CHAPTER III
EXPERIMENTAL

3.1 Materials

Bisphenol-A ($C_{15}H_{16}O_2$) was purchased from Aldrich, Germany. Formaldehyde (CH_2O) was purchased from Merck, Germany. Tetraethylenepetamine (TEPA, $C_8H_{23}N_5$) was purchased from Fluka, Switzerland. 1,4- Dioxane ($C_4H_8O_2$) was purchased from Labscan, Ireland. All chemicals were used without further purification to synthesize polybenzoxazine aerogel. The model trace contaminants were chromium(II), cadmium(II), copper(II), iron(II), manganese(II), nickel(II), lead(II), tin(IV), zinc(II) and phosphate. Solutions containing metal salts in the form of nitrate: chromium(II), copper(II), iron(II), manganese(II), nickel(II), lead(II) and zinc(II) were of analytical grade and purchased from Merck, Germany; except cadmium(II) nitrate was purchased from Fluka, Switzerland. Tin(IV) in the form of chloride was purchased from Merck, Germany. Sodium phosphate was purchased from Carlo Erba Reagent, Italy. Concentrated hydrochloric acid and sodium hydroxide (J.T. Baker, USA and Carlo Erba, Italy, respectively) were used to adjust pH. Phosphate was analyzed following the ascorbic acid method described in the standard methods for the examination of water and wastewater. Reagents which were used for determine amount of phosphate are potassium antimonyl tartrate ($K(SbO)C_4H_4O_6 \cdot {}^1/_2H_2O$) purchased from Riedel-de Haen, Germany, amonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot H_2O$) purchased from Lab-Scan, Thailand, ascobic acid ($C_6H_8O_6$) purchased from POCH, Poland. All solutions were prepared by using deionized water.

3.2 Measurements

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

A Fourier Transform Infrared Spectroscope (FT-IR), Nicolet 670, was used to identify structural characteristics of polybenzoxazine-based aerogel. Potas-

sium bromide (KBr) pellet technique was applied in the preparation of powder samples.

3.2.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (DSC), Perkin-Elmer DSC 7, was used to study the thermal behavior of partially-cured and fully-cured polybenzoxazine. The samples were heated from 30 °C to 280 °C at a heating rate of 10 °C/min under N2 atmosphere with a flow rate of 10 ml/min.

3.2.3 Scanning Electron Microscopy (SEM)

Surface morphology of polybanzoxazine-based aerogel was investigated by using a scanning electron microscope, Hitachi S-4800, surface morphology of polybanzoxazine-based aerogel with an accelerating voltage of 15-40 kV. Samples were coated with platinum under vacuum before observation.

3.2.4 Inductive Coupled Plasma Spectrometry (ICP)

Inductive Coupled Plasma Spectrometer, Perkin Elmer Optima 4300V, was used for the quantitative analysis of metal ions in the model wastewater. The calibration method was applied in analysis.

3.3 Experimental

3.3.1 Preparation of Polybenzoxazine-based Aerogel

The polybenzoxazine-based aerogel was synthesized by dissolving bisphenol-A in dioxane, followed by adding formaldehyde solution and TEPA. The mixture was stirred continuously while the reaction was cooled with an ice bath until the homogeneous yellow viscous liquid was obtained. The mole ratio of bisphenol-A: formaldehyde:diamine was 1:4:1. The precursor was left at room temperature until the gel was formed. After that it was placed in an oven at 80°C before solvent being removed by supercritical drying. The obtained polybenzoxazine-based aerogel was then fully cured in an oven.

3.3.2 Characterization of Polybenzoxazine-based Aerogel

The structural characteristics of polybenzoxazine-based aerogel were identified by using FTIR. The morphology was observed by SEM. Furthermore, the thermal property was measure using DSC.

3.3.3 Adsorption Experiments for Heavy Metals

Batch adsorption experiments were performed to determine the heavy metals adsorption. Different heavy metal solutions with different amounts of polybenzoxazine-based aerogel in a range of 50-80 mg were mixed in glass bottles. The mixtures were stirred continuously for 4-48 hours at room temperature and constant rate of stirring. The pH of the mixtures were maintained in a range from 4-5.The mixture were then filtered through Whatman No.42 filter paper. The filtrates were then quantified by using ICP. The adsorption of metals onto the polybenzoxazine-based aerogel was calculated from the difference between initial and final concentration of heavy metals in solution. The adsorption isotherms for each metal were obtained by varying the initial concentration of the metal solutions while the amount of the adsorbent was kept constant.

3.3.4 Adsorption Experiments for Phosphate

Metal-loaded polybenzoxazine was used as a polymeric ligand exchanger for phosphate removal. The adsorption of phosphate on metal-loaded polybenzoxazine was studied by batch experiments. The known weight of metal-loaded polybenzoxazine was equilibrated with known concentration of phosphate solution in a glass bottle. The solution pH was adjusted and maintained at 8-9 during the test. After the equilibrium was attained, the suspension of adsorbent was separated from the solution by flitration using Whatman No.42 filter paper. The remaining concentration of phosphate was analyzed by applying the ascorbic acid method described in the standard methods for the examination of phosphate in wastewater.