CHAPTER III

EXPERIMENTAL

3.1 Preparation of TiO_2 and ZnO

3.1.1 Synthesis of titania particles

Titania (TiO_2) was prepared by sol-gel method, according to the method proposed by Tian et al [5]. Tetrabutyltitanate (TBT, 97%, Fluka) was used as the starting material. First, 5 ml of TBT was dissolved in 20 ml ethanol and stirred for 30 minutes to get the precursor solution. Then, a mixture of 0.26 ml distilled water, 3.4 ml glacial acetic acid, 0.18 ml hydrochloric acid and 5 ml ethanol were added to the precursor solution under vigorous stirring. After stirring about 1 hour, the solution became transparent yellow. Now, titania sol was obtained. The titania sol was gelled at room temperature about 24 hours and dried at 80°C for 12 hours in an oven. Then, ammonia solution with mass fractions of 0%, 7% or 28% was dropped into the gel and left for 24 hours at room temperature. After that, the obtained product was calcined at 500°C for 2 hours in a box furnace with the heating rate of 1°C/min.

3.1.2 Synthesis of zinc oxide particles

Zinc oxide (ZnO) was prepared according to the method proposed by Tian et al. [5] as well. Zinc acetate (99.5%, UNIVAR) was used as a precursor to prepare ZnO sol. At first, 3.29 g of zinc acetate was dissolved in 20 ml ethanol and stirred for 5 min at 50°C to get the precursor solution. A mixture of 0.26 ml distilled water, 1.58 ml diethanolamine (98.5%, UNILAB), 0.18 ml hydrochloric acid, and 5 ml ethanol was dropped into the precursor solution under vigorous stirring. After stirring for 2 hours, a transparent ZnO sol was obtained. The ZnO sol was gelled at room temperature about 24 hours and dried at 80°C for 24 hours in an oven. Then, ammonia solution with mass fraction of 0%, 7% or 28% was dropped into the gel and left to rest for 24 hours at room temperature. After that, the obtained product was calcined at temperature in the range of 500°C for 2 hours in a box furnace with heating rate of 1°C/min.

3.1.3 Characterizations of photocatalysts

Synthesized photocatalysts were characterized by various techniques.

Phase composition of the powder was determined by X-ray diffraction (XRD) by a Siemens D5000 X-ray diffractometer using Ni-filtered CuKa radiation. The measurements were carried out in the 2θ range of 20-80 degree at the scan step of 0.04 degree. The crystallite size calculated from the half-height width of the diffraction peak of XRD pattern using the Debye - Scherer equation.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{27}$$

where D is crystal size, λ is wavelength of X-ray, β is full width at half maximum, θ is diffraction angle.

The particle morphology was investigated by Scanning Electron Microscopy (SEM) model JSM-6400 at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University.

The surface area, pore volume and pore size were measured by Belsorp-Mini II adsorption analyzer using nitrogen as the adsorbate at the Center of Excellence on Particle Technology, Chulalongkorn University. The operating conditions are as follows:

Sample weight	~ 0.1- 0.2 g
Degas temperature	200°C
Vacuum pressure	< 10 mmHg

The thermal behavior was analyzed by Thermo-gravimetric analyzer (TGA) Model NETZSCH STA 409. The operating conditions are heating rate of 10°C/min from room temperature to 1000°C in air.

Finally, The ultraviolet–visible reflectance of all samples was analyzed by a UV – vis spectroscopy (Lambda 650, Perkin Elmer, USA).

3.2 Adsorption Studies

All adsorption equilibrium experiments of diuron on the TiO_2 and ZnO surface were carried out in 250 ml pyrex reactor under strong stirring and in the absence of light. Studies were conducted with suspensions prepared by mixing 550 ml of solution of diuron in various initial concentrations (1-20 ppm) and photocatalyst concentration of 1 mg/10 ml diuron solution at room temperature (27-30°C) for 3 hours. Changes of diuron concentration were measured by (HPLC), model Class VP (Shimadzu) and C18 column (Phenomenex Luna 5 μm particle size, 250×4.6 mm). The mobile phase was consisted of 70% acetronitrile and 30% deionization water with flow rate of 1.5 ml/min. Function groups of diuron solution after adsorbed by catalyst were identified by using Fourier Transform Infrared Spectrophotometer (FT-IR) Model Spectrum One (Perkin Elmer). Infrared spectra were recorded between wavenumber of 400 and 4000 cm^{-1}. The changing in the structure of diuron after adsorbed by catalyst was identified by using Fourier Transform Nuclear Magnetic Resonance (NMR, ^{13}C: 125.777MHz, ^{1}H: 500.157 MHz) Model INOVA (Varia). In all experimentals, CD_3OD were used as solvent.

3.3 Photocatalytic Degradation Procedure

The photocatalytic activities of the synthesized photocatalysts were determined from the photodegradation of diuron (99.5%,N-(3,4-dichlorophenyl)-N,N-dimethyl urea) under UV irradiation. The photodegradation was conducted in a 600 ml pyrex reactor (the set up of the reaction system is shown in Figure 3.1), in which 550 ml of diuron solution (with predetermined concentration) and photocatalysts were added. The content of the photocatalyst was kept at 1 mg of the catalyst per 10 ml of the solution (initial diuron concentration 10 ppm). The mixture was kept in dark for 30 min to allow the complete adsorption of diuron on the surface of catalysts, prior to the reaction. After that, the solution was irradiated with six UV-A lamps (Phillips TLC 15w/05). During irradiation, agitation was maintained by a magnetic stirrer to keep the catalyst uniformly dispersed within the solution. The suspension was periodically sampled to monitor the concentration of diuron via a reverse-phase liquid chromatography (HPLC), model Class VP (Shimadzu) and C18 column (Phenomenex Luna 5 μm particle size, 250×4.6 mm). The mobile phase was consisted of 70% acetronitrile and 30% deionization water with flow rate of 1.5 ml/min.The organic matter within the sample was measured by Totoal Organic Carbon (TOC) analyzer model TOC-V_{CPH} (carier gas flow rate 150 ml/min, 680°C catalytically-aided combustion oxidation/non–dispersive infrared detection). Identification of the reaction intermediates formed during the photocatalytic degradation of diuron was done by LC-MS analysis (LC/MSD SL, Agilent technologies) with UV detector and MS detector (Single Quadrupole,Model G1956B, Agilent technologies). For the LC-MS analysis, column was Phenomenex Luna, 3 μm particle size, 150×2 mm, while the mobile phase was 70% acetronitrile mixed with 30% water. The mass spectral data were obtained in both negative and positive ion mode, using fragmentor potential of 120 V.

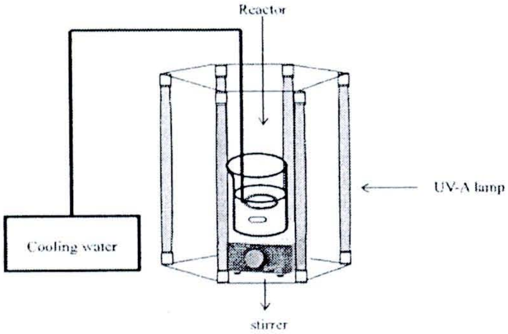

Figure 3.1 Diagram of the equipment setup for the photocatalytic degradation.