CHAPTER 2

EXPERIMENTAL

CHAPTER 2

2.0 EXPERIMENTAL

The dithizone anchored polymeric support used in the present study was synthesized by suspension polymerization technique. The details of the synthesis are discussed later. The chemicals used in the present work are listed below.

2.1 Chemicals used

1. dithizone (Extra pure, Merk India Ltd., Bombay)
2. 4-vinyl pyridine (A. R. Grade, Fluka, Switzerland)
3. divinyl benzene (A. R. Grade, Fluka, Switzerland)
4. copper chloride (A.R.Grade, BDH, Bombay)
5. nickel acetate (A.R.Grade, BDH, Bombay)
6. zinc acetate (A.R.Grade, Merk India Ltd., Bombay)
7. mercuric chloride (A.R.Grade, ExelaR Qualigens Fine Chemicals, Bombay)
8. lead acetate (A.R.Grade, BDH, Bombay)
9. cadmium acetate (A.R.Grade, ExelaR Qualigens Fine Chemicals, Bombay)
10. gold chloride (G.R.Grade, Loba, Bombay)
11. palladium chloride (A.R.Grade, ExelaR Qualigens Fine Chemicals, Bombay)
12. chloroplatinic acid (G.R.Grade, Loba, Bombay)

The solvents and acids used were of A.R. Grade and were used without further purification.

2.2 Synthesis of the chelating resin

Dithizone anchored poly (vinyl pyridine) resin was synthesized from chloromethylated copolymer of 4-vinyl pyridine-divinyl benzene. The resinous material was synthesized in three steps following the method reported by Grote and Kettrup[2].

2.2.1 Synthesis of poly (vinyl pyridine)

A cross linked polymer of 4-vinyl pyridine and divinyl benzene was prepared through suspension polymerization following the standard procedure. In a three neck round bottom flask 90 g of monomer and 10 g of 50 % divinyl benzene were mixed. To this 0.4 g of α, α' azo bis isobutyronitrile, free radical initiator was added. The mixture was stirred at constant temperature 65-70° C for 20 min. At the first appearance of the milkyness which indicates the beginning of polymerization, the mixture was poured rapidly into 600 cm^3 of 20 % sodium chloride solution containing 6.0 g of sodium dodecyl sulphate. The suspension was heated to 80° C with efficient stirring to get desired bead size. The reaction was further continued for 8 hours to ensure the complete polymerization. The polymer was then filtered, washed with water to remove surfactant, then with dimethyl formamide to remove unreacted monomer and finally again with deionised water before drying.

2.2.2 Chloromethylation of crosslinked poly (vinyl pyridine)[1]

For chloromethylation of cross linked poly (vinyl pyridine), 50 g of poly (vinyl pyridine), 30 g of 88 % paraformaldehyde, 5 g of anhydrous $AlCl_3$, 300 g of 1,2 dichloroethane and 25 g of acetic anhydride were mixed in a 1 litre three neck round bottom flask and the contents were heated to ~40° C. Hydrochloric acid gas was bubbled through the reaction mixture and then the reaction mixture was heated to ~60°C for 25 hours with continuous stirring. The colourless chloromethylated poly (vinyl pyridine) was washed with 150 cm^3 of aqueous 1:1 dioxane followed by a mixture of 100 cm^3 of aqueous 1:1 dioxane and 10 cm^3 of concentrated HCl and finally with 150 cm^3 of methanol and deionised water to make it free from chloride and methanol.

The product was dried at 70° C for 8-10 hours and the chlorine content in the product was determined gravimetrically by Volhard's method[5] and Volumetrically by Mohr's method[5].

2.2.3 Anchoring of dithizone to the chloromethylated poly (vinyl pyridine).

For anchoring of dithizone to the chloromethylated poly (vinyl pyridine), 30 g of chloromethylated poly (vinyl pyridine) was treated with 100 cm^3 of freshly distilled dimethyl formamide (DMF) in a 250 cm^3 erlenmeyer flask. To it, 10 g of dehydrodithizone, an oxidised product of dithizone[3] dissolved in 50 cm^3 of DMF was added. The mixture was covered with aluminium foil and was shaken mechanically at room temperature. After 15 days, the orange coloured resin was filtered out and was washed successively with 500 cm^3 of DMF; a (1:1) mixture of DMF and water; water; 1 M hydrochloric acid and finally with water.

The wet resin was stirred with a mixture of 100 cm^3 of 0.5 M ascorbic acid and 50 cm^3 of 1 M sodium hydroxide in an erlenmeyer flask for 30 min. The pH of the solution was adjusted to 6.5. The brown resin was filtered and washed successively with 500 cm^3 of water, 0.01 M sodium hydroxide, water, 0.1 M hydrochloric acid and finally with water. The resin was stored in 0.01 M hydrochloric acid in a brown bottle.

2.3 Resin Characterization

The synthesized resin was thoroughly characterized by spectral and thermal techniques and elemental analysis.

2.3.1 Elemental analysis

% Chlorine content

The % chlorine in the chloromethylated poly (vinyl pyridine) was estimated gravimetrically by Volhard's method.

The chloromethylated poly (vinyl pyridine) (1 g) was taken in a nickel crusible. To it, 2 g of sodium peroxide (Na_2O_2) was added. Initially the mixture was heated gently and then strongly for one hour. The contents of the crusible were transferred quantitatively with deionised water into a measuring flask and volume was made to 100 cm^3 with deionised water.

25 cm^3 of this solution was taken in a 100 cm^3 beaker and was neutralised with HNO_3 (pH 4.5). To it 25 cm^3 of 4 % $AgNO_3$ solution was added with continuous stirring. The contents were left overnight. The precipitate of AgCl was filtered and dried at 120-125° C and weighed.% Chlorine was calculated from the weight of AgCl precipitate.

$$\% \text{ Cl} = \frac{\text{Weight of AgCl} \times \text{Atomic weight of Cl}}{\text{Mol. weight of AgCl} \times \text{Weight of chloromethylated poly (vinyl pyridine)}} \quad (2.1)$$

The results were also confirmed volumetrically using Mohr's method.

Carbon, hydrogen analysis was carried out by using a Coleman elemental analyser and nitrogen analysis by Duma's method.

2.3.2 % Moisture content

Moisture content of the sample can be determined precisely and accurately by Karl Fisher method. But due to the non availability of the instrument and as this property of the resin being less important in the present study moisture content was determined by following method[4].

A known amount of resin (W_1) was washed with water and separated from water and dried to constant weight at 105° C in an oven. The heated resin (W_2) was weighed after cooling in a desiccator. The % moisture was calculated from the difference in the weights.

$$\% \text{ moisture} = \frac{(W_1 - W_2)}{W_1} \times 100 \quad (2.2)$$

$$\% \text{ solid} = 100 - \% \text{ moisture} \quad (2.3)$$

2.3.3 True density of the resin (d_{res})

True density of the resin was determined by using a specific gravity bottle as reported by Inczedy[4]. A known quantity of the resin was taken in a previously weighed specific gravity bottle (W). The bottle was weighed along with the resin (W_r). The bottle was filled with water in the presence of resin and was reweighed (W_{rs}). The weight of the specific gravity bottle filled only with water was also noted (W_s). The true density of the resin was determined by using following relationship,

$$d_{res} = \frac{(W_r - W) \cdot S}{(W_s - W_{rs}) + (W_r - W)} \qquad (2.4)$$

Where S is the density of water, taken as 1.

2.3.4 Apparent density or Column density of the resin (d_{col})

Apparent density or Column density of the resin was determined following the literature method[4].

A known quantity of the resin was suspended in water for 8 h. The slurry of the resin was slowly poured in the column. The resin was allowed to settle down and the excess water was drained off. The volume of the resin in the column was measured. The column density (d_{col}) was calculated as follows.

$$d_{col} = \frac{\text{Weight of the dry resin}}{\text{Volume of the resin bed}} \qquad (2.5)$$

2.3.5 Void volume fraction

Void volume fraction can be calculated by three methods as suggested by Inczedy[5].

(a) simple volume measurements

(b) titration method or

(c) calculation from density data

We have followed the third method which utilises density data. The void volume fraction was calculated by using the relationship,

$$\text{Void volume fraction} = 1 - \frac{d_{col}}{d_{res}} \tag{2.6}$$

2.3.6 Concentration of the fixed ionogenic groups (Cr)

This can be calculated as follows[4],

$$Cr = \frac{d_{res} \times \%\ \text{solid} \times \text{CEC}}{100} \tag{2.7}$$

where, CEC is the cation exchange/chelating capacity.

In the present study Cr will be concentration of chelating groups.

2.3.7 Volume capacity of the resin (Q)

This can be determined by using equation[4],

$$Q = (1 - \text{Void volume fraction}) \times Cr \tag{2.8}$$

2.3.8 Reusability of the resin

For industrial applications the extent of reusability of the resin is important. The resin stability for repeated use was determined in terms of variation in copper exchange capacity. 0.1 g of the resin was equilibrated with 25 cm^3 of known concentration of copper chloride solution for 24 h. The copper exchange capacity was determined by estimating the amount of copper left in supernatant liquid. The copper was eluted with 0.5 M HCl and the resin was regenerated and used again for copper exchange. The procedure was repeated 25 times to study the resin stability towards repeated use.

2.3.9 Thermal stability

For the determination of thermal stability of the resin, 1.0 g of the resin was heated in the oven for 8 h at different temperatures ranging from 30° to 150°C. The copper exchange capacity of the heated resin was determined by taking 0.1 g of the resin sample and following the standard procedure[4] as discussed in sec. 2.3.8.

2.4 Preconcentration of metal ions

The synthesized resin was further used for the preconcentration and recovery of metal ions. The various conditions for the exchange of copper(II), nickel(II), zinc(II), lead(II), cadmium(II), mercury(II), gold(III), platinum(IV) and palladium(II) were optimised. The methods used for the estimation of metals are given in Table 2.1

Stock solutions of 10 mg cm^{-3} concentration of the metal ions : (Cu(II), Ni(II), Zn(II), Pb(II), Cd(II) and Hg(II)) were prepared by dissolving required quantity of the corresponding salts into deionised water and making the volume of the solution to 100 cm^3. Where as stock solutions of gold(III), platinum(IV) and palladium(II) were prepared by dissolving 1.0 g of the corresponding salt into deionised water and making the volume with deionised water to100 cm^3. All these solutions were standardised following the literature methods[5-7]

Table 2.1 : Methods and conditions used for estimation of metal ions

Sr. No.	Metal ion	Method used for estimation	Condition	Reagent and indicator used	Reference
1	Cu (II)	Complexometric titration	liq. ammonia	EDTA,Fast sulphon black	5
2	Ni (II)	Complexometric titration	pH - 10	EDTA,Muroxide	5
3	Zn (II)	Complexometric titration	pH - 6	EDTA,Xylenol orange	5
4	Pb (II)	Complexometric titration	pH - 6	EDTA,Xylenol orange	5
5	Cd (II)	Complexometric titration	pH - 6	EDTA,Xylenol orange	5
6	Hg (II)	Complexometric titration	pH - 6	EDTA,Xylenol orange	5
7	Au (III)	Spectrophoto metric	475 nm	Sodium diethyl dithio carbamate	6
8	Pt (IV)	Iodometric	pH - 7	EDTA, KI, Starch	7
9	Pd (II)	Complexometric titration	0.1 M KOH	EDTA, Eriochrom black T	5

2.4.1 Optimisation of pH for exchange of metal ions

Known quantity (~0.1 g) of the resin was taken and equilibrated with buffer solutions of pH 1-7 for 12 h. After decanting the buffer solutions 25 cm^3 of metal ion solution of fixed concentration and of pH 1-7 was equilibrated with resin for 24 h. The metal exchange capacity was determined by estimating the concentration of metal ion in supernatant liquid as well as after eluting the metal from resin.

From the initial concentration (C_A) and equilibrium concentration (C_B), capacity (Q) of the metal ion exchange per g of the resin was calculated as[4]

$$Q = \frac{(C_A - C_B) \times 100}{\text{Weight of the resin} \times \text{\% solid}} \qquad (2.9)$$

The pH at which maximum exchange takes place was used as optimum pH for further studies.

The distribution coefficient Kd of the metal ions was calculated by using the relationship,

$$K_d = \frac{(C_A - C_B) \times V}{C_B \times \text{weight of the resin}} \qquad (2.10)$$

Where 'V' is the volume of the solution taken

'C_A' is the initial concentration of metal ion

'C_B' is the equilibrium concentration of metal ion

2.4.2 Effect of metal ion concentration on exchange process

Effect of metal ion concentration on preconcentration was studied in terms of metal exchange capacity. For the study 25 cm^3 of metal ion solutions of optimum pH and of varing concentrations were equilibrated with known quantity (~0.1 g) of the resin. After 24 h solutions were decanted and metal ion concentration in the solution was estimated. The capacity in mmol g^{-1} of resin as well as distribution coefficient (Kd) were calculated using equation 2.9 and 2.10.

2.4.3 Rate of metal ion exchange

Exchange process of metal ions was studied according to the method reported by Helfferich[8]. In a series of 150 cm^3 capacity erlenmeyer flasks ~0.1 g of the resin was equilibrated with 25 cm^3 of buffer of predetermined pH for 12 h. The buffer solutions were decanted and 25 cm^3 of metal solutions of the same pH and known metal concentration were added to each flask and allowed to remain in contact with the resin for different periods of time (5, 10, 20, 30 ,40, 50, 60 min and 2, 3, 6, 9, 12, 15, 18 h) with intermittent shaking. After predetermined time the amount of metal ion taken up by the resin was determined by a differential method as well as by eluting the metal from the resin. The metal exchange capacity of the resin or % exchange was plotted against time. Time required for achieving 50 % exchange ($t_{1/2}$) was determined from the plot.

2.4.4 Nature of exchange process

The exchange of metal ions is governed by two types of diffusion processes:

(i) particle diffusion and

(ii) film diffusion

which can be differentiated through interruption test[8]. In this test same procedure was followed as described in sec.2.4.3 upto 20 min time intervals. For the remaining sets exchange process was interrupted by separating the resin particles from the solutions for 10 min. After 10 min the resin was again reimmersed in the solutions and the exchange rate was continued to be determined for 30, 40, 50 and 60 min time intervals. From the results of % exchange with and without interruption nature of exchange process was determined. For the confirmation of the results obtained the method reported by Nativ et al[9] was also used for the study of nature of exchange process.

2.4.5 Measurement of activation energy

From the extent of metal uptake at different temperatures the rate constant and activation energy for the metal exchange can be determined by following the standard procedure[10].

In a 100 cm^3 erlenmeyer flask ~0.1 g of the resin was equilibrated with 50 cm^3 of the buffer of predetermined pH for 3 h at 30, 35, 40, 45 and 50° C temperatures. 50 cm^3 of metal solutions of fixed concentrations maintained at the same temperatures were added to these flasks after decanting the buffer solutions. The rate of exchange of metal was measured as a function of time. Rate constant k was calculated using the equation for the first order exchange reaction[10].

$$-\log(a-f) = \frac{kt}{2.303} \qquad (2.11)$$

where 'a' and 'f' are the initial and final concentrations of metal ions.

The activation energy for the exchange process was determined using Arrhenious equation[10].

$$k = A\,e^{-\Delta E/RT} \qquad (2.12)$$

2.4.6 Effect of eluting reagents

For the quantitative elution of metal ions from the resin 15 cm^3 solutions of various acids, alkalies, electrolytes and complexing agents of different concentrations were added to the metal loaded resin. The amount of metal ion eluted was determined as mentioned earlier.

2.5 Column chromatographic studies

Preconcentration and separation of various metal ions from mixtures was studied by using dynamic column chromatography.

2.5.1 Preparation of column

A graduated glass column of 30 cm length and 1.0 cm i.d. with porous glass frit at the bottom was used for the study. A known weight of resin was kept in water for 12 h and resin slurry was poured into the column. The resin particles were allowed to settle properly to form a compact resin bed (column) to avoid eddy diffusion. The resin column was kept under water during storage.

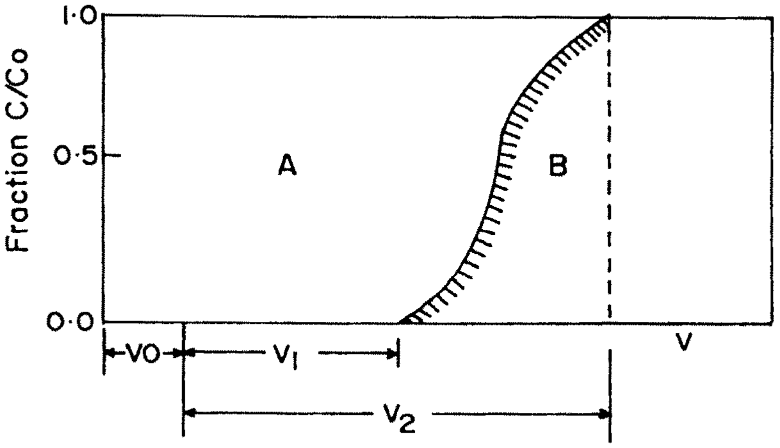
2.5.2 Column characterization

To measure initial break through and total column capacity, metal solutions of 1 mg cm^{-3} of Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) at predetermined pH were passed through the resin bed at 1 cm^{-3} min^{-1} flow rate. Metal ions from each fraction of the column effluent were determined following the process described in Table 2.1. Isoplanes[4] were plotted from the results of equivalent fractions of metal ion (C/Co) against the volume of the effluent from the column.

Where C = amount of metal ions in the column effluent cm^{-3}

Co = amount of metal ion added to the column cm^{-3}

Break through capacity which is one of the characteristic data for the column operations is always lower than total exchange capacity and is designated as A at V_1 in the figure. Total exchange capacity which is the total amount of metal ion taken by the resin is designated as B at V_2 in the figure. The void volume of the column was calculated as $V_o = \alpha X$, where α is the void volume fraction and X is the column volume. The degree of column utilisation was calculated from the ratio of break through and total exchange capacity of the column.



2.5.3 Separation of binary and ternary mixtures of metal ions

Binary and ternary mixtures of various metal ions of fixed concentrations were prepared. 30 cm^3 aliquotes of these mixtures were passed through the resin column at the flow rate of 1 cm^3 min^{-1}. The column was washed with water and metal from the resin was eluted using appropriate eluting reagents. During the process different fractions of column effluent were collected for the measurement of metal ions. The elution isotherms were plotted in terms of % elution against volume of effluent from the column. From the plot percentage recovery of metal ions was calculated.

References

1. Spivack, J. D. and Vauey, S.; *US pat. 3281505*, 1966.
2. Grote, M. and Kettrup, A.; *Anal. Chim. Acta.*; 1985, **172**, 223.
3. Irving, H.M.N.H.; Kiwan, A. M.; Rupainwar, D. C. and Sahena, S. S.; *Anal. Chim. Acta.*, 1971, **56**, 205.
4. Inczedy, J.;*'Analytical Application of Ion Exchangers'*, Pergamon press, London, 1966.
5. Vogel, A. I.; *'A Text Book of Quantitative Inorganic Analysis'*; Longman, London, 1975,
6. Fries, J. and Getrost, H.; *'Organic Reagents for Trace Analysis'*; E Merk, 1977.
7. Scott, W. W.; *'Standard Methods of Chemical Analysis'*; D. Van Nostrand Company, INC., Princeton, New Jercy, 1939.
8. Helfferich, F.; *'Ion Exchange'*, Mc Graw-Hill, New York, 1962.
9. Nativ, M.; Goldstein, S. and Schmuckler, G.; *J. Inorg. Nucl. Chem.*; 1975, **37**, 1951.
10. Barrow, G. M.; *'Physical Chemistry'*, McGraw Hill Book Company, Inc., London, 1961, p 468.