

CHAPTER III

EXPERIMENTAL SECTION

3.1 Chemicals

Chemicals used in this experiment were listed in Table 3.1.

Table 3.1 Chemical lists

Chemicals	Suppliers / Grade
Chloromethylated styrene/divinylbenzene copolymer 1% cross-linked, 100-200 mesh, 4.42 mmol Cl ⁻ /g	Aldrich
Cysteamine hydrochloride	Fluka / purum \geq 97% (RT)
1,2-Dibromoethane	Merck / for synthesis
1,3-Dibromopropane	Merck / for synthesis
1,4-Dioxane	Carlo Erba Reagenti / ACS
Dichloromethane	Fisher Chemicals / AR
Dimethyl sulfoxide (DMSO)	Merck / for synthesis
Ethyl alcohol absolute anhydrous	Mallinckrodt (Baker) / ACS
Hydrochloric acid 37%	Merck / ACS
Hydroxylamine hydrochloride	Carlo Erba Reagenti / ACS
Methanol	Merck / ACS
Ninhydrin	Merck / GR
Nitric acid 65%	Merck / ACS
Phenol	Merck / ACS
Potassium cyanide	Merck / GR
Potassium hydroxide	Merck / ACS

Table 3.1 Chemical lists (cont.)

Chemicals	Suppliers / Grade
Pyridine	Merck / GR
Single standard solution for Pb, Zn, Cu and Cr (1000 mg L ⁻¹)	BDH SpectrosoL [®]
Single standard solution for Co, Cd and Ni (1000 mg L ⁻¹)	Fisher Chemicals
Sodium hydrogen carbonate (NaHCO ₃)	Merck / GR
Sodium hydroxide anhydrous pellets	Carlo Erba Reagenti / ACS
Sodium metal, lumps	RDH
Sodium sulphate anhydrous	Carlo Erba Reagenti / ACS
Triethylenetetramine	Fluka / purum ≥ 97% (RT)

3.2 Apparatus

3.2.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectrometer (FT-IR) model Nicolet FT-IR Impact 410 was used for the characterization of all polymers and chelating ligands. Infrared spectra were recorded from 400 to 4000 cm⁻¹ in transmittance mode by KBr pellet technique (for polymers) and neat technique (for chelating ligands).

3.2.2 Fourier transform raman spectroscopy

Fourier transform raman spectrometer (FT-Raman) model Spectrum GX (Perkin-Elmer) was used for characterization of all polymers.

3.2.3 Flame atomic absorption spectrometer

Metal concentrations were determined using flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin-Elmer). The instrumental parameters are shown in Table 3.2.

Table 3.2 FAAS conditions for determination of metal concentration in solutions

Operating conditions	Cd	Cu	Pb	Zn	Ni	Co	Cr
Wavelength (nm)	228.8	324.8	283.3	213.9	232.0	240.7	357.9
Slit width (nm)	0.70	0.70	0.70	0.70	0.20	0.20	0.70
Lamp type	HCL ^a	HCL ^a	HCL ^a	HCL ^a	HCL ^a	HCL ^a	HCL ^a
Lamp current (mA)	4	15	10	15	25	30	25
C ₂ H ₂ flow-rate (mL/min)	3	3	3	3	3	3	3
Air flow-rate (mL/min)	10	10	10	10	10	10	10

^aHallow Cathode Lamp.

3.2.4 Nuclear magnetic resonance spectrometer

Nuclear magnetic resonance spectrometer (NMR) model Varian Mercury+ 400 was used for the characterization of chelating ligands. NMR spectra were recorded in CDCl₃.

3.2.5 CHNS/O analyzer

CHNS/O analyzer PE 2400 Series II (Perkin-Elmer) was used for elemental analysis of all polymers.

3.2.6 pH meter

A pH meter model pH 211 (Hanna instruments) was used for pH measurements.

3.2.7 Mechanical shaker

A shaker model SA-31 (Yamato shaker) was used to shake the solution.

3.2.8 Thermogravimetric analysis (TGA)

Thermogravimetric measurements were performed using Simultaneous Thermal Analyzer (STA) model 409 (Netzsch) at a heating rate of 10 °C/min under nitrogen atmosphere.

3.3 Methodology

3.3.1 Preparation of chemicals and reagents

All solutions were prepared by using deionized water.

a) Working standard solutions

Stock standard solutions 1000 mg L⁻¹ of Pb(II), Ni(II), Zn(II), Cu(II), Cd(II), Co(II) and Cr(III) were used to prepare working standard solutions by stepwise dilution to required concentrations.

b) Potassium hydroxide solutions

The KOH solutions (1%, 5%, 10% and 20% w/v) were prepared by dissolving the appropriate amount of KOH in deionized water.

c) Nitric acid solutions

Nitric acid solutions were prepared daily by direct dilution from the concentrated solution.

3.3.2 Preparation of chelating ligands

a) 2-[3-(2-Amino-ethylsulfanyl)-propylsulfanyl]-ethylamine (AEPE)⁵²

Sodium metal (1 g, 43 mmol) was dissolved in absolute ethanol (20 mL) and then cooled to 15 °C. The cool solution was added to cysteamine hydrochloride (2.3 g, 20 mmol) and stirred for 15 minutes under nitrogen atmosphere. 1,3-Dibromopropane (1.0 mL, 9.8 mmol) was added and stirred for 4 hours at 40 °C. The mixture was evaporated and then sodium hydroxide (5 g in 15 mL water) was added. The solution was kept in a refrigerator overnight. The solution was extracted with dichloromethane, the dichloromethane phase was washed with water. The dichloromethane phase was separated by an evaporator. The product was obtained in yellow oil and characterized by ¹H-NMR, ¹³C-NMR and FT-IR.

b) 2-[2-(2-Amino-ethylsulfanyl)-ethylsulfanyl]-ethylamine (AEEE)⁵²

This reaction was prepared by the same methodology as 3.3.2 a) but 1,3-dibromopropane was replaced with 1,2-dibromoethane (1.0 mL, 11.6 mmol) and cysteamine hydrochloride (2.7 g, 23.6 mmol) was used. The product was obtained in yellow oil and characterized by ¹H-NMR, ¹³C-NMR and FT-IR.

3.3.3 Preparation of polymer support aldehydic styrene/divinylbenzene copolymer⁵³

Chloromethylated styrene/divinylbenzene copolymer (Cl-PS-DVB, 5g, 4.42 mmol Cl/g, Aldrich) was stirred in 40 mL of dimethyl sulfoxide and 2.11 g of sodium bicarbonate for 6 hours at 155 °C. The resin was then filtered, washed with dimethyl sulfoxide, hot water, and dioxane-water (2:1), then rinsed with dioxane, acetone, ethanol, methylene chloride, and benzene. The resin was dried at 100 °C under vacuum, labeled as CHO-PS-DVB.

3.3.4 Preparation of chelating polystyrene

3.3.4.1 Polystyrene containing Schiff base AEPE ligand, AEPE-PS-DVB

The CHO-PS-DVB (1 g) was swelled in dichloromethane (10 ml) for 1 hour. 2-[3-(2-Amino-ethylsulfanyl)-propylsulfanyl]-ethylamine (0.5131 g, 2.64 mmol) in 10:1 dichloromethane-acetonitrile (30 mL) was added dropwise over a period of 30-45 minutes using the addition funnel with constant stirring. The reaction was refluxed under N₂ for 6 hours. The resins were filtered, washed thoroughly with methanol, dichloromethane and vacuum dried, labeled as AEPE-PS-DVB.

3.3.4.2 Polystyrene containing Schiff base AEEE ligand, AEEE-PS-DVB

This reaction was proceeded by the same methodology as 3.3.4.1 but 2-[3-(2-Amino-ethylsulfanyl)-propylsulfanyl]-ethylamine was replaced with 2-[2-(2-Amino-ethylsulfanyl)-ethylsulfanyl]-ethylamine (0.4761 g, 2.64 mmol) in 10:1 dichloromethane-acetonitrile (30 mL). The product was labeled as AEEE-PS-DVB.

3.3.4.3 Polystyrene containing Schiff base triethylenetetramine ligand, TETA-PS-DVB

This reaction was proceeded by the same methodology as 3.3.4.1 but 2-[3-(2-Amino-ethylsulfanyl)-propylsulfanyl]-ethylamine was replaced with Triethylenetetramine (0.3860 g, 2.64 mmol) in dichloromethane (30 ml) and the reaction was done at room temperature. The product was labeled as TETA-PS-DVB.

3.3.5 Ninhydrin test

Ninhydrin-based detection systems are the well-known method for quantitative and qualitative determination of amino acid groups. In this work, ninhydrin method was used to detect terminal primary amine (uncoupled terminal amine group of the chelating ligands). Ninhydrin test in this research was adapted

from the literature^{54,55}. The ninhydrin solution was prepared by dissolving 500 mg of ninhydrin in ethanol 10 mL and stored the solution in darkness. Then, a few resin beads were washed 3 times with ethanol, transferred into a small glass test tube and 3 drops of ninhydrin solution was added. The mixture was mixed well and heated to 100 °C for 5 minutes. The resin beads and the solution turn dark blue when free primary amine is present. The resin remains their colour and the solution stays yellow when no free primary amine is present.

3.4 Characterization

3.4.1 Characterization of chelating agents

The chelating agents were characterized by ¹H-NMR, ¹³C-NMR and Fourier transform infrared spectroscopy (neat technique).

3.4.2 Characterization of resins

All resins in each stage were characterized by elemental analysis, Fourier transform infrared spectroscopy (with KBr pellet technique), Raman spectroscopy and thermogravimetric analysis.

3.5 Metal adsorption study

The study of metal adsorption of chelating resins was done in batch method. The effect of pH on metal adsorption was studied.

3.5.1 pH Effect on adsorption

TETA-PS-DVB, AEPE-PS-DVB or AEEE-PS-DVB (0.050 ± 0.001 g) was added into a test tube. An aliquot of Pb(II) solution (5.0 mL) containing 5 mg L⁻¹ was placed in the test tube after being adjusted its pH ranging from 1.0-7.0 and the mixture was shaken for 1 hour. The resins were separated. The remained amount of Pb(II) in the solution was determined by FAAS.

The studies of Zn(II), Ni(II), Cu(II), Cd(II), Co(II) and Cr(III) adsorption were performed in the same procedure but the initial concentration of Cu(II), Cd(II), Zn(II), Ni(II), Co(II) and Cr(III) was 3, 1, 1.5, 2, 4 and 4 mg L⁻¹, respectively.