

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Materials and Chemicals

- 1) Phenol (AR grade purchased from TS Interlab Limited)
- 2) Formaldehyde 37 % (AR grade purchased from TS Interlab Limited)
- 3) Diethylenetriamine (DETA) (purity 99% purchased from Sigma-Aldrich)
- 4) Pentaethylenehexamine (PEHA) (Technical grade purchased from Sigma-Aldrich)
- 5) Chloroform (AR grade purchased from RCI Labscan Limited)
- 6) Xylene (AR grade purchased from RCI Labscan Limited)
- 7) Sodium hydroxide (NaOH) (AR grade purchased from RCI Labscan Limited)
- 8) Sodium sulfate (Na_2SO_4) (AR grade purchased from TS Interlab Limited)
- 9) Silicone oil
- 10) Acetone (AR grade purchased from RCI Labscan Limited)
- 11) Carbon dioxide (CO_2) (purity 99.99 % purchased from Praxair Inc.)
- 12) Helium (purity 99.999 % purchased from Praxair Inc.)

3.1.2 Equipment

- 1) Fourier Transform Infrared Spectrometer (FTIR) (Thermo Nicolet, Nexus 670)
- 2) Differential Scanning Calorimeter (DSC) (PerkinElmer, model DSC)

- 3) Thermogravimetric Analysis (TGA) (PerkinElmer TG/DTA, model II Diamond)
- 4) Surface Area Analyzer (SAA/Sorptomatic) (Thermo Finnigan, Sorptomatic 1990)
- 5) CHN Analyzer (Leco, model TruSpec Micro CHNS)
- 6) X-ray Photoelectron Spectroscopy (XPS) (Kratos Axis Ultra DLD)
- 7) Scanning Electron Microscope (SEM) (TM3000/Hitachi and JEOL-JSM 8000LV)
- 8) Simultaneous Thermogravimetric Analyzer (STA) (Netzsch STA 449 Jupiter)
- 9) Volumetric adsorption apparatus

3.2 Experimental Procedures

3.2.1 Preparation of Benzoxazine Monomer

Benzoxazine monomer was prepared from phenol, formaldehyde and diethylenetriamine (DETA), using the method suggested by Hirikamol (2013). The synthesis was started by mixing phenol, formaldehyde and DETA in the mole ratio of 2:4:1 in a three-necked flask. Then, chloroform was added and refluxed with stirring for 6 hours. After that, the yellow product was obtained. This yellow product was washed several times by 1N NaOH solution and rinsed with distilled water until neutral. The products were dried with 10 mg sodium sulfate (Na_2SO_4) and filtered. The solvent product was eliminated by evaporation under reduced pressure in the rotary evaporator. Finally, a pale yellow solid product was obtained.

Another benzoxazine precursor was prepared from phenol, formaldehyde and pentaethylenehexamine (PEHA) in the mole ratio of 2:4:1 and prepared following the method previously reported. Both synthesis reactions of benzoxazines were shown in Figure 3.1.

3.2.2 Preparation of Polybenzoxazine Aerogel

Porous polybenzoxazine via sol-gel technique was prepared, using the method suggested by Lorjai *et al.* (2009). In the beginning, benzoxazine monomer

was mixed with xylene to obtain the benzoxazien solution which was kept at 30 wt%, 35 wt% and 40 wt%. Then, the mixture was moved into vials and sealed. These vials were placed in an oven at a temperature of 130 °C for 16 hours. After this, these obtained products were partially cured to obtain benzoxazine hydrogels. In order to remove the remaining xylene from benzoxazine matrix, the benzoxazine hydrogels were exchanged with acetone for 4 days. After that, the porous benzoxazines were fully cured at 160 °C for 1 h and 180 °C for 45 minutes in an oven. Finally, polybenzoxazine aerogels were obtained after they were left to cool down to room temperature.

3.2.3 Preparation of PBZ Aerogel Loading with Non-ionic Surfactant

Benzoxazine monomer was mixed with 6 wt% of PEG-PPG-PEG block copolymer (non-ionic surfactant) in xylene. The concentration of benzoxazine monomer was kept at 30 wt%. After this, this mixture was prepared via a sol-gel technique as mentioned in the previous subsection.

3.2.4 Preparation of Carbon Aerogel or Activated Carbon from PBZ

Polybenzoxazine aerogel or bulk PBZ was carbonized in a quartz reactor under an inert atmosphere of nitrogen with a flow rate of 100 ml/min. The flow ramp cycle was started from 30 to 200 °C with a heating rate of 3 °C/min, 200 to 700 °C with a heating rate of 1 °C/min, 700 to 800 °C with a heating rate of 3 °C/min, and finally holding at 800 °C for 1 hour. After that, carbon aerogel was activated in a CO₂ atmosphere at 800 °C for 2 hours. Finally, the activated carbon from polybenzoxazine aerogel was obtained.

Another carbon aerogel or bulk PBZ was activated at 900 °C for 2 hours under CO₂ atmosphere which was denoted as CA-X, where X is the activating temperature.

3.3 Characterizations of Benzoxazine and Adsorbents-derived from PBZ

3.3.1 Fourier Transform Infrared Spectrometer (FTIR)

Fourier Transform Infrared Spectrometer (FTIR) was employed to receive the absorption spectra and to analyze the functional groups of all materials derived from PBZ. In case of benzoxazine monomer, it was placed on the ZnSe plate and then dried in an warm air drier. After this, it was run in the ratio mode allowing for subtraction of a pure ZnSe baseline. In particular, the spectrometer was set to collect 64 spectra in the range between 500-4000 cm^{-1} with a resolution of 4 cm^{-1} . Finally, the absorption spectra of the sample was performed.

To obtain FTIR spectra from polybenzoxazine, benzoxazine monomer was placed and fully cured on the ZnSe plate in an oven at the curing conditions of 120 °C for 30 min, 160 °C for 60 min, and 180 °C for 45min. Then, it was operated by the FT-IR analyzer with the same parameters as the characterization of benzoxazine monomer. After the test, an infrared spectrum of adsorption was provided.

3.3.2 Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) was employed to examine the curing behavior of the benzoxazine to determine whether a synthesis of PBZ was fully cured. In this method, each sample was used about 5-9 mg. First, the sample was sealed in an aluminum pan and then analyzed using the temperature ramp rate of 10 °C/min under nitrogen atmosphere. After this, the exothermic peak of benzoxazine was observed and evaluated.

3.3.3 Thermogravimetric Analysis (TGA)

The TGA thermogram of each sample was obtained using the thermogravimetric analyzer (PerkinElmer TG/DTA) with a model SII Diamond. The experimental condition was started from 30 °C to 800 °C or 900 °C by a heating rate of 20 °C/min under an inert atmosphere of nitrogen with a flow rate of 20 ml/min.

3.3.4 Surface Area Analyzer (Sorptomatic)

Surface Area Analyzer (Sorptomatic 1990 Analyzer) was employed to determine the specific surface area, total pore volume, pore size, and pore size distribution of the samples. In all adsorption tests, the carbon materials were degassed under vacuum at 300 °C for 18 hours to remove any volatile adsorbed gases existed on an adsorbent surface. Then, carbon material was placed in the analysis station and operated with N₂ gas under the temperature of -196 °C to obtain an adsorption isotherm. The BET surface area of the sample was measured from the Brunauer-Emmett-Teller (BET) equation. The calculated micropore volume could be obtained by using the HV (Horvath Kawazoe) theory. Furthermore, the calculation of mesopore volume was received by using the BJH (Barrett-Johner-Halendar) theory.

3.3.5 CHN Analyzer

CHN analyzer (LecoTruSpec) was employed to measure three elemental compositions including carbon (C), hydrogen (H) and nitrogen (N) of all materials from PBZ. Before the test, each sample should be dried overnight in a vacuum oven to remove all moistures. In the preparation of sample, each sample was suggested about 0.15 g and placed on a tin foil. Then, it was wrapped and put into the CHN machine for analyzing at 950 °C. Finally, ultimate analysis of each sample was performed.

3.3.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was employed to determine the number and functional groups presented on the surfaces of all adsorbent from PBZ. In the beginning, the samples were placed on the stub bar and brought to degas under an ultra-high vacuum condition in the XPS machine. Then, they were run using a wide scan by resolution pass energy of 160 eV. After all considered components were inspected, the narrow scans were operated at a resolution pass energy of 20-40 eV in order to determine the amount and types of functional groups (e.g., carbon (C 1s), oxygen (O 1s), and nitrogen (N 1s)) on the surface of adsorbents.

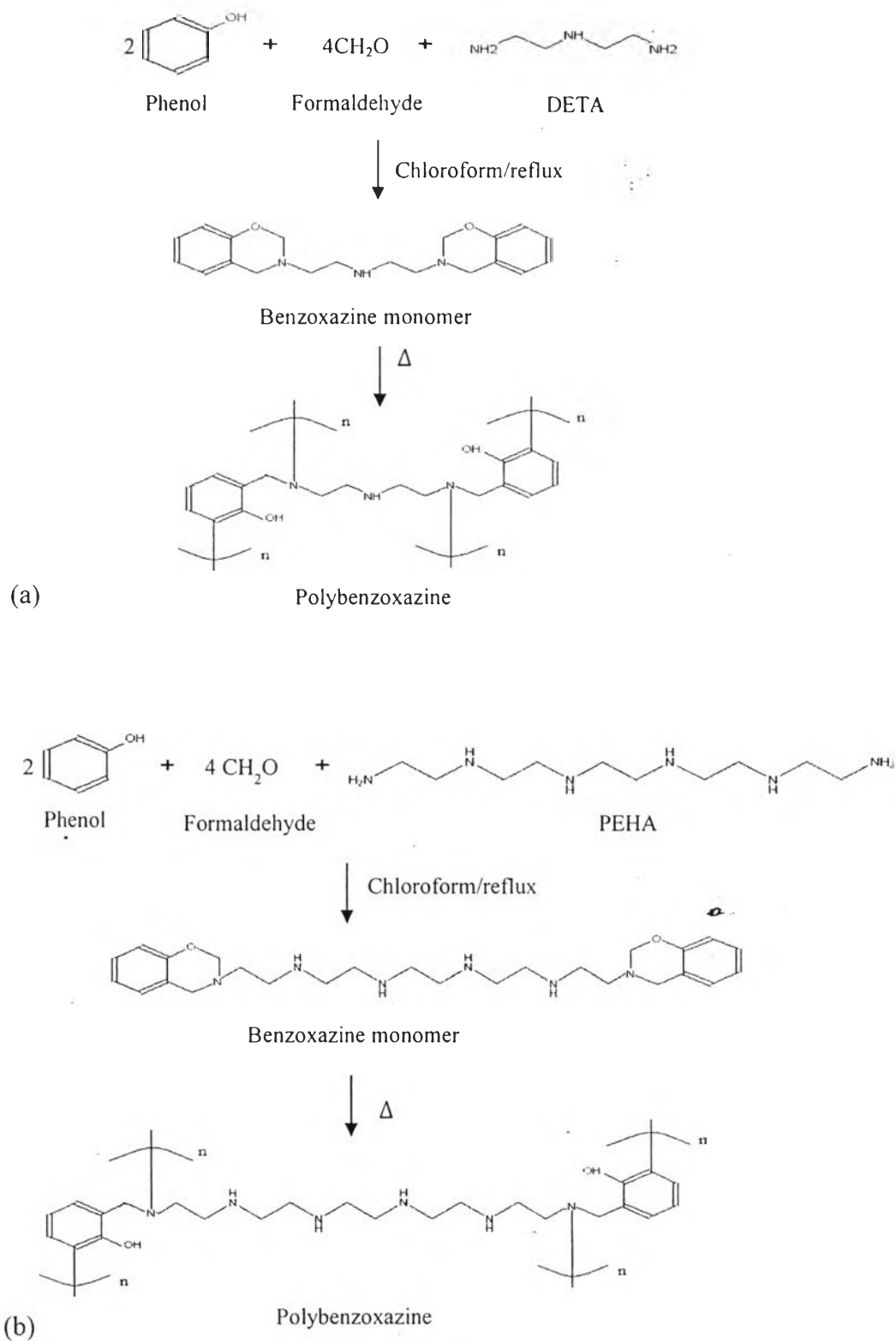


Figure 3.1 The polybenzoxazine synthesis reactions (a) Polybenzoxazine-based on DETA and (b) Polybenzoxazine based on PEHA.

3.3.7 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) was employed to investigate the surface morphology of all adsorbents from PBZ. First, the samples were placed on a carbon sticky tape and then coated with gold before the microstructure image of the sample was taken. After this, all parameters were set and the image of sample was captured by a magnification from 600 to 5,000 times.

3.4 Adsorption Measurement

3.4.1 Pressure Decay Method

The adsorption apparatus was employed to measure the amount of CO₂ adsorption in the adsorbent. All tubings and fittings were made of high quality stainless steel to avoid corrosion along the process. The sizes of reservoir and sample cell were 150 and 10 ml, respectively. Also, the volume of sample cell was measured using helium expansion and calculated from the ideal gas law (shown in Equation 3.1). The temperature was controlled at the same value throughout the reservoir and the sample cell. At first, the sample was placed in the sample cell and heated up to the desired temperature. Then, the sample was degassed to remove the residual gas moisture. After that, the lower needle valve was closed and fed with the CO₂ for pre-expansion pressure. The lower needle valve (NV-2) was closed to isolate the sample cell. The reservoir was then charged with CO₂ and the top needle valve (NV-1) was closed. After the pressure and temperature were stabilized, the lower needle valve was opened and the adsorption experiment was started and run until the equilibrium was reached. Then, the CO₂ adsorption capacity was determined by measuring the beginning pressure and equilibrium pressure. After that, Equation 3.2 was used to determine the amount of CO₂ adsorption.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (3.1)$$

Where P_1 = Pressure of helium before expansion
 V_1 = Volume of the system excluding sample cell

T_1 = Temperature before helium expansion

P_2 = Pressure of helium after expansion

V_2 = Total Volume, $V_1 + V_{\text{sample cell}}$

T_2 = Temperature after helium expansion

$$n_{ad} = \frac{P_i V_1}{z_i R T_i} - \frac{P_f (V_1 + V_{\text{sample cell}} + V_{\text{solid adsorbent}})}{z_f R T_f} \quad (3.2)$$

Where

- n_{ad} = Amount of CO_2 adsorbed in the adsorbent
- P_i = Initial CO_2 pressure, before experiment
- P_f = Final CO_2 pressure, at equilibrium
- V_1 = Volume of the system excluding sample cell
- $V_{\text{sample cell}}$ = Volume of the sample cell
- $V_{\text{solid adsorbent}}$ = Volume of the solid adsorbent
- z_i = Compressibility factor of CO_2 adsorbed before experiment

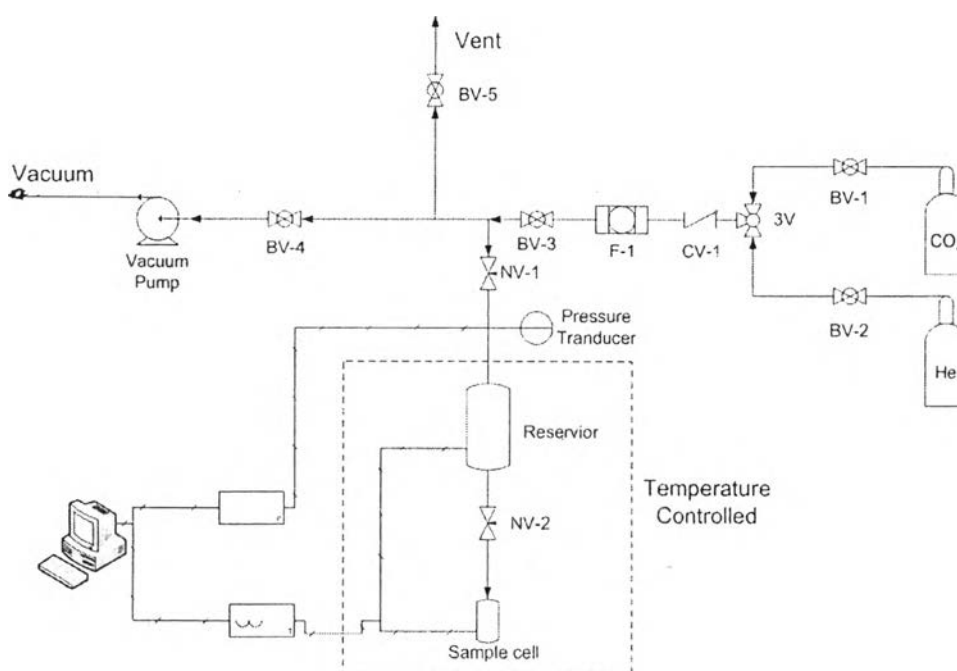


Figure 3.2 Schematic diagram of the adsorption system.

3.4.2 Gravimetric Method

Simultaneous Thermal Analyzer (STA) (Netzsch STA 449 F3 Jupiter) was employed to measure the adsorption and desorption capacities of each adsorbent.

- Approximately 10 mg of adsorbent was loaded in a Al_2O_3 crucible and placed into the STA analyzer. Then, the adsorbent was heated to remove moisture and adsorbed gas at $100\text{ }^\circ\text{C}$ under 100 mL/min of N_2 flow and hold for 30 min. After that, the sample was heated to the desired temperature at $5\text{ }^\circ\text{C/min}$ and hold for 30 min to ensure that the temperature was stabilized. Then the gas flow was switched to CO_2 at 100 mL/min and started determining the adsorption capacity. Finally, CO_2 was switched to N_2 at the same flow rate to determine desorption capacity at the same temperature.