

CHAPTER 3

EXPERIMENTAL

3.1 INSTRUMENTATION

A model Analyst 400 (Perkin Elmer, Germany) flame atomic absorption spectrometry (FAAS) equipped with an air acetylene burner and chromium electrodeless discharge lamp (EDL) was used for the determination of chromium. The pH measurements were performed with Eutech model (Singapore) pH meter. FTIR spectra of the polymers were recorded using FTIR spectrophotometer (Perkin Elmer, United Kingdom) in KBr pellets. A model Thermal Gravimetric Analysis (TGA), Perkin Elmer (Pyris series) TGA 6 was performed at scan rates of 20 °C/min and characterized by the measured weight loss from 30 to 900°C.

3.2 CHEMICAL AND MATERIALS

1,5 Diphenylcarbazide (DPC) (Acros) solution was prepared daily by dissolving appropriate amount of DPC (Sigma) in 25 mL of acetone (Fisher). Cr(IV) stock solutions (1000 mg/L) were prepared from K₂CrO₄ (Merck) and H₂SO₄ (37%) (Fisher).

β-cyclodextrin (β-CD) (Acros), silica gel (Acros), 1,6-hexamethylene diisocyanate (HMDI) (Sigma), toluene-2,4-diisocyanate (TDI), dimethylformamide (DMF), acetone were purchased from Acros and all other chemicals used were of analytical grade. The ultra pure water used during experiment was purchased from Elga.

3.3 SYNTHESIS OF POLY- β -CYCLODEXTRIN (β -CDP-HMDI AND β -CDP-TDI)

5 g β -CD was dissolved with 15 mL of DMF in 500 mL round bottom flask at room temperature. A calculated amount of crosslinker 1,6-hexamethylene diisocyanate (HMDI) or toluene-2,4-diisocyanate (TDI) was added dropwise into the mixture. The mixture of β -CD and HMDI or TDI was prepared in the ratio of 1:10 and 1:7 mmol, respectively. The mixture solution was stirred at 70°C for 4 hours. Finally, the polymer was precipitated and washed with large excess of methanol. The polymer was filtered off by suction and dried overnight at 80°C in an oven.

3.4 IMMOBILIZATION OF β -CYCLODEXTRIN ON SILICA (SI-TDI- β -CD)

Immobilization of β -cyclodextrin on silica was performed in two steps.

Step 1 : Introduction of isocyanate group on silica surfaces

1 g of silica (150°C) and 2 g of TDI were mixed using magnetic stirrer in 40 mL toluene (dried by molecular sieve 24 hours) and the functionalization was undertaken in a dry nitrogen at room temperature for 4 hours. In order to remove all the substances physically adsorbed on the surface of the particle, the sample was separated by filtration and sequentially rinsed with toluene and was dried in the oven for 24 hours. The sample was marked as Silica-TDI.

Step 2 : Immobilization of cyclodextrin on Silica-TDI

1 g of Silica-TDI was suspended in 40 mL of dry hexane and stirred for 30 min at room temperature. To this suspension, β -cyclodextrin in ratio 0.25 mmol was added and

stirred at room temperature for 24 hours. The bonded material was filtered and washed with toluene, acetone and distilled water. Then, the sample was dried in the oven at 80°C, and the immobilized β -cyclodextrin on Silica-TDI was obtained. The sample was marked as Si-TDI- β -CD.

3.5 CHARACTERIZATION OF β -CDP-HMDI, β -CDP-TDI, Si-TDI- β -CD.

3.5.1 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR experiments were carried out in the 4000-400 cm^{-1} region with a spectral resolution of 2 cm^{-1} on a Perkin Elmer spectrometer with a KBr pellet technique.

3.5.2 Thermal Gravimetric Analysis (TGA)

Thermal analysis was performed using Perkin Elmer (Pyris Series) TGA 6 at scan rates of 20 °C/min and the amount of sample was characterized by the measured weight loss from 30-900°C of 5 mg of samples.

3.6 OPTIMIZATION OF Cr-COMPLEX WITH DPC

In this study, only β -CDP-HMDI was used for optimization study since the main objective in this study to get the optimum condition of Cr-complex with DPC.

3.6.1 Effect of acidity

0.05 g of β -CDP-HMDI was shaken with 20 mL of mixture 5 mg/L of Cr(VI) and 0.0025 mol/L of DPC with different molarity of acid in between ranges 0.007-0.015 mol/L

sulfuric acid in 100 mL volumetric flask. The mixture was shaken for 24 hours and the polymer was filtered off by suction, and the filtrate was analyzed using FAAS.

3.6.2 Effect concentration of chelating reagent

0.05 g of β -CDP-HMDI was shaken with 20 mL mixture of 5 mg/L Cr(VI) and DPC complex in acidic medium (0.008 mol/L). The concentration of 1,5-diphenylcarbazide (DPC) in the ranges of 0.001-0.015 mol/L in 100 mL volumetric flask. The polymer was shaken for 24 hours and filtered off by suction. The filtrate was analyzed using FAAS.

3.7 ADSORPTION EXPERIMENTS

Adsorption capacities and kinetics were conducted using the batch method. Experimental data were obtained at different temperatures of 25, 45 and 65°C by varying the concentration of Cr-complex with DPC in aqueous solution from 10 to 30 mg/L. In each experiment, a series of 20 mL of Cr-complex with DPC was added to 0.05 g of β -CDP-HMDI, β -CDP-TDI or Si-TDI- β -CD at a known initial concentration. The mixture was then stirred in a water bath on a constant agitation speed of 180 rpm continuously at different temperatures. Studies were conducted at various time intervals to determine when adsorption equilibrium was reached. The solid phase was separated by filtration. The final concentration of filtrate was determined by flame atomic absorption spectrometry (FAAS).

Adsorption capacity of the adsorbent was calculated from the equation given by:

$$Q = \frac{(C_o - C_f)V}{m} \quad [1]$$

where Q is the adsorption capacity of adsorbent (mg/g), C_o and C_f are the initial and final concentration of the chromium(VI) solution (mg/L) respectively and m is the mass of β -CDP-HMDI, β -CDP-TDI or Si-TDI- β -CD (g).