CHAPTER II

This chapter is broadly divided into two sections. First section provides details of the chemicals and instruments used and second section gives the details of the synthesis and spectral characterization of extractant used in the present study.

2.1 Methods and materials

2.1.1 Apparatus

Glass wares used were made up of pyrex and corning glass. The burette, pipette, and standard flasks were calibrated in accordance with the method described by Vogel [1].

2.1.2 Instruments

pH Meter

For the measurement of pH, Systronics digital pH Meter Model No. 802 was used throughout the work.

Spectrophotometer

All measurements of absorption spectra were made on the JASCO V-530 UV-Vis spectrophotometer with 1 cm quartz cells. The calibration of spectrophotometer was checked by measuring absorption spectrum of 0.0058% solution of potassium permanganate in 1 M sulphuric acid. The observed spectrum is in good agreement with the spectrum reported in the literature [2].

2.1.3 Chemicals

All the chemicals used were of A. R. grade. Double distilled water was invariably used throughout the measurements. It is prepared by distilling water in all glass apparatus containing alkaline potassium permanganate.

2.1.4 Preparation of metal salt solutions

Rhodium solution

A stock solution of Rhodium(III) was prepared by dissolving 1 gm of Rhodium tri chloride tri hydrate(RhCl₃.3H₂O) in dilute analytical reagent grade hydrochloric acid (1M) diluted to 100 ml with distilled water and standardized gravimetrically [3].

A working solution of 200µg ml⁻¹ of Rhodium(III) was prepared by diluting the stock solution with distilled water. An aliquot of this solution was used for the determination of Rhodium(III) by stannous chloride method [4].
Palladium solution

A stock solution of Palladium(II) was prepared by dissolving 1g of Palladium dichloride hydrate in dilute analytical reagent grade hydrochloric acid (1M) diluted to 100 ml with distilled water and standardized gravimetrically. A working solution of 100 µg ml\(^{-1}\) was prepared by diluting the stock solution with distilled water. An aliquot of this solution was used for the determination of Palladium(II) by spectrophotometrically with pyrimidine-2-thiol [5,6].

Aurium (Gold) solution

A stock solution of Gold(III) was prepared by dissolving of 1 g of HAuCl\(_4\) in analytical reagent grade hydrochloric acid (1M) diluted to 100 ml with distilled water and standardized gravimetrically. A working solution of 100 µg ml\(^{-1}\) was prepared by diluting the stock solution with distilled water. An aliquot of this solution was used for the determination of Gold(III) by stannous chloride method [7].

Platinum solution

A stock solution of Platinum(IV) was prepared by dissolving 1 g of Platinum tetrachloride hydrate in dilute analytical reagent grade hydrochloric acid (1M) diluted to 100 ml with double distilled water. The required concentration of this solution was prepared by further dilution.

Ruthenium solution

A stock solution of Ruthenium(III) was prepared by dissolving of 1 g of Ruthenium tri chloride, (RuCl\(_3\).3H\(_2\)O) in analytical reagent grade hydrochloric acid (1M), diluted to 100 ml with distilled water and standardized gravimetrically[4].

Solutions for interference studies

Solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in distilled water.

2.2 Synthesis and characterization of extractant

Synthesis of mesoporous MCM-41:

Magnetic material present in fly ash was removed and remaining portion of fly ash was used as precursor for the synthesis of MCM-41. An alkali fusion method reported by Kumar et al [8] was adopted to obtain the alkali fused coal
fly ash (CFA) powder. The fusion process was carried out by mixing as received CFA powder and sodium hydroxide at a ratio of 1:1.2 and then mixture was heated in oven at 850 K for 4 hour. The resultant product was cooled and milled overnight after that, the obtained alkali fused CFA powder was mixed with deionised water and aged for at least one day under stirring condition in an air atmosphere. The mixture was subsequently filtered to obtain sodium silicate solution. The cetyltrimethyl ammonium bromide (CTAB) was dissolved in 140 ml of warm deionized water and to that sodium silicate was added with constant stirring up to 4 hour, pH of the resulting solution was adjusted to 8-9 by using 1M HCl, resulting gel was poured in to Teflon packed glass bottle and heated at 373 K for 48 hour. White solid so obtained was filtered, washed with deionized water and dried at 60°C overnight. The template was removed by calcinations at 550°C for 4 hours to obtain surfactant free mesoporous material MCM-41 [9-10].

The synthesized extractant belongs to the class of high molecular weight amines (HMWA). High molecular weight amines (HMWA) popularly known as liquid anion exchangers, uniquely combines some of the advantages of liquid – liquid extraction and ion exchange techniques.

There are several general features, which are essential for an extraction, if it has to achieve the selective extraction of metal. The high molecular weight amine systems were used for liquid-liquid extraction of many metals from different aqueous solutions. High molecular weight amines have found wide applications in the separation chemistry. The separations of metals were carried out from both mineral acid as well as organic acid media by taking an advantage of the difference in the KD values of anionic complexes of metals. The basis for the separation devised was by exploiting the inability of some elements to form the complexes. The parameters which govern the formation of anionic complex are the effect of acidity, effect of salting out agents and stability of the complex. Among the organic acids, such as oxalic, malonic, citric, tartaric acids, succinic, salicylic acids have been extensively used as complexing ligands. The extent of extraction depends on the pH, nature and the concentration of amine as well as that of the ligand. The extractions involving organic acids are more selective and specific [11-12].
2.2.1 Synthesis of N-n-decylaminopyridine:
The ligand was synthesized in two steps:

**Step-1**
N-n-decylaminopyridine was synthesized using equimolar proportion of N-decylaldehyde and 4-Aminopyridine in 20 ml DCM and 0.1 mg of metal catalyst was refluxed for 3-4 hrs. The product was separated and recrystallized from hot ethanol as white shiny needles (M.P 68-70).

**Step-2**
Product of step1 (Schiff base) is reduced by NaBH₄, using equimolar amounts of Schiff base and NaBH₄ in absolute methanol and refluxed for 30 minutes, product was separated and recrystallized from hot ethanol (M.P - 245°C).

The purity of compound was monitored using H¹ NMR, FT-IR and Mass spectrum. H¹ NMR (CDCl₃): 0.87(3H,t-CH₃), 1.87(2H,d-CH₂), 1.26(2H,d-CH₂), 4.1 (1H,s,-NH),6.5 (2H,d, J 8 Hz, aromatic protons), 8.2 (2H, s, J 8 Hz, aromatic protons). IR (cm⁻¹): 2922 (=C-H), 1331(C-N), 1513-1640 (C=C), 3429 (N-H). Mass m/e: 236 (100.0%) (M⁺). The obtained spectral data is in agreement with the structure of the extractant.
SPECTRAL ANALYSIS

Fig 2.1: The H¹ spectrum of N-n-decylaminopyridine
Fig 2.2: IR spectrum of N-n-decylaminopyridine
Fig 2.3: Mass spectrum of N-n-decylaminopyridine
CHAPTER II

References


5) M. A. Anuse, N. A. Mote and M. B. Chavan, Talanta, 30 (1983) 323.


