1 Airlift reactor system

A lab-scale internal loop air-lift reactor (see Figure 4.1) was designed and was constructed for this study. The reactor was made of transparent Pyrex glass (wall thickness 3 mm) to avoid absorption of the UV light by the reactor. A main column was 9.4 cm in internal diameter and 65 cm in height with a nominal working volume of three liters. A draft tube was installed inside the main column. The internal diameters of the draft tubes were either 4.6 cm or 6.6 cm and the height was 40 cm. The mixing in the reactor was carried out by feeding air into the bottom of reactor through a sparger using an air pump. The air flow rate was measured by a rotameter. UV irradiation was provided by eight black light bulbs (Philips Actinic blue 20W), which were evenly placed around the reactor with 4.5 cm away from the reactor in the configuration shown in Figure 4.1.

4.1.2 Bubble column system

For the bubble column system (see Figure 4.2), all of the equipments were similar to the airlift reactor system described in Section 4.1.1 except for the absence of a draft tube.

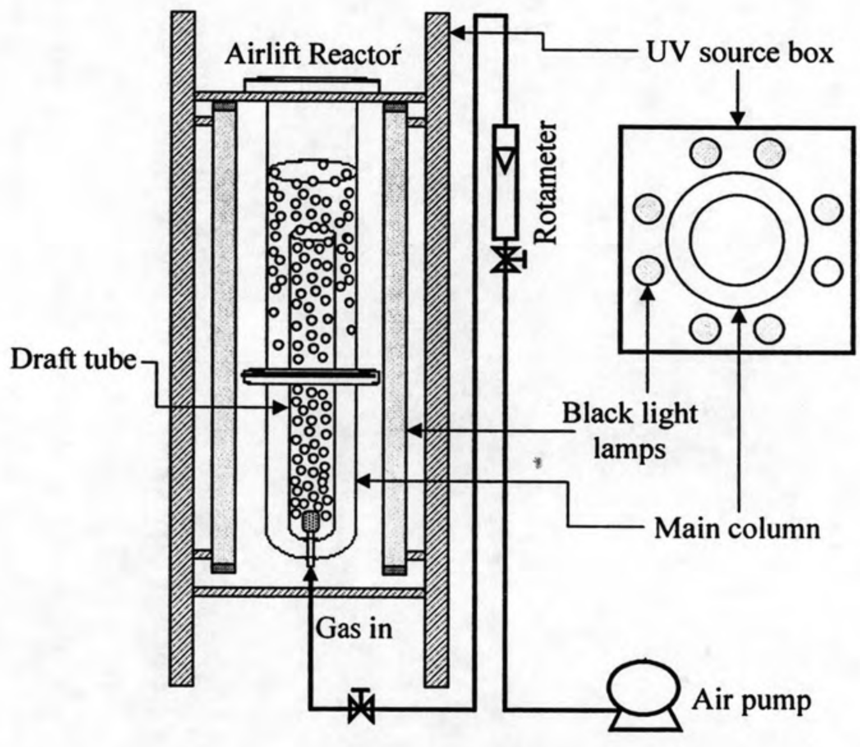


Figure 4.1 Schematic representation of the airlift reactor system. A top view of the system is shown on the right.

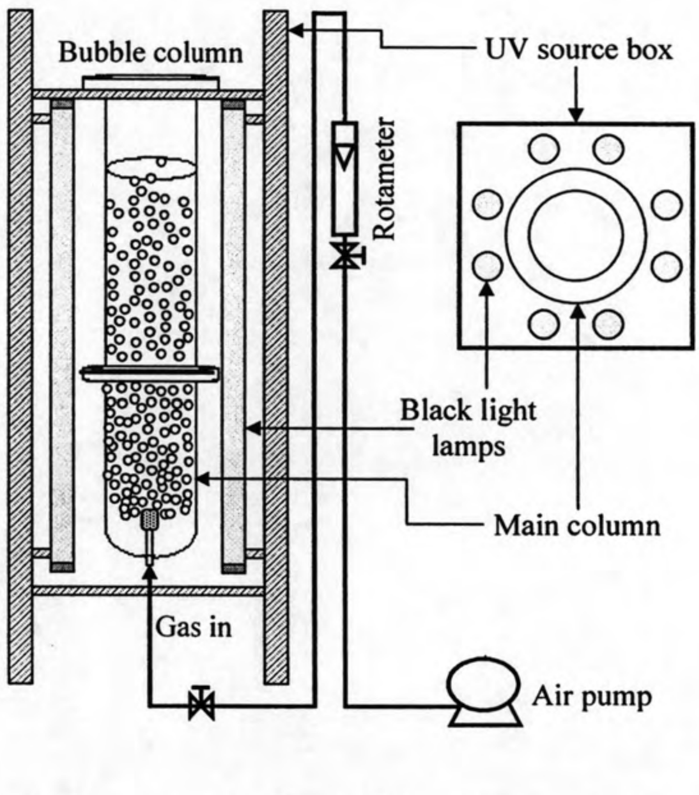


Figure 4.2 Schematic representation of the bubble column system. A top view of the system is shown on the right.

4.1.3 Stirred tank reactor system

For the stirred tank reactor system (see Figure 4.3), the magnetic stirrer was used to mixing the dye solution in the Pyrex beaker that has the same internal diameter as a main column of airlift reactor in order to maintain the same intensity of UV-irradiation reaching both reactors. The magnetic stirrer and the beaker were put in the middle of the UV source box. Air was fed into the system by an air pump.

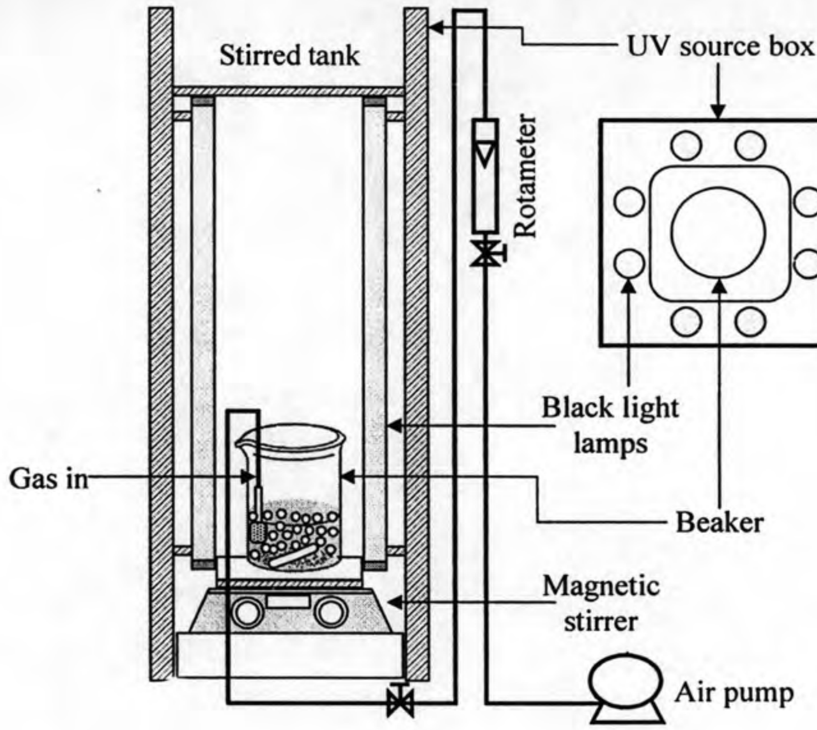


Figure 4.3 Schematic representation of the stirred tank reactor system. A top view of the system is shown on the right.

For the three systems, to avoid the heating of the solution, a blower was used to blow the air from the top through the bottom of the UV source box so as to remove the heat from the light source.

4.2 Preparation of titanium dioxide

Titanium dioxide was synthesized via a sol-gel method and titanium isopropoxide (Aldrich Chemical, Milwaukee, WI) was employed as a precursor. First, 3.14 ml of 70% nitric acid (Asia Pacific Specialty Chemicals Limited) was added into 1,000 ml of distilled water. While the acidic solution was stirring, 83.5 ml of titanium isoproproxide was added slowly dropwise, and the white precipitate occurred. The suspension was stirred continuously at room temperature for about 3-4 days until clear solution was obtained. After that, the sol was dialyzed in a cellulose membrane with a molecular weight cutoff of 3500 (Spectrum Companies, Gardena, CA). Prior to use, the dialysis tubing was washed in an aqueous solution of 0.001M EDTA and 2% sodium hydrogen carbonate. The wash solution was prepared by dissolving 0.372 grams of EDTA (Asia Pacific Specialty Chemicals Limited) and 43 grams of sodium hydrogen carbonate powder, 99.93% (Fisher Scientific Chemical) in one liter of distilled water. Dialysis tubing was cut into sections of 32 cm in length and was submerged in the wash solution. Then the membrane was heated to 80 °C and held at that temperature for 30 minutes while simultaneously being stirred. After the solution was cooled to room temperature, the tubing was again washed with distilled water. The tubing was again immersed in one liter of fresh distilled water while being stirred continuously, and was heated to 80°C. The tubing was rinsed one more time and was stored in distilled water at 4 °C until needed. The clear sol was placed in dialysis tubing. Then the tubing containing the sol was submerged in distilled water using a ratio of 100 ml of sol per 700 ml of distilled water. The dialyzed water was changed daily for 3-4 days until the pH of the water reached 3.5. To remove solvents, the dialyzed sol was left in ambient atmosphere for overnight, the solvents are completely evaporated, then titanium dioxide gel was obtained and was dried at 110°C for 12 hours. The resulting gel was then ground. Finally, titania nanoparticles were calcined at 200 °C for an hour. The preparation procedure is shown schematically in Figure 4.4.

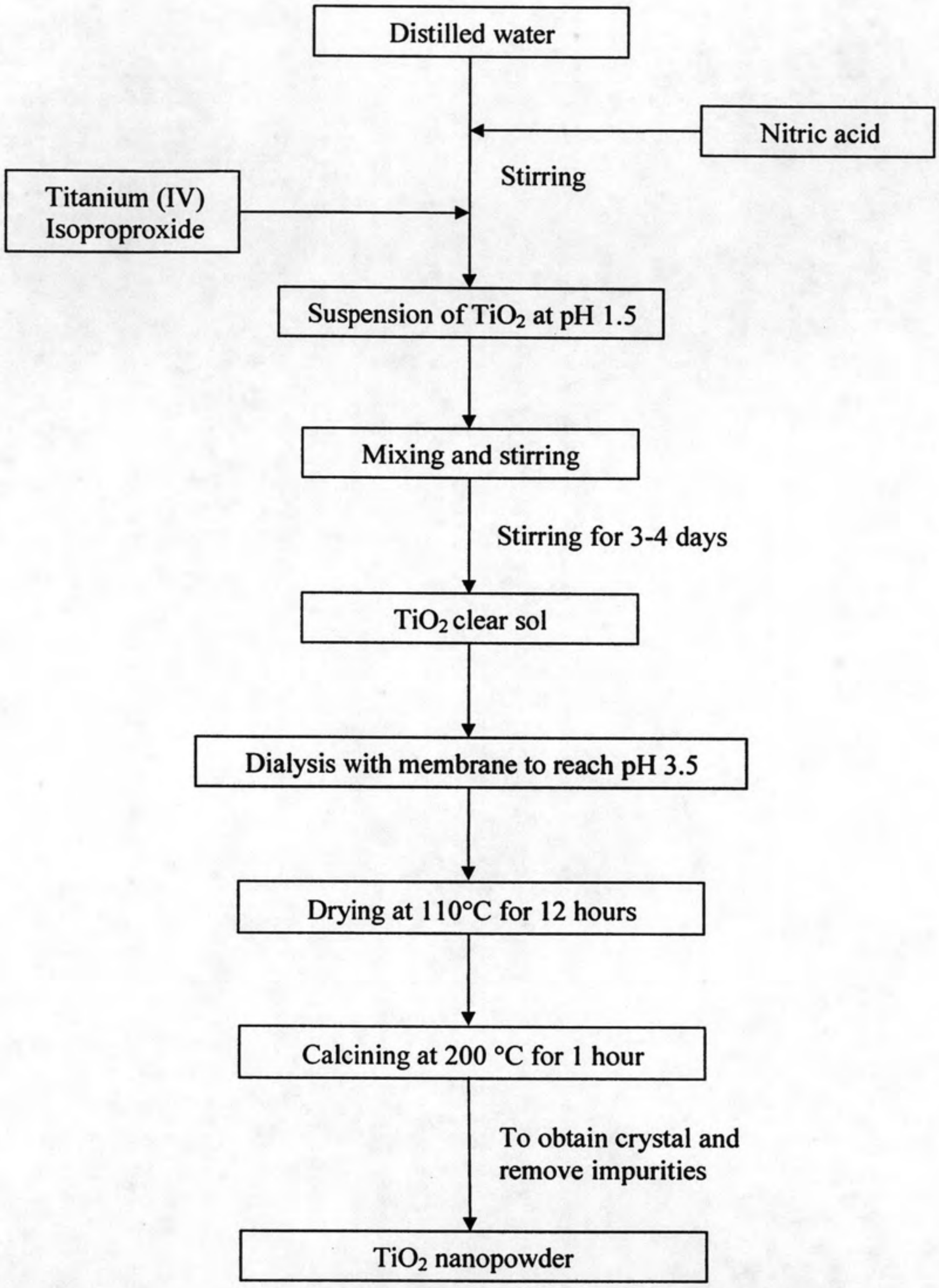


Figure 4.4 Schematic diagram for the preparation of TiO_2 via a sol-gel method

4.3 Catalyst characterizations

In order to determine physical and chemical properties of catalysts, various characterization techniques were employed. Such techniques are discussed in this section.

4.3.1 X-ray diffractometry (XRD)

XRD was performed to determine crystal phase and crystallite size of titanium dioxide. It was conducted using a SIEMENS D500 X-ray diffractometer with CuK_{α} radiation (λ = 1.54439 A°) with Ni filter. The spectra were scanned at a rate of 0.02° min^{-1} in the 2θ range of 20-80°.

4.3.2 Nitrogen physisorption

Specific surface area was measured through nitrogen adsorption in a continuous flow method at liquid nitrogen temperature. A mixture of nitrogen and helium was employed as the carrier gas using Micromeritics ChemiSorb 2750 Pulse Chemisorption System instrument. The sample was thermally treated at 200 °C for 1 hour before each measurement.

4.4 Photocatalytic degradation of organic dyes

The apparatus, materials, and experimental procedures employed to evaluate the performance of photocatalytic degradation of organic dyes in an airlift reactor is described in this section. In this study, two different dyes were used. The effect of two parameters of concerns in airlift reactor, i.e., draft tube diameter and aeration rate, were investigated. The effect of initial concentration of dyes, pH of dye solution and different types of photoreactor systems were also studied.

4.4.1 Apparatus

The three different photoreactor systems were already described in Section 4.1. Figure 4.5 shows the airlift reactor system used in this study.

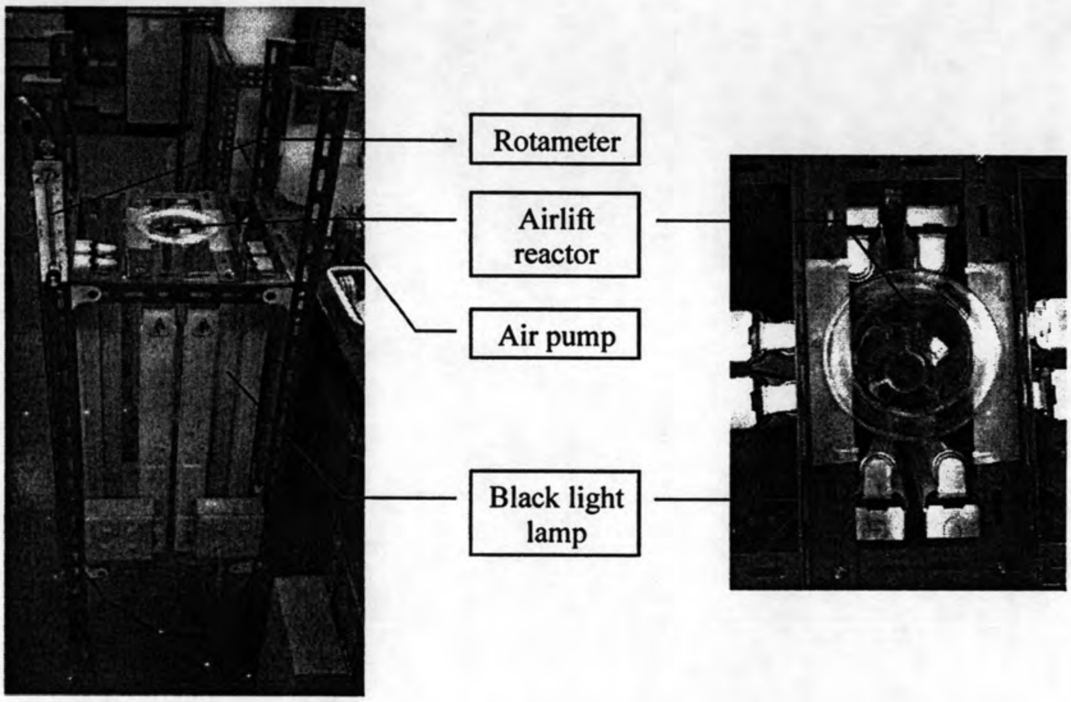
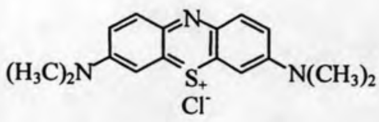
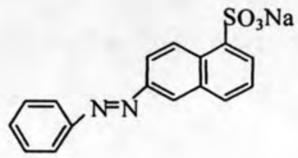


Figure 4.5 Airlift reactor system. A top view of the system is shown on the right.

4.4.2 Material

Titanium dioxide was synthesized by a sol-gel method and was used as the photocatalyst. Two dyes namely, Crocein Orange G (Sigma-Aldrich) and Methylene blue (Unilab, Asia Pacific Specialty Chemicals Limited) were used in the study. The dye solutions were prepared using water from a Millipore Waters Milli Q purification unit. Table 4.1 shows the characteristics of the two dyes.

Table 4.1 Characteristics of the two dyes.

Dye	Chemical formula	Chemical structure	MW (g/mol)	λ_{max} (nm)
Crocein Orange G (OG)		azoic	350.33	495
Methylene Blue (MB)		hetero-poly aromatic	356	660

4.4.3 Procedure

The volume of the aqueous solution of each dye in an airlift ractor was 3000 ml. The initial concentrations of dye use one 5 ppm, 10 ppm, and 15 ppm. Approximately 3 g of powder TiO_2 was added (1 g/l) to the reactor. The suspension was first stirred in the dark for 60 min before irradiation to reach adsorption equilibrium as deduced from the constant concentrations. First, investigation of the effect of draft tube diameter was performed. Each draft tube diameter was placed in an airlift reactor and the photocatalytic degradation study was performed. After that, the draft tube diameter with the better performance was chosen for subsequent experiments. To study the effect of aeration rate, three aeration rate were employed, i.e., 6 l/min, 9 l/min, and 12 l/min. The pH of the solution was adjusted by using either NaOH or HNO_3, the detail of which is displayed in Table 4.3. Then, the best conditions for each parameter were chosen to study the photocatalytic degradation of each dye in different of photoreactor systems. The procedure as described above is shown schematically in Figure 4.6

Table 4.2 Experimental details for airlift systems with two draft tubes diameter.

Draft tubes diameter (cm)	Riser area, A_r (cm^2) (Draft tubes area)	Downcomer Area, A_d (cm^2)	A_d/A_r
4.6	16.63	49.78	3.05
6.6	34.23	30.93	0.90

Table 4.3 Experimental details for adjustment of the solutions pH

Dye solutions	pH	Adjusted by
Crocein Orange G	2	HNO_3
	4	HNO_3
	5.57	Natural pH
	8	NaOH
Methylene Blue	4	HNO_3
	5.37	Natural pH
	8	NaOH
	10	NaOH

For the photocatalytic degradation in stirred tank reactor, the volume of the aqueous solution of each dye in the stirred tank reactor was reduced to 1500 ml, in which 1.5 g of powder TiO_2 was added (1 g/l).

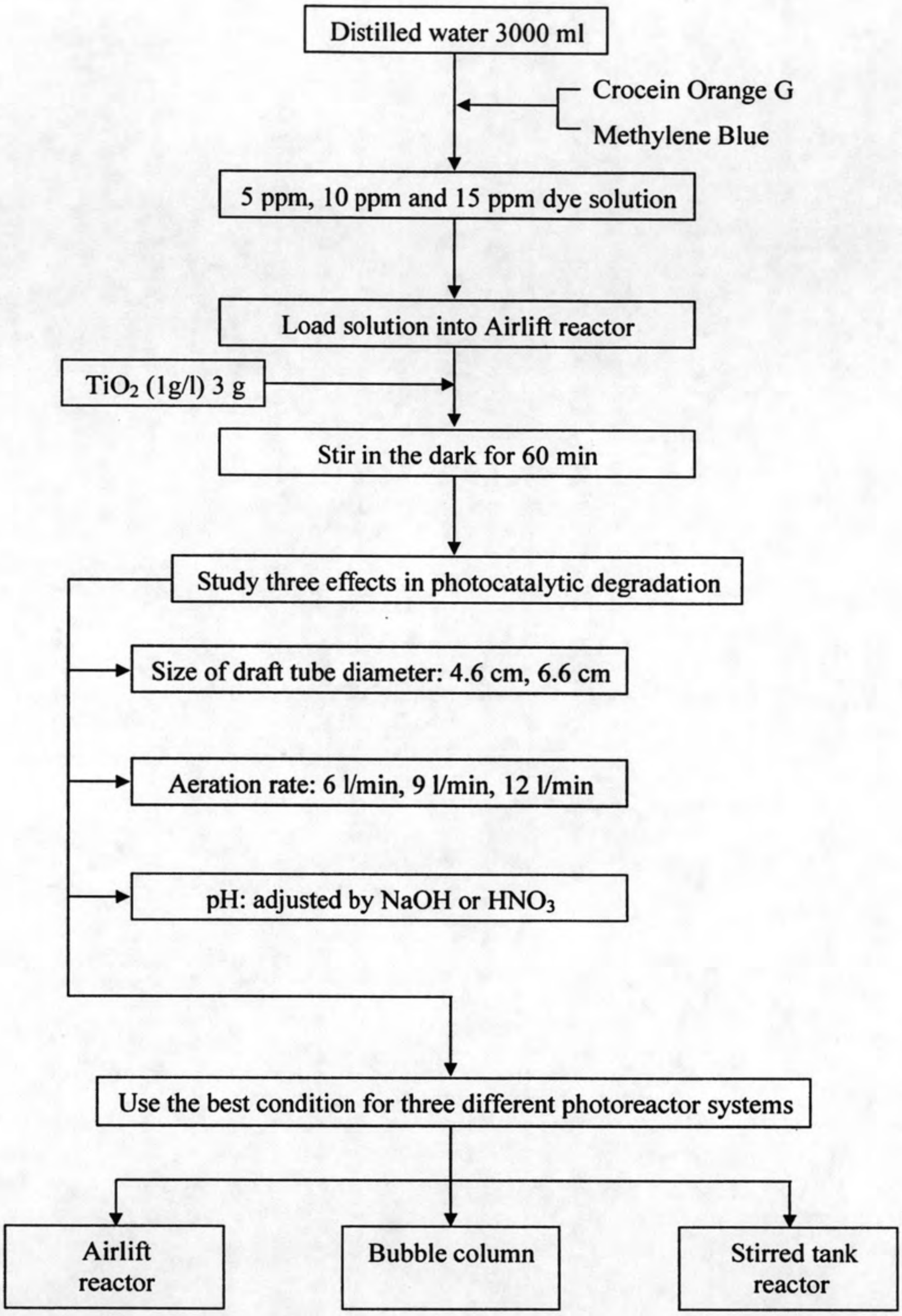


Figure 4.6 Schematic diagram of the experimental procedure.

4.4.4 Analytical methods

The photocatalytic degradation of each dye was monitored through the disappearance of color using UV–visible spectrophotometer (Perkin Elmer Lambda 650). The calibration curves of crocein orange G and methylene blue solution based on Beer–Lambert's law was prepared at 495 and 660 nm in wavelengths, respectively in order to determine the concentration of dyes at different reaction time by converting the absorbance of the sample to dyes concentration.

Samples (5 ml) were taken out directly from the photoreactor systems using a syringe. Then the sample was centrifuged to separate TiO_2 agglomerates from the solution before analysis.

The amount of dissolved oxygen in solution was measured using Mettler Toledo O_2 Transmitter 4500.

The light intensity was measure by International Light IL 1700 Research Radiometer connected with the SED005#973 detector, WBS320#27818 filter, and W#11513 input optic with the response wavelength in range 250-400 nm.