

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipments

#### 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) Pentaethylenhexamine (PEHA) (Technical grade purchased from Sigma-Aldrich)
- 5) Chloroform (AR grade purchased from RCI Labscan Limited)
- 6) Sodium hydroxide (NaOH) (AR grade purchased from RCI Labscan Limited)
- 7) Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) (AR grade purchased from TS Interlab Limited)
- 8) Acetone (AR grade purchased from RCI Labscan Limited)
- 9) Carbon dioxide (HP grade, purity 99.99% purchased from Praxair Inc.)
- 10) Nitrogen (HP grade, purity 99.99% purchased from Praxair Inc.)
- 11) Activated carbon (supported by Carbokarn Co., Ltd.)

#### 3.1.2 Equipments

- 1) Valves and fittings (purchased from Swagelok)
- 2) Surface area analyzer (Sorptomatic)
- 3) Simultaneous thermal analyzer (STA)
- 4) Fourier transform infrared spectrometer (FTIR)
- 5) X-ray photoelectron spectroscopy (XPS)
- 6) CHN analyzer
- 7) Scanning electron microscope (SEM)

## 3.2 Experimental Procedures

### 3.2.1 Preparation of Benzoxazine

Benzoxazine was synthesized from phenol, formaldehyde and two types of amines by using the method that was modified from the work of Su and Chang (2003). Briefly, phenol: formaldehyde: amine in the mole ratio of 2:4:1 were mixed in a three-necked flask, and chloroform was added as a solvent. The reaction mixture was refluxed with stirring for a varying time about 4-6 days. The yellow product was obtained. Then the product was washed several times by 1N NaOH solution and then was rinsed with distilled water until neutral. The base washed products was dried with 10 mg sodium sulfate and filtered. The solvent was then evaporated by using rotary evaporator. Finally light yellow solid product of benzoxazine monomers derived from DETA and PEHA was obtained.

### 3.2.2 Impregnation of Adsorbent

The adsorbent using activated carbon is impregnated by benzoxazine by adapting wet impregnation method (Arenillas *et al.*, 2005) as follows:

- a. A desired amount of benzoxazine was dissolved in 10 mL of chloroform.
- b. Dissolution of the benzoxazine was performed by mechanical mixing for 15 min.
- c. An amount of activated carbon that made the mixture to 2 g is added.
- d. The resultant slurry was mechanically mixed for a further 30 min to ensure a complete penetration of benzoxazine into activated carbon.
- e. The impregnated activated carbon is cured at 120 °C for 90 min and following by 180 °C for 90 min.

### 3.2.3 Carbonization and Activation of Polybenzoxazine Adsorbent

The polybenzoxazine adsorbent was prepared by carbonizing and activating itself as follows:

- a. Benzoxazine was cured to form polybenzoxazine at 120 °C for 90 min and following by 180 °C for 90 min in the oven.

b. Polybenzoxazine was carbonized at varying temperatures (200 °C, 300 °C, and 400 °C) with a heating rate of 10 °C/min and hold for 1 hr under N<sub>2</sub> atmosphere.

c. Finally, the product was heated at 10 °C/min to 800 °C and activated by CO<sub>2</sub> for 1 hr.

### 3.3 Characterization of Polybenzoxazine-based Adsorbent

#### 3.3.1 Surface Area Analyzer (Sorptomatic) (Thermo Finnigan, Sorptomatic 1990)

The series of polybenzoxazine impregnated activated carbon and polybenzoxazine activating sorbent were characterized by Surface area analyzer (Sorptomatic) to determine the BET surface area, pore volume and pore size distribution. The sample was out gassed under vacuum at 150 °C around 15 hours to remove any water or adsorbed gas on the surface. Then N<sub>2</sub> was purged to adsorb on the surface and adsorption isotherms are performed at -196 °C. The BET surface area, S<sub>BET</sub>, was determined from the linear part of the Brunauer-Emmett-Teller (BET) equation and the calculation of pore size distribution was performed using Horvath Kawazoe (HK) equation using the full isotherms method.

#### 3.3.2 Simultaneous Thermal Analyzer (STA) (Netzsch STA 449 F3 Jupiter)

Simultaneous Thermal Analyzer (STA) was employed to determine the decomposition of polybenzoxazine series. Each adsorbent was heated to 800 °C with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere (100 mL/min flow-rate).

#### 3.3.3 Fourier Transform Infrared Spectrometer (FTIR) (Thermo Nicolet, Nexus 670)

Fourier Transform Infrared Spectrometer (FTIR) was employed to obtain an infrared spectrum of absorption and evaluate the functional groups of benzoxazine. The benzoxazine sample was put on the ZnSe plate and put them to the holder. The polybenzoxazine sample was prepared by curing benzoxazine that is on the ZnSe plate at 120 °C for 90 min and following by 180 °C for 90 min in the oven.

The samples were run in spectrometer and were collect at 64 spectra in the range between 400-4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

#### 3.3.4 X-ray Photoelectron Spectroscopy (XPS) (Kratos Axis Ultra DLD)

X-ray photoelectron spectroscopy (XPS) was employed to determine the surface functional groups presented on the surfaces of the modified adsorbent before and after  $\text{CO}_2$  adsorption. The sample was out gassed under an ultra-high vacuum condition and a wide scan was performed at resolution pass energy of 160 eV. For high resolution or narrow scans are performed at resolution pass energy of 20-40 eV for determining the quantity and functional groups (C1s, O1s and N1s) on the surface of sample.

#### 3.3.5 CHN Analyzer (Leco TruSpec)

CHN analyzer was used to analyze the 3 elemental compositions including carbon (C), hydrogen (H) and nitrogen (N). A 0.15 g of impregnated adsorbent was put in the tin foil and wrapt it. Then put the foil pack of adsorbent into the CHN analyzer and analyzed at 950  $^{\circ}\text{C}$ .

#### 3.3.6 Scanning Electron Microscope (SEM) (Hitachi. TM 3000)

Scanning electron microscope (SEM) was employed to analyze the surface morphology of the untreated activated carbon, both polybenzoxazine and impregnated adsorbent. The sample was placed on the carbon tape then it was coated with platinum under vacuum. The SEM images were captured at a magnification of 9,000 times from the range of 40 to 20,000 times.

### **3.4 Adsorption System**

The adsorption and desorption capacities of each adsorbent were measured from gravimetric method by Simultaneous Thermal Analyzer (STA) (Netzsch STA 449 F3 Jupiter).

a. 10 mg of adsorbent was loaded in a  $\text{Al}_2\text{O}_3$  crucible and placed into the STA analyzer.

b. The adsorbent was heated to remove moisture and adsorbed gas at 100  $^{\circ}\text{C}$  under 100 mL/min of  $\text{N}_2$  flow and hold for 30 min.

c. The sample was heated or cooled to the desired temperature (40 °C, 75 °C, and 140 °C) at 5 °C/min and hold for 30 min to ensure that the temperature was stabilized. Then the gas flow was switched to CO<sub>2</sub> at 100 mL/min and started determining the adsorption capacity.

d. Finally, CO<sub>2</sub> was switched to N<sub>2</sub> at the same flow rate to determine desorption capacity at the same temperature.