



CHAPTER III EXPERIMENTAL

3.1 Materials

Bisphenol-A (BPA, $C_{15}H_{16}O_2$) was purchased from Aldrich, Germany. Formaldehyde (CH_2O , analytical grade) was purchased from Merck, Germany. Triethylenetetramine (TETA, $C_6H_{18}N_4$) was purchased from Fluka, Switzerland. 1,4-Dioxane ($C_4H_8O_2$, analytical grade) was purchased from Labscan, Ireland. All chemicals were used without further purification. Solutions containing metal salts in the form of nitrate: Chromium(II), Copper(II), Iron(II), Manganese(II), Nickel(II), Lead(II), and Tin(II) were of analytical grade and purchased from Merck, Germany; except Cadmium(II) nitrate was purchased from Fluka, Switzerland. Concentrated hydrochloric acid and sodium hydroxide (J.T. Baker, USA and Carlo Erba, Italy, respectively) were used for the adjustment of pH. Sodium chloride (AJAX Chemicals, Australia) was used for desorption experiments. Deionized water was used in all experimental work.

3.2 Measurements

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of benzoxazine precursor were obtained using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples.

3.2.2 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a Mettler Toledo TGA/SDTA 851e instrument. The sample was loaded on the platinum pan and heated from 30° to 800°C at a heating rate of 10°C/min under N_2 flow of 50 mL/min.

3.2.3 Scanning Electron Microscope (SEM)

Scanning electron microscope, JEOL/JSM model 5200, was used to observe the surface morphology of polybenzoxazine-based aerogel. Specimens were coated with gold under vacuum before observation.

3.2.4 Transmission Electron Microscope (TEM)

Transmission electron microscope, JEOL model JEM-2100, was used to observe the porous structure of polybenzoxazine-based aerogel. TEM samples were prepared using the ultra microtome.

3.2.5 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance was used to characterize the chemical structure of polybenzoxazine. ^1H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. The solvent used was deuterated dimethyl sulfoxide (DMSO).

3.2.6 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30° to 300°C at a rate of $10^\circ\text{C}/\text{min}$ under a N_2 atmosphere with a flow rate of $10\text{ ml}/\text{min}$.

3.2.7 Surface Area Analyzer (SAA)

N_2 adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 150°C during 12 h in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Dubinin-Astakhov DA method micropore analysis.

3.2.8 Inductively Coupled Plasma Spectrometer(ICP)

A 50 ml of 1 ppm Cd^{2+} , Cr^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Sb^{2+} , Sn^{2+} and Zn^{2+} solutions and polybenzoxazine-based aerogel (20 to 80 mg) were placed in a glass bottle and shaken for 4 to 48 hr. The quantitative analysis of metal ions was carried out with Inductively Coupled Plasma Spectrometer (ICP) mass spectrometer, Optima 4300DV model PE.

3.3 Methodology

3.3.1 Synthesis of Organic Aerogel from Polybenzoxazine

The benzoxazine aerogel was synthesized by dissolving bisphenol-A (BPA, $C_{15}H_{16}O_2$) in dioxane ($C_4H_8O_2$). Formaldehyde (CH_2O) and Triethylenetetramine (TETA, $C_6H_{18}N_4$) were then added to the solution. The mixture was stirred continuously while the reaction was cooled with an ice bath; yielding partially-cured benzoxazine which was in the form of homogeneous yellowish viscous liquid until homogeneous viscous liquid was obtained. (The mole ratio of bisphenol A: formaldehyde: diamine is 1:4:1). The precured benzoxazine was then placed in the oven at 80°C for 72 hr. in a closed system to evaporate solvent at ambient condition, followed by fully curing with a heating rate of $10^\circ\text{C}/\text{min}$ for 10 hr. under N_2 atmosphere. The organic aerogel was then obtained.

3.3.2 Characteristics of Polybenzoxazine-based Aerogel

The structural characteristics of polybenzoxazine-based aerogel were measured using FTIR and ^1H - NMR. The thermal properties were measured using DSC and TG/DTA. The morphology was observed by SEM. The porous structure of polybenzoxazine-based aerogel was characterized by TEM. Furthermore, the surface area and pore distribution were measured using SAA.

3.3.3 Metal Sorption Studies

Experimental solutions with different amounts of polybenzoxazine-based aerogel were mixed in glass bottle at a given temperature and constant total ion normality in solutions. Essentially, 50 ml of a solution containing the metal-ions with 1 ppm of initial concentration (C_0) was mixed with polybenzoxazine-based aerogel weighted varied from 10 to 80 mg, under constant magnetic stirring, at 298 K. After a time period from 4 to 48 h, the suspension were filtered through $2.5\ \mu\text{m}$ membrane filters and the metal solutions were analyzed.

The control experiments were done in order to confirm that the adsorption of specific metals on the walls of glass bottle or in the filtration systems was negligible.

3.3.4 Desorption Experiments

The polybenzoxazine-based aerogel (80 mg) with adsorbed Sn, obtained from the metal sorption study, was placed in contact with (a) H₂O or (b) 2% (w/v) NaCl solutions at pH 4, 7, 9 while stirring continuously. After 24 hours, the aqueous phase was separated by filtration and the amount of metal released from the polybenzoxazine-based aerogel was determined.

3.3.5 Quantitative Analysis of The Adsorbed Metal-ion on Polybenzoxazine-based Aerogel

The Inductively Coupled Plasma Spectrometer (ICP) mass spectrometer model PE, Optima 4300DV was used for metal ions analysis. Calibration curves were obtained by using 1000 mg.L⁻¹ stock solutions as standards.