STUDIES ON CHELATING ION-EXCHANGE RESINS

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By
LUCY JOSEPH

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022

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TO MY PARENTS

BROTHERS AND SISTERS

They could not drink of the waters of Marah,
for they were bitter .... and
Jehovah showed him a tree, and he cast it
into the waters, and the waters were
made sweet.

Exodus 15: 23-25

DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of Dr.V.N.Sivasankara Pillai, Reader, Department of Applied Chemistry, Cochin University of Science and Technology and no part of this thesis is included in any other thesis submitted previously for the award of any degree.

15/12/'87

LUCY JOSEPH

Cochin - 682 022,
10th December 1987.

CERTIFICATE

Certified that the work presented in this thesis is based on the bonafide work done by Smt. Lucy Joseph, CSIR Senior Research Fellow, under my guidance, in the Department of Applied Chemistry, Cochin University of Science and Technology and no part thereof has been included in any other thesis submitted previously for the award of any degree.

Dr.V.N.Sivasankara Pillai
Reader
Dept. of Applied Chemistry
Cochin University of Science
and Technology
(Supervising Teacher)

Cochin - 682 022
10th December 1987.

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-LUCY JOSEPH-

PREFACE

Ion-exchange chromatography has emerged as a practical and rapid method of separation and analysis. A review of literature on chelating resins reveals that eventhough investigations on highly selective resins are intensively pursued from early 1940s, such resins are still insufficiently used in analytical chemistry and process technology. This is mainly due to the complexity of their synthesis and high cost. In this context, it is worthwhile to develop novel chelating resins which are specific or at least selective towards a group of metal ions. Synthesis, characterization and analytical applications of two such resins are presented in this thesis.

A thiol-bearing resin, ST-3, which shows high affinity towards mercury (II) and silver (I) was synthesized by a simple three-step procedure. The toxicity of mercury to higher forms of life due to bioamplification prompted us to investigate the applicability of ST-3 resin in mercury removal.

Enrichment of mercury from sea-water and removal from chlor-alkali plant effluents were carried out successfully on the analytical scale.

The thiol group in the resin is stable to air-oxidation which is not the normal case with thiol-bearing resins. This property is attributed to the stabilising action of a prosthetic group. Another attractive feature of the resin is that it competitively takes up mercury (II) or silver (I) from solution of high ionic concentration. The sorbed ions can be conveniently stripped and the resin can be regenerated. Since the resin shows promising properties for process applications and scale up is being attempted, the details of its synthesis are not presented in the thesis.

Anchoring of ionic chelating agents to an ion-exchange resin of desired matrix characteristics, by simple exchange process, seems to be the easiest and cheapest method for synthesizing highly selective chelating resins. Using this principle, we were able to synthesize a selective resin by incorporating pyrogalloldisulfonic acid to a commercially available anion exchange resin. It shows high selectivity towards molybdenum (VI), vanadium (V) and iron (III). Separations of these metal ions from a number of other common metal ions were done successfully. Results of the studies on the preconcentration of molybdenum (VI) for estimation by AAS or ICP-AES are also presented.

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CHAPTER - I

INTRODUCTION

1.1 GENERAL INTRODUCTION

The first scientific description of the phenomenon of ion-exchange was given by Thomson and Way in their work on the exchange of cations on soil.[1] The stoichiometry of the reaction was demonstrated by Lemberg.[2] Later, such materials found applications in water softening and related fields in industrial operations.

A new era in ion-exchange technology began with the development of organic ion-exchangers by Adams and Holmes.[3] These ion-exchange resins exhibited properties much better than the ion-exchange materials available until then. The period after 1940 was marked by hectic activity in the synthesis of more sophisticated ion-exchange materials based on polymer matrix. A wide variety of polymers were tried as back-bone structures. Porosity and particle size of the ion-exchange resins were controlled by modifying polymerization conditions. The versatility of ion-exchange resins could be attributed to the nature and number of the fixed ionic groups and the degree of cross-linking that could be controlled according to the intended applications.

Most of the current industrial and laboratory applications of ion-exchange are based on synthetic organic ion-exchange resins. The superiority of these resins over natural and synthetic mineral ion exchangers lies in their better chemical and mechanical stability, higher ion-exchange capacity, faster exchange kinetics and versatility. However, with the development of nuclear reactors and radiochemical engineering, attention was once again focussed on inorganic exchangers due to their better thermal stability and resistance to radiation.[4]

Majority of work on ion-exchange chromatography has been concentrated on metal ion separations. Efforts to achieve separation of very similar components such as rare-earth metals and transuranium elements have resulted in a large number of publications on ion-exchange separations alone. Compared to conventional precipitation method, ion-exchange provides advantages such as greater speed and ease of operation as well as applicability to the separation of trace constituents without need for the addition of carriers. The basic method of ion-exchange separation by elution with an electrolyte has undergone a lot of modifications and has proved to be an efficient separation process. The use of complexing agents, buffers and aqueous-organic solvent mixtures have added new dimensions to the overall picture.

Today, ion-exchange has grown to the extent that it is firmly established as a unit operation. Its applications range from water treatment and purification of cane sugar to production of ultrapure water for the microelectronics industry, recovery of valuable materials from sewage effluents and pollution control. Hydrometallurgical applications as diverse as treatment of plating wastes, tonnage production of uranium are also noteworthy. Extrapolation of its application to physiological chemistry and biophysics is definitely of much technological importance.

The idea of introducing complexing groups into the resin phase was a break through in the search for highly selective resins. Researchers, with the aim of preparing a set of polymer sorbents specific for each kind of ion, synthesized a large number of chelating resins selective to a group of metal ions. A large number of papers have appeared during the last forty years on synthetic organic resins whose functional groups are chelate forming. But the possibility of preparing "specific complexones" is restricted by the non-availability of an adequate set of functional groups.

The situation appears more hopeful with the recent conceptions of the reactivity of polymers. Sufficient experimental data on specific polymer effects in the chemical reactions of functional groups linked with macromolecules are available now. Using these data, new chelating exchangers can be designed to regulate the selectivity of the sorbents even using a small set of functional groups. The sophisticated idea of "memory complexones" according to Effendiev and Kabanov[5] has opened a new route to the synthesis of resins with higher selectivity.

1.2 FUNDAMENTALS OF ION-EXCHANGE PROCESS

Ion-exchange process involves exchange of ions of like charge, between a solid and a solution, or between two immiscible liquid phases, in contact with each other, in a chemically equivalent amount. At some point during the process an ion-exchange equilibrium is established. The equilibrium constant for the reaction, on a cation exchange resin,

$nR^-A^+ + B^{n+} \rightleftharpoons R_n^- B^{n+} + nA^+$ can be given as,

$$K_{A^+}^{B^{n+}} = \frac{[R_n^- B^{n+}]\,[A^+]}{[R^-A^+]\,[B^{n+}]} \qquad \ldots\ldots\ldots(1.1)$$

where the terms in brackets indicate the ion concentration in moles/l for the solution phase and in moles/g for the resin phase. The term $K_{A^+}^{B^{n+}}$ is dependent on experimental conditions and is referred to as selectivity coefficient.[6] This relationship is useful for determining which ion will exchange in reasonable amounts and for estimating the amount of resin required to remove a given quantity of ions from solution. The preference of an exchanger for one ion (B) over another ion (A) is often expressed in terms of the 'separation factor' or 'selectivity quotient' Qs, where

$$Qs = \frac{[R_n^- B^{n+}]\,[A^+]}{[R^-A^+]\,[B^{n+}]} \qquad \ldots\ldots\ldots(1.2)$$

The weight distribution coefficient, D_g for the exchanged ion A is given by

$$D_g = \frac{[A]_r}{[A]_s} \qquad \text{.......(1.3)}$$

$$= \frac{(\text{mmoles of } A_r)\ (\text{ml of solution})}{(\text{mmoles of } A_s)\ (\text{g of resin})}$$

Where $[A]_r$ and $[A]_s$ are the concentrations of A in the resin phase and solution phase respectively. Selectivity quotient (eq.1.2) can also be written as

$$Qs = \frac{D_g^B}{D_g^A} \qquad \text{.......(1.4)}$$

1.3 GENERAL CHARACTERISTICS OF ION-EXCHANGE RESINS

To be effective, an ion-exchange resin must contain exchangeable ions within their structures, be insoluble in water or other solvents, and provide enough space in their porous structure for ions to pass freely in and out of their polymer matrix. Generally, ion-exchange resins are characterized by their ion-exchange capacity, moisture retension capacity, porosity and density.

1.3.1 Ion-exchange capacity

The capacity of a given resin may be expressed in terms of the total number of ionizable groups per unit mass or volume which is referred to as the "total capacity" and also in terms of its actual performance under specified conditions which is referred to as the "operating capacity".[7] Weight capacity expressed as milliequivalents per gram of dry resin is considered as more accurate and reproducible while commercial quantities are measured by volume capacities (equivalents per litre of swollen bed). The operating capacity depends on experimental conditions and hence is meaningful only when accompanied by a description of experimental conditions. A better way of characterizing a resin is by giving its weight capacity and the pK of its ionogenic group which can be determined by pH titration.

1.3.2 Moisture retension capacity

The capacity of an ion-exchange resin to retain water in its fully swollen state helps to define its hydrophilic character and to indicate the effective pore diameter. The moisture content increases with decrease in cross-linking and with increase in concentration of ion-exchange groups. Conventional cation exchange resins (8% divinyl benzene) in their sodium forms hold 43 to 45% water by weight. Since the degree of swelling represents a balance between osmotic forces and the tension within the elastic resin structure, the nature of counter ions has considerable effect on this property. The effect of counter ions is more pronounced in weak acid and weak base resins. For example some commercial weak base anion exchange resins expand as much as 25% when converted from OH^- form to Cl^- form. Generally, if the equilibrium moisture retension capacity is below 50%, free diffusion into and out of the structure is limited to simple inorganic ions and above 55%, much larger ions can move through the resin phase.

1.3.3 Porosity

Porosity of an ion exchange resin is an index to the rate of exchange and the limiting size of ions which can penetrate a resin matrix. Porosity of a solid may be defined as the ratio of the volume of interstices of the material to the volume of its mass. The effective pore diameter of an ion-exchange resin can be measured by determining the exchange capacity with ions of various size.

1.3.4 Density

Density of an ion-exchange resin may be expressed as the density of the particles which can be determined by measuring the density of a mixture of nonpolar solvents which will just suspend the resin particles. Density of fully hydrated ion-exchange resin varies from about 1.07 for the lightest anion exchange resin to about 1.3 for the heaviest cation exchange resin.

1.4 REACTIVE ION-EXCHANGERS (RIEX)

A sharp distinction between classical ion-exchange and ion-exchange accompanied by chemical reaction was recognized for the first time by Helfferich.[8] The overall process in classical ion-exchange is exclusively a redistribution of counter ions so that the exchanging ion retains its identity. Exchange of counter ions A and B on a cation exchange resins can be given as:

$$R^-A^+ + B^+ \rightleftharpoons R^-B^+ + A^+$$

According to Janauer et al[9] a reactive ion-exchange procedure comprises one or more ion exchange steps accompanied, preceded or followed by reaction(s) resulting in the formation of different chemical species, and by the consumption or transformation of initially present species in all participating phases. Eleven typical examples of this kind are given by Helfferich[8]. They can be classified into four groups.

In group-I the counter ion released by the exchanger is consumed by a reaction. Neutralization of H^+ or OH^- (released by exchanger) with solution of base or acid or formation of undissociated acids or complexes (Reactions I, II & III in table-1) are examples for the same. In ion-exchange of the second type the counter ions originating from solutions is consumed by reactions on the fixed ionic groups. This occurs when salt forms of weak acid or weak base exchangers react with acid or base or when chelating resins in a salt form take up a complexing metal ion (Reaction IV and V). A third situation is the ionization of undissociated fixed ionogenic groups as in the neutralization of weak acid or weak base ion-exchangers with solutions of base or acid respectively or in stripping of complexed metals from chelating resins by stronger chelating agents (reaction VI). A fourth situation is the conversion of an undissociated fixed ionogenic group to a second undissociated form, as in acid-regeneration of metal complexed chelating resin (reaction VII).

Table - 1.1 Types of ion-exchange reactions

I. $R\text{-}SO_3^-H^+ + Na^+OH^- \longrightarrow RSO_3^-Na^+ + H_2O$

II. $RSO_3^-H^+ + Na^+AcO^- \longrightarrow RSO_3^-Na^+ + AcOH$

III. $4RSO_3^+(Ni^{2+})_2 + (Na)_4EDTA^{4-} \longrightarrow 4RSO_3^-Na^+ + Ni_2EDTA$

IV. $RCOO^-Na^+ + H^+Cl^- \longrightarrow RCOOH + Na^+Cl^-$

V. $RN(CH_2COO^-Na^+)_2 + Ni^{2+}Cl_2^- \longrightarrow RN(CH_2COO)_2Ni + 2Na^+Cl^-$

VI. $RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$

VII. $RN(CH_2COO)_2Ni + 2H^+Cl^- \longrightarrow RN(CH_2COOH)_2 + Ni^{2+}Cl_2$

1.4.1 Objectives of reactive ion-exchange resins

Different chemical reactions have been combined with classical ion-exchange process by many workers to solve problems of very specific nature like the separation of actinides at trace levels and concentration and analysis of toxic species in natural waters. The ion-exchange behaviour of anionic metal complexes, the synthesis and properties of polymeric nonionic and ionogenic redox systems, termed "electron exchangers" and the use of soluble chelating agents in conjunction with ion-exchangers have all been the focus of extensive experimental studies. Chelating ion-exchange resins had been an area of early interest and is still in the front row of research topics.

The objectives of RIEX have been classified into five general categories by Helfferich.[8]

1. Isolation, concentration or removal of an individual species from diverse mixtures, e.g., isolation of metals from ore leachings, removal of mercury from a waste stream. Analytical applications at trace levels need both preconcentration and isolation.

2. Separation from each other of several very similar species, e.g., separation of lanthanides or aminoacids. Here also analytical applications are very important.

3. Total removal or concentration of groups of ionic species or of ionogenic species, e.g., removal of cations and anions in water demineralization.

4. Degradation of unwanted chemicals or biological species by transformation into harmless products, e.g., nucleophilic cleavage of organophosphorous pesticide residues before landfill disposal.

5. Catalysis of organic reactions, e.g., acid-catalysed esterification by means of strong acid cation exchangers in the hydrogen form.

1.4.2 Thermodynamics of RIEX

In the ion-exchange reaction

$$A_{resin} + B_{soln} \rightleftharpoons A_{soln} + B_{resin}$$

$$\Delta G^{B/A}_{total} = (\Delta G^{B}_{Coulomb} - \Delta G^{A}_{Coulomb}) + (\Delta G^{B}_{Solvation} - \Delta G^{A}_{Solvation})$$

$$= - RT\ln K^{B/A} \qquad \ldots\ldots\ldots\ldots(1.5)$$

Where K is the selectivity constant. Here, the difference between the two coulombic terms is usually small so that most of the ΔG of a classical ion-exchange can be ascribed to the hydration term. The fact that $|\Delta G|$ values for spontaneous chemical reactions such as chelate formation is high compared to $|\Delta G_{IEX}^{B/A}|$ justifies the possibility of separating two ions A and B by reactive ion-exchange, i.e., by finding suitable chemical reaction(s) which will yield an overall negative ΔG_{total} of sufficient magnitude.[10] The effectiveness of expected separation can be calculated from the ΔG values of the chemical reactions since

$$\Delta G_{total} \approx \Delta G_{reaction}^{B/A}, \text{ assuming that } |\Delta G_{reaction}| \gg |\Delta G_{exchange}|$$

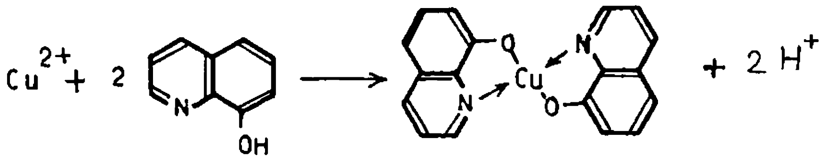
1.4.3 Kinetics of RIEX

A unified treatment of the kinetic aspects for a general RIEX is difficult since there are fundamental differences in the reactions involved. So, the dynamics of chemical reactions, of ion-exchange as such and of ion-exchange process accompanied by chemical reactions all have to be examined separately. The kinetics of exchange process coupled with or accompanied by chemical reactions have been systematically treated by Helfferich.[8]

1.4.4 Advantages of RIEX involving chelation

Chelate formation opens up a vast number of potential applications in RIEX sequences. For the separation, enrichment or removal of transition metal ions, the possibilities are almost unlimited. The masking of multivalent cations using a complexing agent in the solution phase as well as sorption of all but alkali ions from a solution on a chelating resin are obvious applications of chelating reactions.

One of the most striking features of chelates is the enhanced stability. They form ring systems resembling the aromatic rings of organic compounds. A chelating ligand must possess two or more donor atoms. Almost all co-ordinating organic compounds contain -OH, -SH or -NH groups in some form and N,O and S atoms in the molecule can coordinate with metal ions in forming chelate rings. These groups must be located in such positions that the metal ion will be involved in the ring formation without strain. A typical example of such a chelating agent is 8-hydroxyquinoline. The chelate formation with Cu^{2+} can be given as,



Scheme 1.1

The stability of chelate structure will be further enhanced if there are more than two donor group in the compound capable of forming multiple rings. EDTA with six donating groups forms the most suitable chelate structure for metal ions.

Other attractive features of RIEX involving chelate formation are (1) thermodynamic driving forces are usually large and (2) intrinsic selectivities can be further enhanced by pH adjustments. It is because the stability of metal-ligand complex increases with increasing basicity of the ligand. The complex formation can be given as a competitive reaction:

$$M^{n+} + nHL \rightleftharpoons ML_n + nH^+$$

and hence, the degree of complex formation can be controlled by pH. In homologous series, such as primary aliphatic amines the logarithm of the formation constant with a given metal ion increases linearly with pk of the ligand acid, HL.

The separation factor of a chelating ion-exchange resin for one metal ion over another metal ion can be expressed as the ratio of the stability constants, with the resin which refers to the reaction,

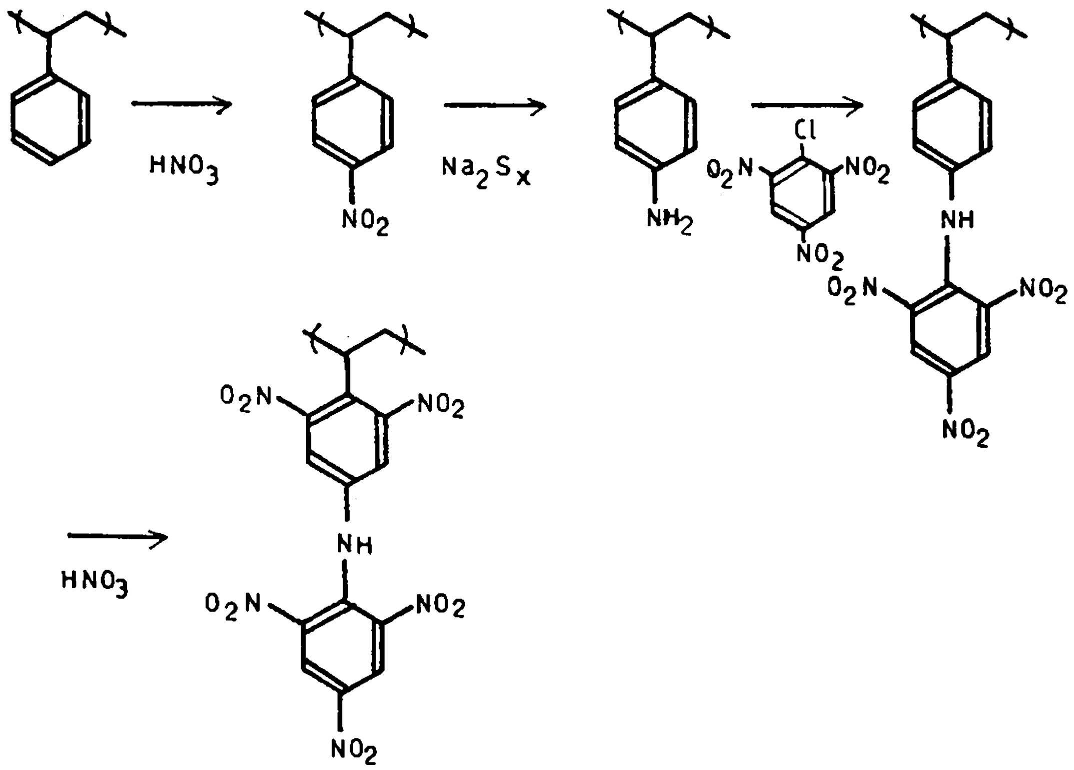
$$M^{2+} + H_2R \rightleftharpoons MR + 2H^+,$$

so that, in principle, selectivity can be calculated from a knowledge of K_{MR} values. Since it is difficult to evaluate K_{MR} values exactly, an alternative is to employ the stability constant of the complex in aqueous solution (K_{ML}) with a model ligand having the same functional groups as on the resin. But the calculated values of selectivity sometimes exceed the observed values and a logical alternative is to measure sufficiently large number of values of K_{MR} to establish a correlation between them and the appropriate values of K_{ML}. Two methods are popular for the measurement of K_{MR}, namely, ligand competition method and proton competition method.[12] The ligand competition method involves competition for the metal ion by the resin and a suitable ligand in solution under alkaline condition (pH 10). For copper and nickel systems with Dowex A-1, the value of log K_{MR} were considerably greater than log K_{ML}, the constant for analogous complex in solution.[13] The proton competition method is based on the competing reactions of metal ions and protons for the resin in slightly acid solution (pH_{2-4}). In this range the values of K_{MR} are close to those of K_{ML} for the systems studied.

1.5 CHELATING ION EXCHANGE RESINS - AN OVERVIEW

The development of chelating resins started in 1939 with the work of Erlenmeyer and Dahn[14] who chromatographed various cation mixtures on a column of powdered 8-hydroxyquinoline. In the same year Griesbach[15] pointed out that a series of exchange resins with any acid strength is available in principle and that the acid groups can be introduced into the resin in a selective way in the form of phenolic hydroxyl groups, carboxylic groups and sulfonic acid groups. He also mentioned the value of introducing complexing groups.

Skogseid attempted to put this idea into practice. His work was based on the observation that all nitrated secondary aromatic amines selectively bind potassium ions and hence an insoluble macromolecular amine of this type, if produced, without any major structural alteration, would possess potassium-selective ion-exchange property. He synthesized a resin with structure similar to that of dipicrylamine.[16] The resin was prepared from polystyrene by nitration, reduction and condensation with picrylchloride and repeated nitration (Scheme 1.2)



Scheme 1.2

Mellor again drew attention to the possibility of making complexing polymers but with a different outlook.[17] He suggested that better selectivity can be achieved by polymerizing organic reagents which are capable of forming stable metal chelates, leaving active groups free.

In 1952 Gregor et al[18] described the first of a new class of ion-exchange resins which consisted of phenol-formaldehyde polymers condensed in the presence of chelate-forming compounds like o-amino phenol and anthranilic acid. They specified four properties required by the chelate-forming molecules, namely:

1. It must be capable of resin formation or substitution in the resin matrix..
2. It must be sufficiently stable to withstand the polymerization procedure.
3. The functional group must be compact so as not to be sterically hindered by the dense resin matrix.
4. Both donor atoms of the chelate-structure must be on the same monomer in proper spatial configuration.

These four criteria are met in 8-hydroxyquinoline molecule and hence polymers incorporating this unit werefurther studied by Parrish, Von Lillin and Davies et al independently. Parrish[19] pointed out that o-aminophenol-formaldehyde resin developed by Gregor et al would be expected to contain substituted amino groups. Parrish prepared a condensation polymer of resorcinol-formaldehyde-oxine which exhibited chelating properties similar to oxine but the capacity of the resin was very low.[19] Later it was shown that the low capacity was due to the high degree of cross-linking.[20] To overcome this, he prepared a lightly cross-linked polystyrene with 2% divinylbenzene and three selective ion-exchange resins were made by incorporating aliphatic thiol, arsonic acid and 8-quinolinol groups. The chelating resin containing 8-quinolinol was prepared by coupling it with diazotized poly(aminostyrene). This resin was selective towards copper, nickel and cobalt but the rate of exchange was very slow.

Following the technique developed by Parrish, Davies et al[21] synthesized metal complexing polymers by coupling units like o-hydroxyphenylarsonic acid, 8-quinolinol, salicyclic acid and kojic acid with diazotized poly(aminostyrene). Here, polystyrene containing 1% DVB was used and was found to show much faster kinetics than the resin developed by Parrish which required two weeks for equilibration.

Many polymers with special functional groups have been prepared but they are characterised by low capacity, slow exchange rates, large volume changes and lack of expected selectivity. Bayer stressed the point that ligands attached to polymers show greater selectivity than in solution due to the restricted geometric arrangement in the resin.[22] A resin containing iminodiacetic acid functional group was reported from the Chemical Research Laboratory at Teddington in 1953 and was described as having considerable affinity for polyvalent ions.[23] Later they reported various amino carboxylic resins based on chloromethylated polystyrene.[24] Dowex A-1 containing iminiodiacetic acid was the first commercially available chelating resin.[24] The functional group sorbed many metal ions by chelation but selectivity could be improved only by adjusting pH. It was inconvenient to use this resin in columns since it underwent considerable volume change when conditions were changed. Hirsch, Gancher and Russo[25] prepared an iminodiacetic acid resin of higher cross-linking that underwent very little volume change and was suitable for column operations. A large number of chelating resins have been introduced by various workers and are included in section 1.5.1.

1.5.1 CLASSIFICATION OF CHELATING RESINS

A survey of chelating ion-exchange resins reveals that only a few elements like N, O, S and As can function as electron donors in chelating groups (Table1.2). A brief classification of some important chelating resins according to the donor atoms of their functional groups is given below.

(i) Chelating resins with nitrogen as the donor atom

The number of chelating resins with nitrogen as the sole donor atom is comparatively small. A polymeric aliphatic amine, prepared by cross-linking water soluble polyaziridine with dibromoethane shows high affinity for copper (II).[65] Poly(N-vinylimidazol) introduced by Gold and Gregor shows good selectivity towards copper (I) and silver (I).[66]

Recently several chelating resins incorporating pyridine derivatives have been prepared which show selectivity towards copper. Thus 2-pyridyl methylamine and N-2-(2-pyridyl ethylenediamine) have been incorporated into styrene-divinylbenzene copolymer beads.[67] A selectivity order of Cu(II) $>$ Ni(II) $>$ Co(II) $>$ Zn(II) was observed for these resins. 2,2'-bipyridine is another versatile bidentate ligand which has been introduced into polymer matrix.[68]

Sl. No.	Chelating Group	Matrix	Elements	Ref.
1.	8-Quinolinol	Polystyrene, Silica gel	Cu, Ni, Co, Zn, Fe, Al, U, Pb, Mn	20, 21 26-29
2.	4-(2-Pyridylazoresorcinol	Polystyrene	Cu, Zn, Fe, V, Co, Ni, U, Au, Al	30
3.	Hydroxamic acid and N-substituted hydroxamic acid	Acrylic polymers Amberlite XAD-4 Sephalex	Fe, Cu, Zn, Ag, Hg, Al, Pb, Ti, Cd, Mn, Ni	8-12
4.	Mercaptogroup	Polystyrene, St DVB	Hg, Ag, As,	36, 37 20
5.	2-Mercaptobenzothiazole	Glass leads	Cu, Pb, Zn, Cd	38
6.	(N-Acryloylaminomethyl)-mercaptoacetamide	Polyacrylamide	Heavy metals	39
7.	Thiol	Glycolmethacrylate	As, Sb, Bi	40
8.	Thiol (Speheron thiol)	Hydroxyethyl methacrylate gel (macroporous), polyacrylamide	Zn,	41-43
9.	Chromotropic acid	Cellulose	Fe, Cu, Zn, Ti	44
10.	Thioglycolate	Sucrose methacylate	Ag, Hg	45
11.	Thiosemicarbazide	Polystyrene	Pt, Pd, Rh, Ru, Ir	46

12.	Acylthiosemicarbazide	Acrylic polymer	Cu, Ag, Cd, Hg	47
13.	Triazol thiol	Polyacrylic acid	Cu, Ag, Cd, Hg	47
14.	Bis dithiocarbamate	Silica	Cu	48
15.	Dithiocarbamate	Polystyrene	Ag, Cu, Zn, Ni, Co	50
16.	Hexyl thioglycolate	Polystyrene	Ag, Hg, Au, Bi, Cu	51
17.	Arsonic acid	Polystyrene	Cu^{2+}	21
18.	O-Hydroxy phenyl arsonic acid	Polystyrene	Cu^{2+}	21
19.	Benzylisothiouronium chloride	St-DVB	Pt, Ir, Os, Pd	52
20.	Diethyl vinyl phosphonic acid ("memory complexone")	Acrylic polymer	Cu^{2+}	5
21.	Phenyl arsonic acid	Cellulose	Cu, Ni	53
22.	Maleic anhydride	Styrene-acrylonitrile	Fe, Cu	54
23.	Hydrazone	Silica gel		55
24.	Biscarboxy methylamino group	Polystyrene	Ga, In, Al	56
25.	1-Nitroso-2-naphthol	Silica, Polystyrene (macroreticular)	Co, Cu, Fe, Ni, Pd, U	57,58

Sl. No.	Chelating Group	Matrix	Elements	Ref.
26.	β-Diphenylglyoxime	Polystyrene	Pd	59
27.	Ethylene diglycol dibutyl ether	Polystyrene	Au	60
28.	N,N-(Di-n-butyl propionamide)	Polystyrene	U, Th, Zr, Au, Pd	61
29.	Pyrogallol	Condensation polymer with formaldehyde	Be, Ge, Zr, Hf, Ta, Mo, W	62
30.	Isonitrosoacetamide	St-DVB	Pd, Cu, Hg, U, Ag, Pb	63
31.	Dithizone	Polystyrene	Au, Pt-group metals	64

Polyethylene polyamines such as ethylene diamine, diethylene triamine and triethylene tetramine have been attached to cross-linked chloromethylated styrene by amination.[69] These polyethylene polyamines show selectivity towards Cu(I), Cu(II), Ni(II), Zn(II) and Cd(II) ions.

(ii) Chelating resins with nitrogen and oxygen as donor atoms

The largest number of chelating resins comes under this class, the widely used iminodiacetic acid resins forming a major group. Other important ligands are hydroxamic acids, oximes, 8-hydroxyquinoline derivatives and Schiff's bases. A great deal of effort has been extended to study the various synthetic, analytical and theoretical aspects and applications of polymers with iminodiacetic acid functionality. Iminodiacetic acid and other aminocarboxylic acid resins as chelating exchangers have been reviewed.[70] Commercially available iminodiacetic acid resins are listed in Table 1.3. B, B^1-iminopropionic acid, ethylene diamine tetracetic acid, 2,6-pyridine dicarboxylic acid and propylene diamine tetracetic acid are a few such compounds studied.[71-74] These resins have been used for the selective separation of various metal ions from alkali and alkaline earth metals at graded pH.[75,76]

Resins incorporating 8-quinolinol are known for the last thirty years. However, Parrish who was a pioneer in the work involving this particular type of resin has emphasised the fact that their properties have never been completely satisfactory, due to low capacity and slow exchange rate.[77] Condensation of oxine-resorcinol and formaldehyde and coupling of diazotized poly(aminostyrene) with oxine are the two basic methods of synthesis of the resin. In a commercially available resin "Spheron Oxine 1000" (Koch-Light) oxine is bound through azo group and the flexible side chain is of a hydrophilic macroporous copolymer of glycoldimethacrylate and glycol monomethacrylate. This resin shows an exchange capacity of 0.2-0.3 mmol/g.[77] Parrish showed that better kinetics and capacity could be obtained by preventing the loss of water during curing and by incorporating sulfonic acid group. He succeeded in synthesizing a macroporous resin impregnated with oxine which gave better results than Spheron Oxine.[77]

Another ligand which has been extensively used in polymer complexones is hydroxamic acid. The hydroxamic acid group is well known for its ability to form highly stable chelates with heavy metal ions, particularly iron. The study on this type of chelating exchangers was pioneered by Deuel et al.[78] They prepared hydroxamic acid derivatives of poly(methacrylic acid) resins.[78-80] Since then a number of resins have been synthesized with hydroxamic acid as the functional group. However, so far none of the hydroxamic acid resins is commercially available. Winston and Mazza and Vernon[81] have reviewed various aspects of the polymeric hydroxamic acids. Acrylo-, methacrylo-, crotono-, and cinnamo-hydroxamic acids have been prepared by the reaction of the corresponding esters with hydroxylamine. These monomers can be polymerized under a variety of conditions.

The work of Vernon and Eccles in this area is quite significant.[81-83] Their method of synthesis involved partial hydrolysis of macroporous acrylonitrile - DVB copolymer to poly(acrylamide), followed by hydroxylaminolysis. They succeeded in obtaining several analytical separations and recovery of uranium from sea water. Wan Yunus[84] produced a cross-linked polyhydroxamic acid (PHA) exchanger in the form of a macroporous microbead with higher metal capacities and improved exchange kinetics. In order to prepare the microbead form of the resin, an acrylonitrile-ethylacrylate - DVB mixture had to be polymerized. Separation of gold and silver at trace levels have been achieved on this PHA resin. In a further study, Vernon has reported the purification and recovery of uranium using this resin.

The effect of N-substitution on the complexing property of PHA resin has been studied by Fritz and coworkers.[85,86] They studied N-phenyl, N-methyl and N-unsubstituted PHA group attached to Amberlite XAD-4 resin and suggested that in strong acid medium N-substituted hydroxamic acid is a more effective functional group than the N-unsubstituted analogues. The extraction behavior of N-methyl hydroxamic acid resin with 19 metal ions and various applications are reported.

Resins incorporating oxime derivatives are found to be very useful due to their strong chelating properties. A number of attempts have been made to incorporate vicinal dioxime into ion exchanger to obtain resins selective for nickel(II) and palladium(II).

Stamberg et al prepared several such resins using polystyrene as starting material.[87] One disadvantage of resins with oxime group is their limited stability towards chemical influences.

Another interesting group of resins are those based on carboxylic acid hydrazides developed by Blasius, Laser, and Brozio.[73,88] These resins have a strong affinity towards transition metals. A resin with maleic acid hydrazide is specific for mercury(I) and mercury(II).[88]

(iii) Chelating resins with oxygen as the donor atom

Polyhydroxy compounds, polycarboxylic acids, ethers, 1,3-diketones, fluorones and flavones are some important groups of chelating compounds containing oxygen as the sole donor atom. Polycondensation of phenols with formaldehyde is the simplest route for synthesizing such resins. Thus pyrogallol,[19] 2,3,4-trihydroxybenzoic acid, resorcinol and salicyclic acid have been incorporated into the resin matrix.[89-91] Polycarboxylic acid resins have also been obtained from acrylic or methacrylic acids.[92,93]

De Geiso et al have reported the synthesis of a copolymer of 5-methyl-5-hexene-2, 4-dione and styrene that has affinity for Fe(III).[94] Sahni and Reedijk have described in detail the various chelating resins with oxygen as donor atom.[95] Phosphonic and arsonic acid exchangers are the other chelating resins with oxygen as donor atom. Kennedy and co-workers synthesized several resins by phosphorylation of chloromethylated polystyrene.[21] Phosphonic acid resins are important as they have affinity for uranium. Parrish synthesized a resin with arsonic acid functional group by Baht reaction with polyaminostyrene.[19]

(iv) Chelating resins containing crown ether and related ligands

Crown ether and related compounds are increasingly being used in liquid-liquid extraction for separation or concentration of trace metals or isotopes, in ion-selective electrodes and membranes, electrophoresis and many other areas. A variety of macroheterocycles such as crown ethers including cyclic compounds containing nitrogen, sulfur, or phosphorous atoms instead of oxygen atom, acyclic polyethers and cryptands (bicyclic crown ethers) have been incorporated into different types of polymer supports.[96] A detailed review on chelating resins containing macrocylic and related ligands, has been published by Sahni and Reedijk.[97] Blasius et al have prepared a large number of polymeric or polymer-supported crown ethers and reviewed their synthesis,properties and applications.[96] Diaza-crown ethers and cryptands incorporated into condensation polymers have also been studied.[98] Warshawsky et al synthesized a number of polymers described as "polymeric pseudocrown ethers" (PDCE) based on a one-step cyclisation reaction between a chloromethylated styrene-divinylbenzene copolymer and polyoxyalkylene under the conditions of Williamson ether synthesis.[99]

A polymer-bound macrocylic hexaketone has been used for uranium extraction from sea-water while polymer-bound diazacrown ether and cryptand have been used to separate alkali and alkaline earth metal ions.[100] Two cryptands, Kryptofix 221B and Kryptofix 222B, bound to chloromethylated styrene-divinylbenzene copolymer, are now commercially available. Several chelating polymers with sulfur or sulfur and oxygen as ether linkages have been reported to be selective towards mercury(II) and other toxic metal ions.[101]

(v) Chelating resins with sulfur or sulfur and nitrogen as donor atoms

Chelating resins having a sulfur atom in their functional group should show high affinity for soft metals and several such resins have been studied extensively. Gregor et al[36] and Overberger and Lebovits[102] reported the synthesis of poly(thiolstyrene) almost simultaneously. Parrish synthesized a cross-linked poly(thiolmethyl styrene) by treating chloromethylated polystyrene with thiourea followed by hydrolysis with alkali.[19] This resin was found to be specific for mercury(II). In general thiol-based resins might be used to remove those metals which form mercaptides from a mixture of metal ions.

Another important sulfur containing ligand is the dithiocarbamate and related compounds which are capable of forming exceptionally strong complexes with a large number of metal ions.[103] Okawara and Sumitomo briefly described the preparation of dithiocarbamate resins starting with chloromethylated polystyrene.[104]

Recently Hiratani et al also reported the synthesis of four kinds of dithiocarbamate resins by treating chloromethylated polystyrene with the sodium salt of the corresponding dithiocarbamic acid in dimethylformamide.[50] The resin containing N-methyl-N-carboxymethyl dithiocarbamate showed maximum sorption capacity of 4.17 $meqg^{-1}$ for copper(II) and the reactivity towards metal ions was in the order Ag(I) > Cu(II) > Zn(II) > Ni(II) > Co(II).

Dithiocarbamate derivatives of cellulose have been prepared by Murthy et al by reaction of substituted amine derivatives of cellulose with sulfurdioxide in ammonia solution.[105] These cellulose derivatives showed better metal-sorption capacities. they used the trien-dithiocarbamate cellulose to preconcentrate Cu(II), Cd(II), Hg(II) and Pb(II) from sea and tap-water.

Novel routes for synthesizing polymers containing pendant multidentate ligands having two dithiocarbamate groups and a number of solid thioether based resins have been studied very recently.[106]

The resin prepared by Koster and Schmuckler containing isothiouronium functionality has excellent selectivity towards gold and platinum.[52] But elution of the metals was difficult and the resin had to be destroyed to recover.

In recent years, a number of other chelating resins incorporating ligands containing sulfur and nitrogen as donor atoms have been investigated. A chelating resin bearing mercapto and azo group was prepared by treating a commercial resin Amberlite IRA-400 with azothiopyrine disulfonic acid 4,4'-(4-diazenediyil-5-mercapto-3-methyl 1,2-diazacyclopenta-2,4-dien-1-yl)dibenzene disulfonic acid.[107] This resin is selective towards Hg, Cu and Cd and can be used for treatment of waste water containing mercury(II). The sorbed mercury can be eluted using thiourea solution and the resin can be reused. Fritz et al prepared a chelating resin by attaching hexylthioglycolate group into macroporous XAD-4 resin.[51] This resin showed favourable K_D values for gold(III), silver(I), mercury(II) and bismuth(III). Graded elution was used to separate mixtures of metal ions.

1.5.2 Thiol resins

The sulfur containing groups act as selective ligands with a high bond stability for transition metal ions. Several papers describe the immobilization of thiol groups on various matrices particularly styrene-DVB or polymethacrylate resins.[40, 42, 51, 107] The behaviour of thiol resins differs markedly from that of other chelating polymers such as Dowex A-1 for which the fixation of metal ion can be done with a highly swollen basic form with shrinking. In contrast to this, thiol-bearing resins complex at neutral pH without affecting the degree of swelling. Slight shrinkage was observed in acid medium.[42]

However, thiol group is slowly oxidized by oxygen during storage and thus resulting in a decrease in capacity. Synthesizing chelating resins with stable thiol group is a possibility worth exploring.

Slovak and co-workers tried to synthesize thiol derivatives of some hydrophilic hydroxyethyl methacrylate gels assuming that the hydrophobicity of polystyrene-based thiol derivatives affects the

sorption process unfavourably.[40] When the sorption of heavy metal ions on thiol derivatives of the polystyrene and methacrylate types was compared, better results were obtained for the latter.[40]
A hydrophilic glycolmethacrylate (now commercially available under the trade name Spheron Thiol) with bound thiol group was synthesized and was found to be selective for Hg(II), Sb(II), Bi(III), As(III), Ag(I), Cu(II) and Pt(IV) in acid solutions. The equilibrium was attained within five minutes and a sorption capacity of 0.5 to 1 mmol/g was observed in the case of Hg. The resin regeneration was possible with 10% thiourea in 0.1 M HCl. In a further study they have described the sorption of As(III), Sb(III) and Bi(III) from 1 M sulfuric acid and have optimized the condition for the electrothermal AAS of these metals sorbed on the resin.[24]

A similar resin has been investigated by Deratani & Sebille.[39] The thiol function has been grafted to the polyacrylamide matrix through a methylenediamide linkage which is supposed to be very stable in a wide pH range. Heavy metals and copper exhibit a high affinity towards the thiol function of the resin with fast fixation kinetics due to the hydrophilic matrix. The resins were prepared by thiolation via thiol ester group formation of various cross-linked polymers of N-acryloylaminomethyl chloroacetamide.

The synthesis and sorption studies of various metal ions on a macroreticular poly(acrylic acid) - based resin containing triazolethiol group has been described by Sugii et al.[47] The resin is resistant to air oxidation and can be used for the concentration of silver and gold from sea-water.

1.5.3 Ionically anchored chelating agents

The idea of synthesizing highly selective chelating resins by ionically anchoring anionic chelating agents to anion exchange resins is a new one. Aromatic chelating agents with sulfonic acid group and their complexes with metal ions undergo exchange on anionic resins due to the presence of sulfonic acid group. When such a chelating agent is loaded on the resin, the resin shows a high degree of selectivity to metal ions depending on the nature of the loaded reagent. Brajter et al were the first to recognize the potentiality of electrostatically loaded reagents.[108] More than ten reagents loaded on anion exchange resins have been investigated by various workers and these are discussed in more detail in part II.

1.6 SYNTHESIS OF CHELATING ION-EXCHANGE RESINS

The two main tasks involved in the synthesis of chelating ion-exchange resins are synthesis of a suitable polymeric matrix and incorporation of chelating groups into the matrix. Usually, it is done either by functionalisation of a pre-formed polymer or by using a chelating monomer in the polymerization process. A combination of the two methods are also used. The various methods of polymer modification and functionalisation have been exhaustively reviewed.[109-111]

The synthesis of an ion-exchange resin must yield an insoluble three-dimensional net-work of hydrocarbon chains carrying the functional groups. The polymerization should be carried out in such a way that the cross-links are formed at appropriate intervals, the ion-exchange resin so formed is insoluble and the counter ions are able to move freely in the matrix.

1.6.1 Matrix modifications

Among the various polymeric matrices used for preparing ion-exchangers, synthetic organic polymers possessing styrene-divinylbenzene copolymer has found most wide application. Condensation polymerization and addition polymerization are the two basic methods of synthesis of such resins. In the case of condensation polymers, the synthesis involves condensation of p-substituted phenol with formaldehyde and if an unsubstituted phenol is added a cross-linked polymer can be obtained. The degree of cross-linking can be adjusted by varying the content of phenol and formaldehyde in the matrix. Addition polymerization of styrene in presence of divinylbenzene gives a cross-linked matrix. Here the degree of cross-linking can be adjusted by varying the divinylbenzene content of the reaction mixture.

Actually, only in the case of addition polymerization, the degree of cross-linking can be easily adjusted. In the case of polycondensation, the structure of the product depends not only on the composition of the reaction mixture but also on the experimental conditions. Most of the classical work was carried out on condensation type polymers. The more recent addition polymers have almost completely replaced the earlier condensation polymers.

The ease of chemical modification and subsequent ion-exchange process depend largely on the physical properties of the resin itself. The matrix structure of the resin should facilitate diffusion of ions towards the exchange sites, a phenomenon which depends on the extent of swelling or solvation, the effective pore size and pore volume, and the chemical and mechanical stability of the resins under specified conditions. This, in turn, depends on the degree of cross-linking and the conditions employed during the preparation of the resin.

Three main types of resins are identified by Akelah and Sherrington, depending on the matrix structure which in turn depends on the conditions of preparation.[110] They are (a) microporous or gel type resins, (b) macroporous resins and (c) macroreticular resins.

The influence of porosity of macroreticular resins on the sorption of metal ions has been reported by Maeda and Egawa.[112, 113] They have investigated the uptake of zinc ions at low concentrations on a macroreticular resin (RST) with different porosity containing triethylene triamine side chains. Among the four resins of pore radii of 21.0, 24.5, 28.0 and 66.5 nm the resin with pore radius 66.5 nm gave the highest initial sorption rate and the largest breakthrough capacity for zinc ions. They showed that the densely cross-linked macroreticular resin with the largest pore radius was more practical for the removal and recovery of heavy metal ions from industrial effluents because of its fast kinetics and high physical stability.

1.6.2 Functionalisation

Conventional ion-exchangers contain either basic or acidic functional groups which are generally introduced by a substitution reaction. The design and synthesis of selective ion-exchange resins containing chelating groups is a tedious task.

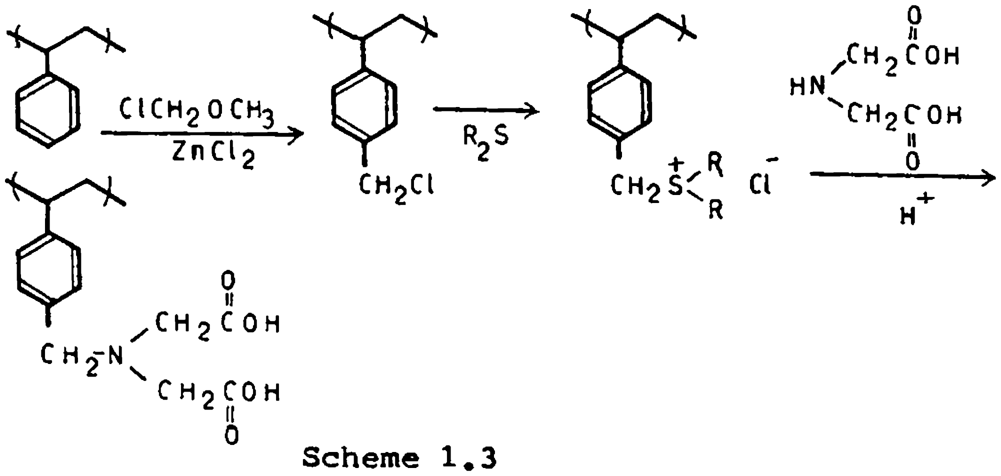
For incorporation into polymer matrix, a chelating agent must satisfy the following requirements. If the chelating group is introduced in the monomer before its polymerization, the group must be stable to withstand the polymerization conditions and must yield a resin gel of sufficient chemical stability. On the other hand if the chelating agent is incorporated by substitution in a preformed polymer matrix, the functionalisation must be achieved in minimum number of steps as each subsequent reaction will progressively clog the pores of the polymer. Care must also be taken to prevent intramolecular reactions within the dense resin gel.

The steric structure of the chelating molecule must be compact so that complex formation with metal ion will not be hindered by the matrix. The co-ordinating atoms in the chelating group must be oriented in such a way that its ability to form chelate is preserved in the resin.

Thus it can be seen that many chelating molecules are unlikely to be incorporated into a resin without loss of their selectivity properties. All chelating agents that do not form 1:1 complexes (e.g., 8-quinolinol) and long chain molecules (e.g., EDTA) have proved to be of restricted use for synthesizing chelating resin.[114]

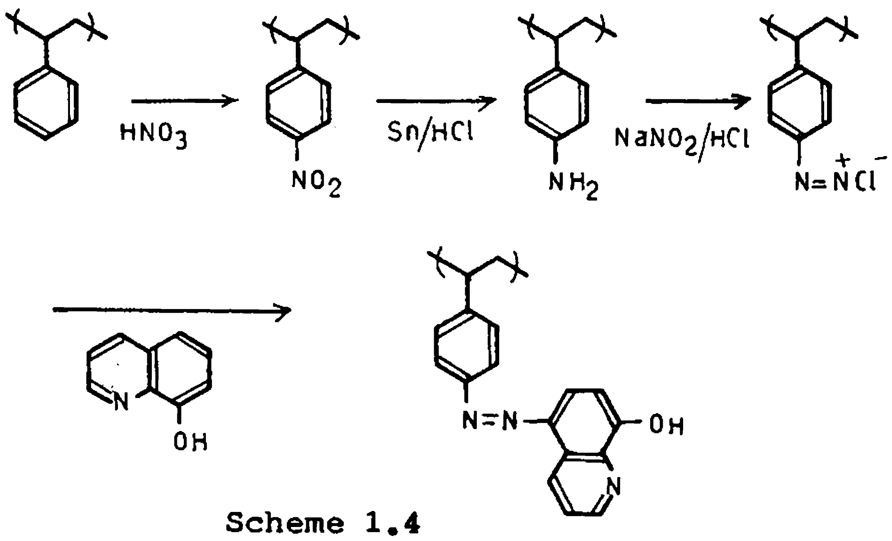
Various methods for the synthesis of chelating ion-exchange resins have been reviewed by Vernon[115] and Hodgkin.[116] The method involving incorporation of chelating groups into preformed polymers is preferred to other methods since commercially available polymers of desired characteristics can be used as starting materials. Majority of the preformed polymers are the copolymers of styrene and divinylbenzene (e.g., XAD-4 (Rohm & Haas Co., Philadelphia).

The most widely used technique for the synthesis of polystyrene-based chelating resins involves chloromethylation followed by substitution of chlorine atom with a suitable group.[117] Thus poly(methylene iminodiacetic acid styrene) can be prepared by the route shown in scheme



Scheme 1.3

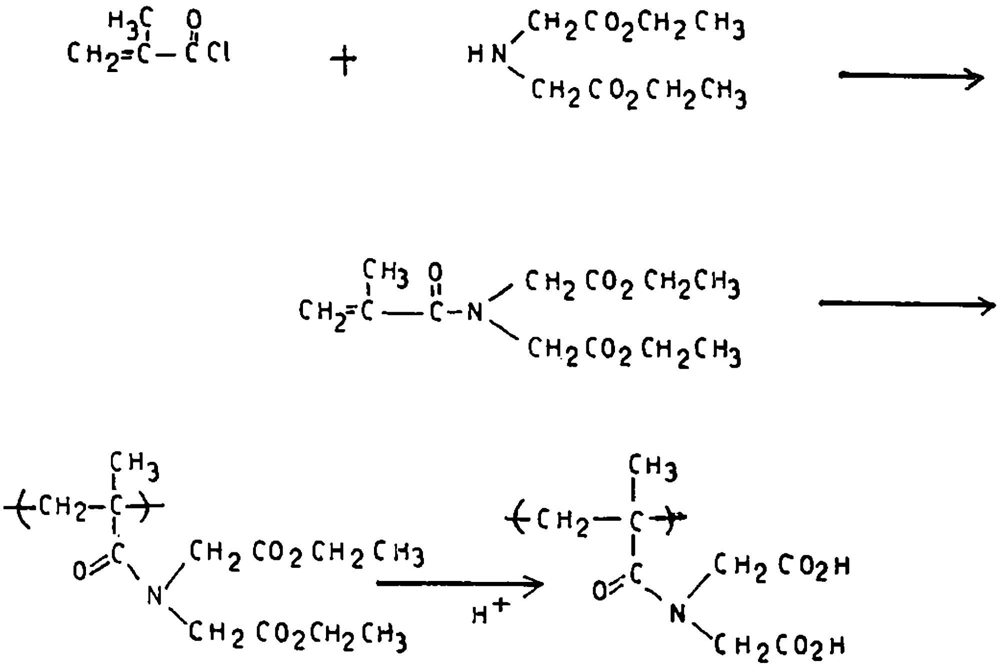
Another popular technique is the azo coupling of various chelating compounds with diazo derivatives of polystyrene.[20,21,118] The polystyrene can be nitrated and reduced to aminopolystyrene which in turn can be diazotized and coupled. The steps involved in the synthesis of an 8-hydroxyquinoline-based resin is given below:



Scheme 1.4

The sorption capacity of chelating resins obtained by transformation of pre-formed polymers depends on the nature of the matrix and the degree of substitution at each stage of the synthesis. Since the reactions proceed more effectively on linear polymers, the chelating group can be introduced into a linear polymer; the reaction can often be carried out in aqueous or aqueous-organic solutions. Dimethyl formamide is found to be most suitable when modification of chloromethylated polystyrene is involved.[119] The functionalized polymer can be further cross-linked to obtain an insoluble sorbent. In some cases these chelating sorbents are supported onto inert materials such as silica, alumina, etc.

In recent years, chelating resins have been prepared by polymerization of chelating monomers in the presence of a cross-linking agent. This approach is exemplified by the synthesis of an iminodiacetic acid derivative given in scheme 1.5.[120]



Scheme 1.5

Vinylpyridine type sorbents that have found extensive application are synthesized by polymerising vinylpyridines with divinyl compounds. The reason for their infrequent use is the difficulty in synthesizing vinyl compounds containing chelating groups.

Polycondensation is another important method for the synthesis of chelating ion-exchange resins. The chelate-forming molecule is copolymerised with phenol and formaldehyde. Resins incorporating anthranilic acid,[121] m-phenylene diamine tetracetic acid,[91] 8-quinolinol[20, 121] and many other monomeric ligands have been used to separate a number of elements. Shortcomings of chelating resins obtained by polycondensation include: uncertainty of the structure of polymers, insufficient selectivity, slow sorption rate, etc. But this method is still being used for the synthesis of new chelating ion-exchange resins.

Cellulose-based chelating resins have been synthesized using the reactivity of its hydroxyl groups.[122] Thus, cellulose sorbents containing iminodiacetic acid, anthranilic acid, aminophenyl arsonic acid, etc. have been obtained by interaction of the corresponding monomers with cellulose derivatives. Diazotisation of the cellulose amino derivative and coupling with compounds containing chelating groups is also employed.

1.6.3 Fibrous Exchangers

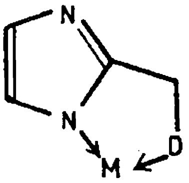
Recently ion-exchange fibers have attracted attention because of their large surface area and the resultant fast kinetics and high capacity. A fibre-type exchanger must satisfy the indispensable conditions: (1) the ionic group and the matrix polymer must be chemically stable, (2) the mechanical strength must be sufficiently high. A series of papers have been published by Yoshioka and Shimamura on ion-exchange fibres which satisfy the above mentioned conditions.[122-124] They have reported for the first time an ion-exchange fibre with high ion-exchange capacity and high mechanical strength. Polystyrene-based exchangers satisfy the first two conditions, however possess poor mechanical strength. A polystyrene-based ion-exchange fibre which satisfies the three conditions has been reported by them by introducing a cross-linking group and an ion-exchange moiety into polystyrene by chemically treating an "island-in-a-sea" type fibre composite.[122] The 'sea' ingredient predominantly comprised of an ion-exchanger based on polystyrene matrix and the 'island' ingredient comprised of polypropylene fibre for reinforcement. It was found that the resulting fibre had high ion-exchange rate and large capacity for macromolecular ionic substances. The surface area of the fibre was found to be about 10 times larger than that of the beadtype resin.

In a later paper Yoshioka has described the synthesis of fibrous chelating exchangers with $-N(CH_2COOH)_2$ and $-N(CH_2CH_2COOH)_2$ groups attached to polystyrene-polypropylene composite fibre.[124] The sorption characteristics of Cu(II) on these chelating fibres and an ordinary resin have been compared. It was found that the rate of sorption on the fibrous material was about ten times higher than that on the bead-type resin and that the former forms more stable complexes with Cu(II) than the latter. It is concluded that the diffusion within the exchanger is the major rate-controlling step in the sorption process. Theoretical explanation of the results has been given using the diffusion equation for ion-exchange on a cylindrical endless fibre by modifying the method used for a spherical resin.

As the resin reinforced with polypropylene fibre has high mechanical strength, it can be converted to various forms viz., filament, cut fibre, knitted fabric, woven fabric, braid, felt, chip and paper. A cylindrical module made of felt is reported to be superior to other forms in the removal of metal ions.[124]

1.6.4 Derivatives of polyvinylimidazole

Studies by Green and Jaskulla[125] have brought to light a further extension of synthesis of chelating exchangers. They employed vinylimidazole as the monomer, taking into account its favourable properties, so that a donor atom was provided in the matrix itself. Other functional groups were introduced after polymerization, with the result that the product could chelate with metal ions.



D = Donor group
M = Metal

(Imidazole-metal complex)

Because the chelating properties of the resins do not occur solely because of the attached active group D, (as they do in the case of polystyrene-based resins) it is reasonable to assume that the structure of D need be less complex than for polystyrene resins.

The method of preparation and nature of the precursor are analogous to those of polystyrene-based resins but there is an advantage of obtaining a useful complexing resin by attaching a single donor atom such as oxygen, nitrogen or sulfur. Using this principle they prepared a number of chelating resins based on poly(vinylimidazole) by treating the halomethylated copolymer of vinylimidazole and divinylbenzene with a variety of reagents containing amine and sulfur groups.[125] These resins showed appreciable capacities and selectivities towards Cu(II), Ni(II) and Co(II). The possibility of using such a resin for the recovery of all the Ni(II) and Co(II) from uranium plant raffinate solution, has also been described.

1.6.5 Memory Complexones

It is practically impossible to have a set of polymer sorbents specific to each kind of metal ion. In most cases the functional groups exhibit selectivity to a large group of ions. It is reported that specific silica gels with improved selectivity can be obtained by forming gels in the presence of active sorbents.[21]

Recently, Effendiev and Kabanov have proposed a method of preparation of polymer complexones with macromolecular prearrangement favourable for the sorbing ions. The method involves treatment of the functionalized linear polymer with the particular ion to be sorbed. The macromolecule still mobile enough takes conformations favourable for sorption. The metal ion-sorbed linear polymer is fixed at the optimum conformation by cross-linking. On removing the template ions, the cross-linked polymer may "keep-in-mind" the conformation advantageous for sorbing the template ions and this would lead to an improvement in fundamental sorption characteristics. Effendiev and Kabanov synthesised a 'memory complexone' or this type using diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA) as the initial monomers and N, N'-methylene diacrylamide as the cross-linking agent.[5]

The investigation of copper ion uptake by the so called "memory complexones" showed that the prearrangement of macromolecules for ion uptake makes it possible to increase the sorption capacity more than twice and significantly improves their kinetic characteristics in comparison with polymer complexones without such prearrangement. Sorption studies of samples prearranged for the uptake of cobalt and nickel showed that in all cases the sorbents exhibited higher selectivity with respect to metal ions for which they were prearranged.

1.6.6 Supported resins

Complexation with organic reagents supported or immobilized on various solids is becoming increasingly popular on account of high selectivity, simplicity of preparation and effectiveness. Large, mechanically stable and highly porous ion-exchange pellets are prepared by cementing small ion-exchanger particles together with an inert binder or by impregnating an adequately strong and stable support such as pumice.[126] The support is impregnated with the liquid reaction mixture and the condensation is completed in situ.

1.7 ANALYTICAL APPLICATIONS

Chelating ion-exchange resins play a vital role in the field of analytical chemistry. Although instrumental methods of analysis are more popular, there are many instances in metal analysis in which the instrumentation cannot fulfil all demands of analytical criteria. The problem can be solved to a considerable extent by the application of chelating polymers which enable preconcentration of metal ions conveniently by an ion-exchange chromatographic procedure. Furthermore, the preconcentration of the sample can be simultaneously connected with a separation procedure which is based on the metal selectivity of the chelating polymers. The selectivity, in turn, can be varied to a large extent by changing experimental conditions such as pH, temperature and addition of complexing agents.

When environmental protection agencies started to enforce strict rules on the control of pollutants in industrial effluents, a sudden spurt occurred in the search for evolving effective methods to remove these pollutants. Removal of toxic metal ions like Hg(II), Cd(II), Pb(II) and As(III) even in μg/l levels also became a serious problem. The study of the removal of metal ions at trace levels from aqueous solutions either for pollution control or for recovery has been assuming importance in recent years. The use of immobilized metal complexing polymers is found to be the simplest method due to good recovery ratio.

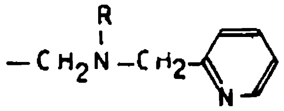
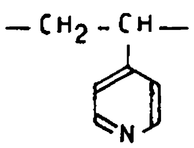
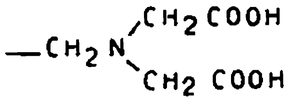
Separation of metal ions from one another or from impurities is also equally important. Due to an increasing demand in semiconductor manufacture, an efficient process is required to extract ultra pure metal ions from low grade ores or industrial scraps. Although solvent extraction procedures are available, solid-liquid systems have attracted much attention for hydrometallurgical process owing to their mechanical convenience over liquid-liquid extraction systems.

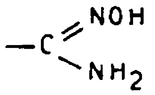
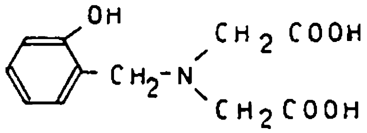
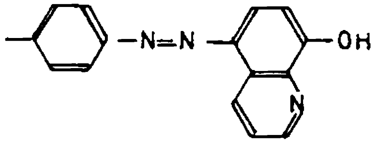
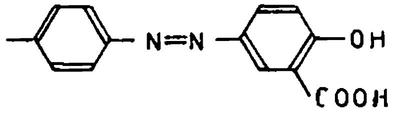
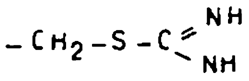
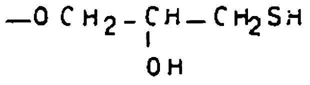
Recently, the analytical behaviour of hydrophilic glycolmethyacrylate gel with bound thiol group (Spheron Thiol) was studied[40,41] and the high selectivity of this resin for sorption of Hg, As, Sb, and Bi from mineral acid solutions was reported. Direct sampling of the resin suspensions for electrothermal AAS determination was an additional advantage of this resin. Complete recovery of 40 ng of As ml^{-1} added to solution of 5% KCl or 5% $MgCl_2$ and to river water was obtained. Today a number of chelating resins are used for separation or pre-concentration of metal ions. Some of the commercially available chelating resins are listed in Table 1.3.

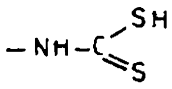
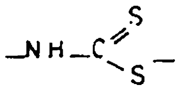
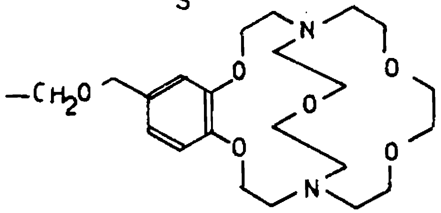
Ion chromatography

Although a large number of papers have been published on ion-exchange methods, the technology of chromatographic separation of inorganic ions lagged behind until recently. Many of the chromatographic separations use resins of large particle size, gravity flow, and require fraction collection and discrete quantitation of separated species. Efficiency of separation is highly improved by using columns of relatively small diameter containing a stationary

Table 1.3 Some Commercially Available Chelating Ion-Exchange Resin

Sl. No.	Chelating Group	Nature of Chelating Group	Polymer Matrix	Commercial Name	Manufacturer
1.		Weakly basic group	Polystyrene (X% DVB)	Dowex XF-4195 Dowex XF-4196	Dow Chemical, USA
2.	$-CH_2-NH-(C_2H_4NH)-H$	Basic (Polyamine)	Polystyrene (X% DVB)	Diaion CR-20	Mitsubishi
3.		Basic (Polypyridine)	Polyvinyl-pyridine (20% DVB)	Sumichelate CR-2	Sumitomo Japan
4.	 $-CH_2N(CH_2COOH)_2$	Iminodiacetic acid	Polystyrene (X% DVB)	1. Dowex A-1	Dow Chem. U.S.A.
				2. Duolite ES 466	Diamond Shamrock
				3. Chelex-100	Bio-rad
				4. IMACSYN 101	Diamond Shamrock
				5. IRC-718 (XE-318)	Rohm & Haas
				6. Wofatit MC 50	VEB Chemie-kombinat Biterfield, DDR
				7. Permutit S-1005	Permutit Co. Ltd. England
				8. TP-207	Bayer, A.G. West Germany

Chelating Group	Nature of Chelating Group	Polymer Matrix	Commercial Name	Manufacturer
 $-C(=NOH)NH_2$	Amidoxime	Polyacrylic (X% DVB)	Duolite ES 346	Diamond Shamrock
	(O-hydroxybenzyl) iminodiacetic acid	Phenol formaldehyde	Unicellex UR-50, UR-40 UR-30 UR-20 UR-10	Unitika Ltd. Japan
	8-hydroxyquinoline	Poly(hydroxyethylmethacrylate-co-ethylene dimethacrylate	Spheron Oxine 1000	Lachema, n.p., Brno
	Salicylic acid	Poly(hydroxyethylmethacrylate-co-ethylene dimethacrylate	Spheron Salicyl 1000	Lachema, n.p., Brno
 $-CH_2-S-C(=NH)NH$	Isothiouronium	Polystyrne (X% DVB)	Srafion NMRR	Ayalon, Haifa, Israel
			Ionac SR-3	Ionac, Sybrom Chem.Div. USA
 $-OCH_2-CH(OH)-CH_2SH$	Thiol	Poly(hydroxyethylmethacrylate CO-ethylenedimethacrylate	Spheron Thiol 1000	Lachema, n.p., Brno

Chelating Group	Nature of Chelating Group	Polymer Matrix	Commercial Name	Manufacturer
-SH	Aromatic thiol	Polystyrene (X% DVB)	IMAC TMR	Diamond Shamrock
-SH	Aromatic thiol	Polystyrene (X% DVB)	Duolite ES 465	Diamond Shamrock
 $-NH-C(SH)=S$	Dithiocarbamic acid		Misso ALM- 525	Nippon Soda
 $-NH-C(=S)-S-$	Dithiocarbamate	Polyacrylic	Sumichelate Q-10R	Sumitomo Japan
	Cryptand	Polystyrene (2% DVB)	Kryptofix 221 B (Polymer found)	Parish Co., Utah, USA

phase of small particles of uniform size and by using small sample volumes, constant eluent flow and continuous detection.

In preparative ion-exchange chromatography particles of 100-200 mesh, packed into columns of 1-2 cm diameter and 10-50 cm length were employed. The packing operation did not demand any special care and flow rate of mobile phase was not maintained constant as gravity flow was often employed. The method of monitoring an ion-exchange separation was discontinuous since the fractions collected were analysed chemically and chromatograms constructed by plotting the amount of solute in each fraction against the fraction number or average volume of eluent in each fraction. Even with gradient elution technique, total elution volumes tended to be as large as several litres in extreme cases.

Modern ion-exchange chromatography is faster, more convenient and has higher resolution than classical methods. The improvement in performance can be attributed to factors like use of more efficient ion-exchange resins and columns, smaller samples, better chromatographic components and above all automated continuous detection systems. The particle size ranges from 5-50μm and columns are of small bore (2.5 mm i.d and 25-100 cm in length). As in organic LC, the columns must be properly packed to attain high performance. The connecting tubes are of small bore ($\approx$ 0.3 mm) to reduce peak spreading. In high performance chromatography the sample volume is small (typically 10-100μl) and the amount of sample component is in the microgram range, the exact amount depending on the capacity of the loaded phase and the sensitivity of the detector. As a result, greatly improved resolution and sharper peaks are obtained.

The most important aspect of modern ion-exchange chromatography is the use of on-column detection systems, which provide a continuous signal output. Several papers have been published in which automatic spectrophotometric detection was used for metal ions separated by ion-exchange chromatography.[128,129] The work by Small, Stevens and Bauman using automatic conductometric detection was a milestone, because, for the first time it made possible the rapid separation and measurement of common inorganic and organic anions.[130]

The name "ion chromatography" has been used by many authors to describe separation of ions in a chromatographic system involving two columns, one used for separation and the other, 'suppressor' column, used to remove the eluent ions, analyte ion in the effluent being monitored by a conductivity detector. Fritz et al have used the term in a broader sense i.e., "for a process in which ions are separated chromatographically for the purpose of analysis in which some form of automatic detection is employed".[131]

The lack of a satisfactory detector system for ions that do not absorb in the uv region probably has held up development of automated ion-exchange chromatography particularly for inorganic samples. However, spectrophotometric detectors employing a colour forming reagent, the recently developed electrochemical detectors and the conductivity detectors provide excellent sensors for monitoring ion-exchange separations.

The design of an automatic detection system involves the careful choice of eluent type, concentration of analyte and a detector compatible with the eluent and sample ions. Conductometric detectors are used widely in ion-chromatography while spectrophotometric and electrochemical detectors are also useful to monitor ion-exchange separation. Detectors may be operated as a direct monitor or as a monitor after post-column-derivatization.

Detailed description of detector hardware, construction of various detector cells and detector operations has been given by Fritz, Douglas, Gjerda and Pohlandt.[132] An exhaustive description of two-column method and one-column method for anions and cations using conductometric detectors is also given.

CHAPTER - II

SYNTHESIS AND CHARACTERISATION OF ST-3 RESIN

2.1 INTRODUCTION

Sulfur-containing ligands are known to be more selective towards heavy metal ions.[51,133] Several sulfur containing resins have been synthesized and investigated for their application in separation, removal and/or recovery of metal ions either for pollution control or for raw material recovery. Of these resins studied, benzyl thiouronium salt introduced by Koster and Schmuckler[52] has proved to be the most successful.

A novel chelating resin (ST-3) bearing stable thiol group was synthesized and characterised. Since polystyrene is readily available and is sufficinetly durable, it was used as the matrix in the synthesis of ST-3 resin. Studies on its nature and sorption behaviour towards Cu(II), Ni(II), Hg(II), Ag(I), Pb(II), Zn(II), Cd(II) and Bi(III) by both batch and column techniques are reported in this chapter.

2.2 EXPERIMENTAL

2.2.1 Synthesis of the resin

ST-3 resin was synthesized by a novel easy route using polystyrene as the starting material. The resin is a derivative of poly(aminostyrene) bearing a thiol functionality as evidenced by IR spectrum. The analytical studies have conclusively proved that ST-3 resin holds promise as a material of choice for the removal of mercury from effluents. Scale up studies are in progress to establish its commercial viability. Hence, the synthetic procedure for its preparation is not presented here.

The resin was characterised by the following physical and chemical methods.

2.2.2 Elemental analysis

A. Sulfur

Sulfur content of the resin was estimated by Schoniger oxygen flask method.[134]

A weighed sample (0.2g) of dry resin was placed in the sample cup of the Schoniger flask. It was covered with a strip of ashless filterpaper having a thin strip for ignition. Sodium hydroxide solution (10 ml, 10%) was used as absorbent and 5 ml of 30% hydrogen peroxide was used as oxidant. The sample cup was lowered into the flask and the flask was flushed with oxygen. The strip was ignited and the flask was closed by lowering the stopper carrying the cup. After ignition, the contents were thoroughly mixed, the solution was acidified with hydrochloric acid and transferred to a 250 ml beaker. Sulfate was estimated gravimetrically as barium sulphate.

B. Nitrogen

Nitrogen was estimated by micro Kjeldhal method.[135] A sample of dry resin (25 mg) was accurately weighed and transferred into the digestion flask. A digestion mixture consisting of 1g potassium bisulfate and 10 ml of concentrated sulfuric acid and a pinch of copper sulfate were added. The contents were digested for about 4 hours, cooled, diluted with water and quantitatively transferred to the distillation tube of the Kjeldhal apparatus. About 20 ml of 50 per cent sodium hydroxide solution was used to generate ammonia. Ammonia was steam distilled and collected in a solution of boric acid and was titrated with 0.05N hydrochloric acid to methyl red-methylene blue end-point.

2.2.3 Functional group analysis

Thiol functionality in the resin was estimated by iodine method. A sample (0.2 g) of the resin was kept soaked in a known volume of standard iodine solution contained in an iodine flask for 2 h with occasional shaking. Residual iodine was determined titrimetrically using standard thiosulfate solution to starch end point. The equivalence of thiol was calculated from the amount of iodine consumed.

2.2.4 Stability of the resin in acid and alkaline media

Stability of ST-3 resin towards acid and alkali of different strength were checked by keeping it soaked in the medium for 24 h. It was then washed thoroughly with distilled water and dried. The sorption cpacity of the treated resin for mercury (II) was compared with that of the untreated resin.

2.2.5 Determination of water regain

A weighed amount of the resin was kept immersed in deionised water for 24 h. The resin was then filtered and air-dried by suction. Weighed amount of the swollen resin was then dried at 80°C for 48 h and reweighed. The water taken up (in g) by 1g of the dry resin was calculated.

$$\text{Water regain \% W/W} = \frac{\text{Wt. of water absorbed}}{\text{Wt. of dry resin}} \times 100$$

2.2.6 Procedures used in sorption studies

Stock solutions of metal ions were prepared using the following salts.

Formula of salt	Manufacturer
1. $CuSO_4.5H_2O$	Glaxo Laboratories, Bombay
2. $(NH_4)_2SO_4$ $NiSO_4.6H_2O$	E.Merck(India) Ltd., Bombay
3. $HgCl_2$	Glaxo Laboratories, Bombay
4. $Zn SO_4.7 H_2O$	Sarabhai M.Chemicals,Baroda
5. $Cd(NO_3)_2.4 H_2O$	E.Merck(India) Ltd., Bombay
6. $Pb (NO_3)_2$	E.Merck(India) Ltd., Bombay
7. $Ag NO_3$	Glaxo Laboratories, Bombay
8. $Bi(NO_3)_3$	E.Merck(India) Ltd., Bombay

All chemicals used were of guaranteed purity and solutions were prepared in doubly distilled water. Stock solutions of 2000 mg/l were prepared and standardised by recommended procedures.

pH of experimental solutions were adjusted using 0.1N sodium hydroxide and 0.1N hydrochloric acid unless otherwise specified. Ionic strength of solutions was adjusted using sodium perchlorate wherever specified.

The sorption characteristics of the resin for various metal ions were studied by batch and column methods. The resin was powdered in a glass mortar and particles of 100-200 mesh size (ASTM) were used for the sorption studies. The resin was washed with distilled water till the filtrate was neutral and dried under vacuum at 80°C for 24 h before use. In all cases capacities and related parameters are expressed in terms of dry weight of the resin.

(a) Batch technique

The dependence of sorption of metal ions on pH and the kinetics of sorption were studied by batch technique. A sample of resin weighing

0.1g was taken in a stoppered conical flask. An aliquot of the metal ion solution of which the pH was adjusted using 0.1N NaOH/HCl was added to it and kept shaken at 28±1°C on a mechanical shaker. pH of the solution was also checked after equilibriation. To ensure attainment of equilibrium, sufficient time was given before sampling the solution for analysis. Generally, it was less than 8 h.

Residual concentration of metal ions in solution was determined by withdrawing the supernatant liquid after 8 h using a filter stick fitted with a G-4 sintered glass filter. The amount of metal present in the resin phase was taken in terms of the difference between the original and residual concentrations in the solution phase. The sorption capacities (millimoles of metal ion taken up by 1g of dry resin) and K_D values for various metal ions at different pH were calculated.

$$(K_D = \frac{C_R}{C_S} \times \frac{V}{M})$$

For studying the kinetics of sorption of metal ions, 0.1g of the resin was kept shaken with aliquots of metal ion solution of which the pH was adjusted to the value where maximum sorption capacity was observed.

(b) Column operations

A glass column, 0.5 x 10 cm, fitted with threaded plexiglass joints was used for the column operations. Polyethylene tubes (2 mm i.d.) were used for interconnections. The resin (100-200 mesh size) was allowed to swell in appropriate buffer for 24 h. The swollen resin was slurry-packed by applying suction at a water pump. The resin bed was conditioned by passage of appropriate buffers. The solution was fed by gravity flow. Flow rate was adjusted using a pinch cock. Fractions were collected in graduated test tubes.

Breakthrough studies of Hg(II), Ag(I), Pb(II), Bi(III) and Cd(II) were carried out. The procedures used are given below.

(i) Mercury (II)

The column was pre-conditioned by running 50 ml of 0.01M hydrochloric acid at a flow rate of 1 ml/min. After pre-conditioning, mercury(II) solution (100 mg/l) at pH 2 was allowed to pass through the column at a flow rate of 0.5 ml/min from the over head reservoir. Fractions were collected in 5 ml lots. The amount of Hg(II) in each fraction was determined spectrophotometrically using potassium thiocyanate.[136]

(ii) Silver (I)

The column was pre-conditioned by running 50 ml of very dilute nitric acid (pH 3) at a flow rate of 1 ml/min. Silver (I) solution (100 mg/l) at pH 3 was allowed to pass through the column at a flow rate of 0.5 ml/min. Fractions were collected in 5 ml lots and the amount of Ag(I) in each fraction was determined spectrophotometrically using dithizone.[137]

(iii) Lead (II)

The column was conditioned at pH 5.5 using acetate buffer and lead nitrate solution [(100 mg/l of Pb(II)] was run through the column at a flow rate of 0.5 ml/min. Concentration of Pb(II) in the fractions was determined spectrophotometrically using dithizone.[138]

(iv) Bismuth (III)

The column packed with the resin was pre-conditioned with 0.5M hydrochloric acid by running 50 ml of the acid at a flow rate of 1 ml/min. Then 100mg/l solution of Bi(III) as nitrate was allowed to pass through the column at a flow rate of 0.5 ml/min. Fractions of 5 ml were collected and concentration of bismuth in each fraction determined spectrophotometrically using thiourea.[139]

(v) Cadmium (II)

The column containing the resin was pre-conditioned at pH 5.5 by running 50 ml of sodium acetate/acetic acid buffer of pH 5.5. A solution of cadmium chloride [100mg/l of Cd(II)] was run through the column at a flow rate of 0.5 ml/min. Fractions were collected in 5 ml lots and concentration of Cd(II) was determined spectrophotometrically using dithizone.[140]

2.2.7 APPARATUS

pH was measured using Model 1400 pH meter (e.s. Research, Madurai). A combination electrode system consisting of glass electrode and silver/silver chloride/saturated potassium chloride electrode was used. Routine adjustments like slope and asymmetric corrections were done whenever necessary.

Metal ion concentrations in various samples were measured by UV-visible absorption spectrophotometry, atomic absorption spectrophotometry (AAS) or inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) as indicated in the corresponding sections.

(a) UV-visible spectrophotometer

A model 200-20 UV-visible spectrophotometer, Hitachi, Japan was used for UV-visible spectrophotometric measurements. Slit width was adjusted at 2 nm. Matched, fused silica cuvettes were used as sample cells.

(b) Atomic absorption spectrophotometer

Model 2380 Perkin Elmer atomic absorption spectrophotometer was used for the quantitation of certain metal ions. Mercury concentration in presence of thiourea was measured by cold vapour atomic absorption using Perkin Elmer, model 50 A instrument. The experimental details are given in corresponding sections. The analytical wave lengths used and other instrumental settings were as per the manufacturer's manual.

(c) Inductively coupled plasma-atomic emission spectrophotometer

Estimation of some of the metal ions were carried out using inductively coupled plasma - atomic emission spectrophotometer, model 8410 Plasma Scan (Labtam). Data were acquired in a computer and concentrations were measured against built-in calibration curves.

2.3 RESULTS AND DISCUSSION

2.3.1 Nature of the resin

ST-3 resin is a nonporous particulate resin with a sulfur content of 8.7% (2.72meq/g). The resin contains 2.2meq/g of thiol groups as determined by iodine method. This is less than the value projected by elemental analysis. The remaining sulfur may be existing in the oxidized forms of thiol, e.g., disulfides (-s-s-), formed during preparation. The nitrogen content of the resin is 6.4% which corresponds to 4.57 meq. of nitrogen per gram of the resin. The primary amine part is derivatized with a pendant group bearing the thiol functionality. It is evident that the mole ratio of nitrogen to sulfhydryl group is 4.5:2.2.

The skeletal structure of the resin contains polystyrene. The resin has sufficient mechanical strength to withstand degradation on mild shaking. It has a water regain of 25% and is suitable for compositing in a porous medium.

2.3.2 Stability of the resin

The resin is insoluble in acid and alkali. Also it does not dissolve in chloroform. The water regain is around 25%. The insolubility is also reflected by the low water regain compared to crosslinked ionic resins. The resin shows excellent chemical stability. It is not degraded by 2M hydrochloric acid or 0.1M alkali. Thus it meets the technological requirements for application with diluted effluents. However it is oxidised with iodine, which usually reacts with all sulfhydril groups.

The thermal stability of the resin was investigated by thermogravimetry in air. The sample shows a slow loss of weight in the region 85-100°C which may be due to the loss of sorbed water (Fig.2.1). Then it shows a stability plateau from 115 to 225°C. From 225°C there is a slow loss of weight in two consecutive overlaping stages. The weight becomes stable at around 540°C. The residual weight above 600°C may be due to the formation of condensed aromatic residue.

2.3.3 Sorption behaviour of metal ions

The resin is an extremely weak acid so that when soaked in media of neutral to low pH it may be assumed that it exists in non-ionic form. A small proportion of free amino group exist as indicated by the analytical results.

Since thiol function is selective towards silver, mercury and lead and shows limited selectivity

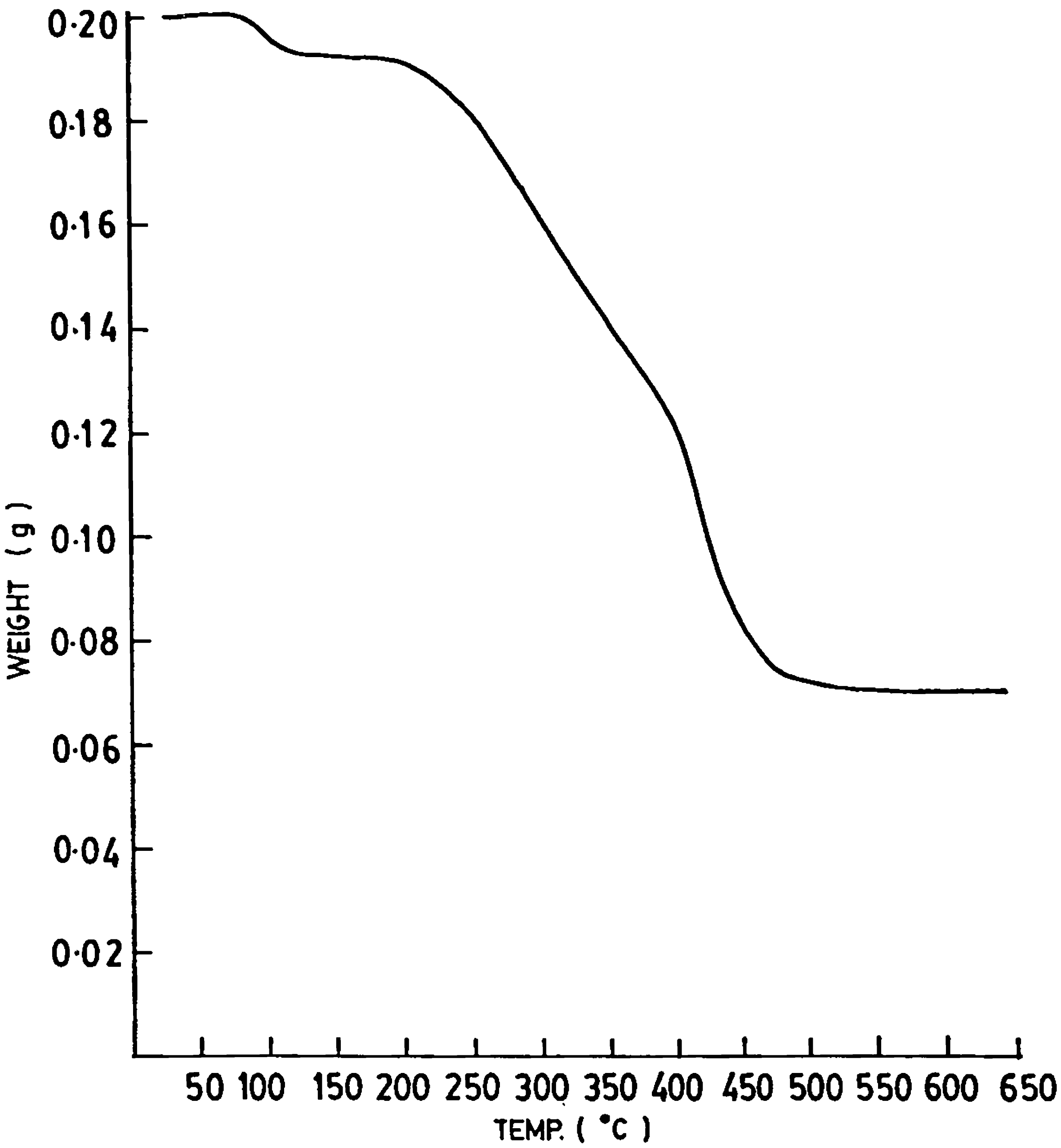


Fig. 2.1 Thermogravimetric trace for ST-3 resin.
Sample weight 0.2g, heating rate 10°C/min., atmosphere - static air.

towards the sulfide group of elements in qualitative analysis, these co-occurring elements have been individually studied to assess the selectivity of sorption of the ions on ST-3 resin. Since most of the metal ions are prone to precipitation at higher pH, studies were limited to below around pH 7. The results are listed in Tables 2.1-2.15.

(a) Sorption of silver ions

Sorption of silver (I) ions on the resin was studied in the pH range 1-6. pH was adjusted using dilute nitric acid and dilute sodium hydroxide solution. pH dependence of sorption remains more or less steady in the pH range studied. There is a very slight increase in sorption observed at around pH range 2-4 and maximum sorption is observed at around pH 3.5 (Fig. 2.2). The corresponding sorption capacity is 0.73 mmol/g. The slight increase in sorption above pH 2 may be explained as follows:

The sorption due to thiol groups may remain constant in this pH range. At low pH, the free amino groups may be protonated.

$$-NH_2 + H^+ \rightleftharpoons NH_3^+$$

As pH is raised, the amino groups are free and they

Tables 2.1-2.7 Sorption of metal ions on ST-3 resin as a function of pH

Amount of ST-3 resin 0.1g, particle size 100-200 mesh, volume of solution 20 ml, amount of metal ion 8.0 mg, shaking time 8h, temperature 28 ± 1^{o}C.

$$K_D = \frac{\text{mg of metal ion per g of resin}}{\text{mg of metal ion per ml of solution}}$$

Table - 2.1 Copper (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
0.5	0.07	1.04
1.8	0.12	1.30
2.8	0.16	1.46
3.4	0.20	1.57
4.0	0.23	1.64
5.0	0.28	1.76
6.0	0.22	1.64

Table - 2.2 Nickel (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.0	0.01	0.20
3.4	0.01	0.20
4.1	0.025	0.58
4.8	0.032	0.68
5.2	0.044	0.83
5.5	0.03	0.65

Table - 2.3 Mercury (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
1.3	0.35	3.18
2.4	0.28	2.70
3.4	0.26	2.60
4.0	0.25	2.54
5.3	0.26	2.60
6.0	0.29	2.72

Table - 2.4 Lead (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.6	0.05	1.53
3.6	0.07	1.65
4.5	0.10	1.84
5.1	0.21	2.37
5.8	0.23	2.47

Table - 2.5 Silver (I)

Equilibrium pH	Capacity (mmol/g)	Log K_D
0.9	0.72	3.46
1.7	0.725	3.70
2.2	0.73	3.86
3.3	0.73	3.85
3.8	0.725	3.66
5.2	0.72	3.46
6.1	0.72	3.49

Table - 2.6 Cadmium (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.0	0.01	0.32
2.6	0.02	0.65
3.5	0.03	0.81
4.8	0.06	1.28
5.8	0.08	1.40
6.5	0.106	1.54

Table - 2.7 Zinc (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.6	0.008	0.10
3.6	0.02	0.45
4.5	0.02	0.59
5.0	0.05	0.93
5.6	0.09	1.23
6.4	0.13	1.39

Table - 2.8 Sorption capacity of ST-3 resin for various metal ions at optimum pH

Metal Ion	Optimum pH	Capacity (mmol/g)
Cu^{2+}	5.0	0.28
Hg^{2+}	1.5	0.35
Ag^{+}	3.0	0.73
Zn^{2+}	6.4	0.13
Pb^{2+}	5.8	0.23
Cd^{2+}	6.5	0.10

Tables 2.9-2.14 Kinetics of sorption of metal ions on ST-3 Resin

Amount of ST-3 resin 0.1g, particle size 100-200 mesh, volume of solution 10 ml, amount of metal ion 4.0 mg, temperature 28 ± 1°C.

Table - 2.9 Mercury (II)

Time (min.)	% Saturation*
5	33.8
10	49.5
20	62.6
40	81.4
60	91.0
80	95.4
120	97.0
180	100

*pH of solution 2.

Table - 2.10 Copper (II)

Time (min.)	% Saturation*
5	43.2
10	54.6
20	68.0
30	79.0
40	88.6
60	100
120	100

* pH of solution 4.

Table - 2.11 Cadmium (II)

Time (min.)	% Saturation*
10	40.2
20	56.1
30	66.5
60	74.7
80	89.5
120	92.5
240	100

*pH of solution 6.5.

Table - 2.12 Silver (I)

Time (min.)	% Saturation*
10	69.4
20	87.5
30	97.8
40	99.7
60	100
120	100

*pH of solution 3.

Table - 2.13 Lead (II)

Time (min.)	% Saturation*
5	36.0
10	65.3
20	85.5
30	94.8
60	100
120	100

*pH of solution 5.

Table - 2.14 Zinc (II)

Time (min.)	% Saturation*
5	45.0
10	57.3
20	74.8
30	86.2
40	93.5
60	99.2
120	100

*pH of solution 3.

Table - 2.15 Time for half saturation for different metal ions on ST-3 Resin

Metal ion	pH	$t_{1/2}$ Sat. (min.)
Cu^{2+}	5.0	10
Hg^{2+}	1.5	10
Ag^{+}	3.0	10
Cd^{2+}	6.5	15
Pb^{2+}	5.8	10
Zn^{2+}	6.4	10

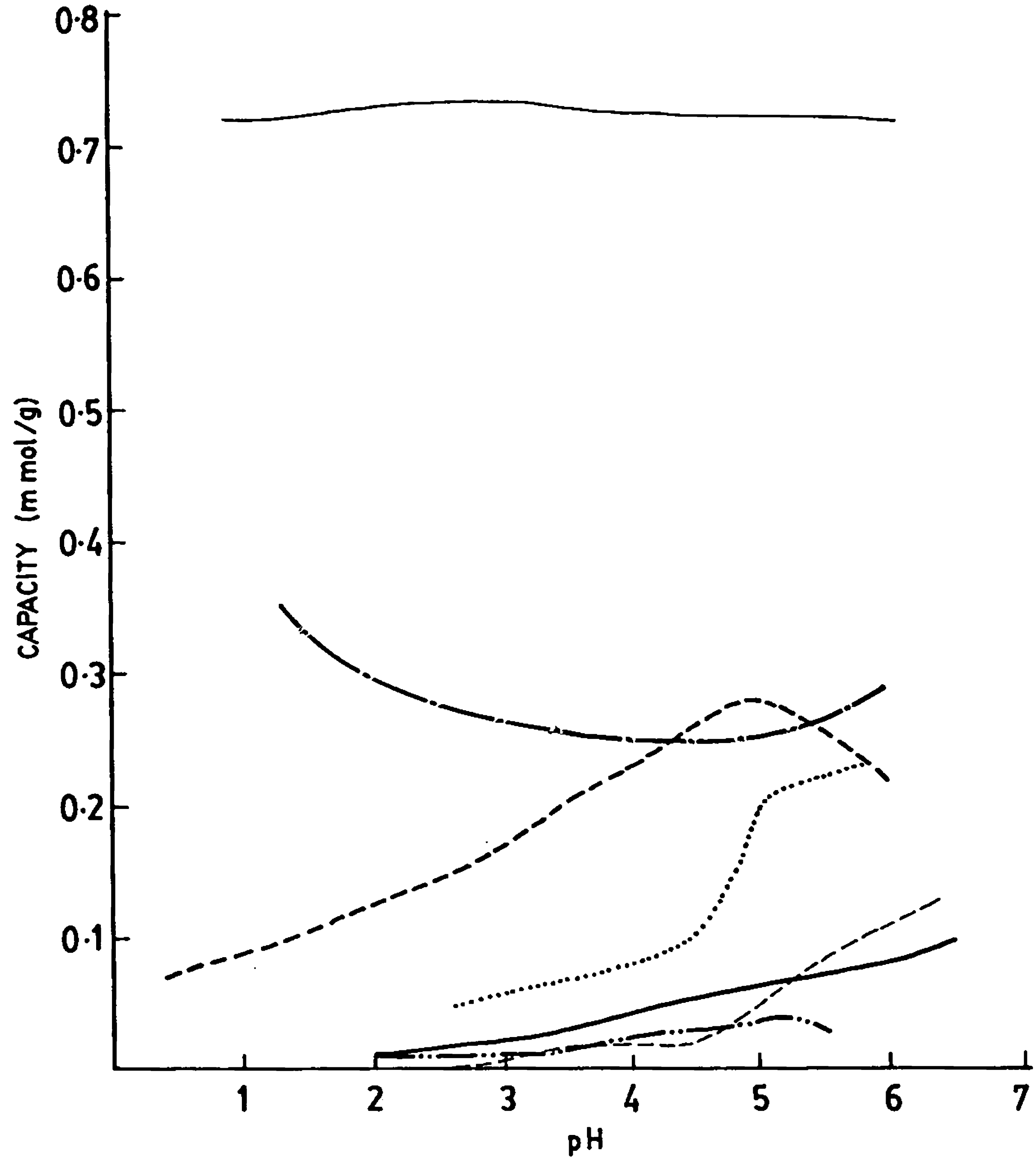


Fig. 2.2 Effect of pH on the sorption of metal ions on ST-3 resin

Amount of resin 0.1g, volume of solution 20 ml, amount of metal ion 8.0 mg, shaking time 8 h, temperature 28 ± 1°C, (——) Ag(I), (—·—) Hg(II), (-----)Cu(II), (·········) Pb(II), (———)Cd(II), (—··—) Ni(II), (----) Zn(II).

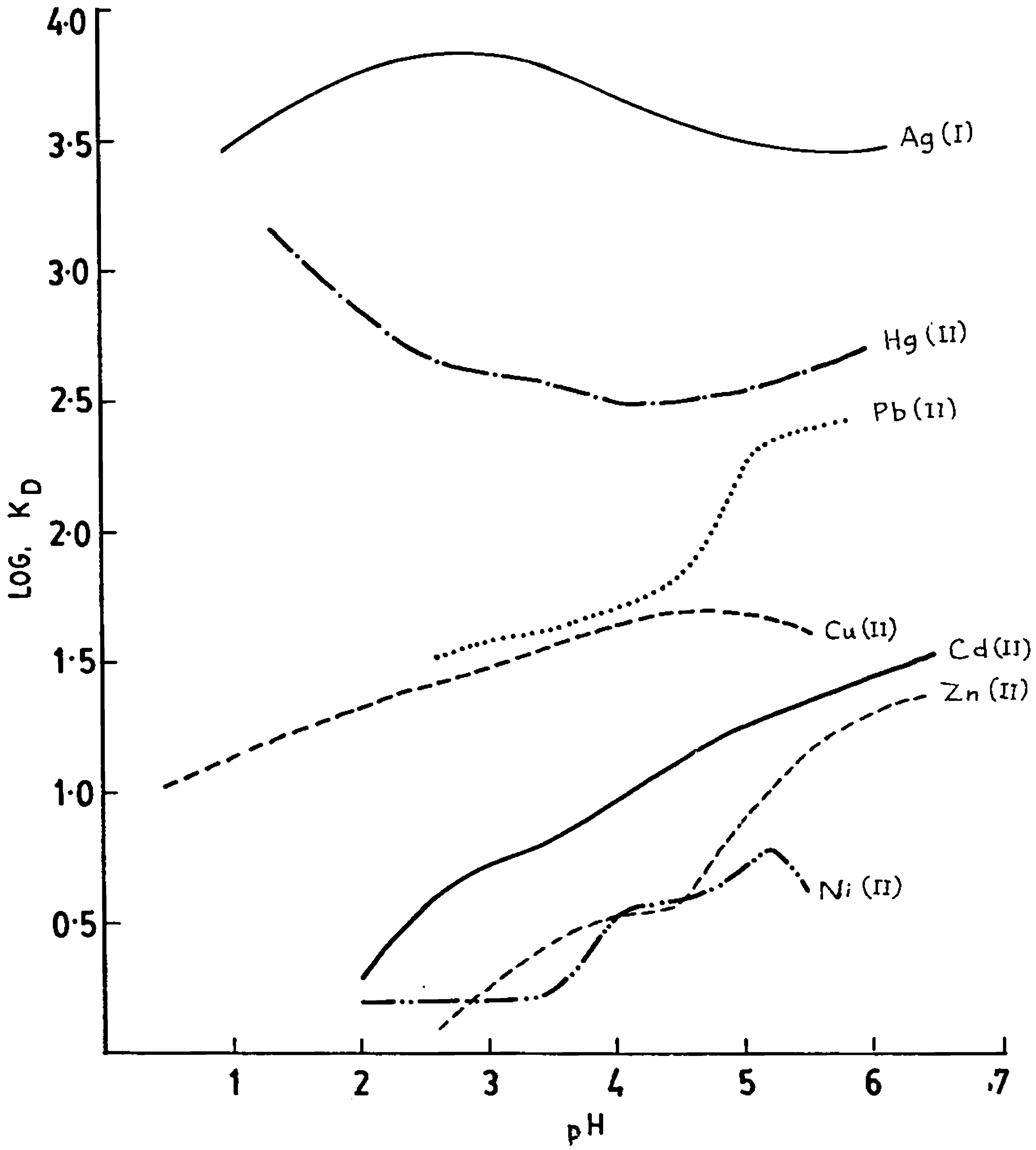


Fig. 2.4 Effect of pH on K_D for metal ions on ST-3 resin.

Conditions same as that of Fig. 2.2.

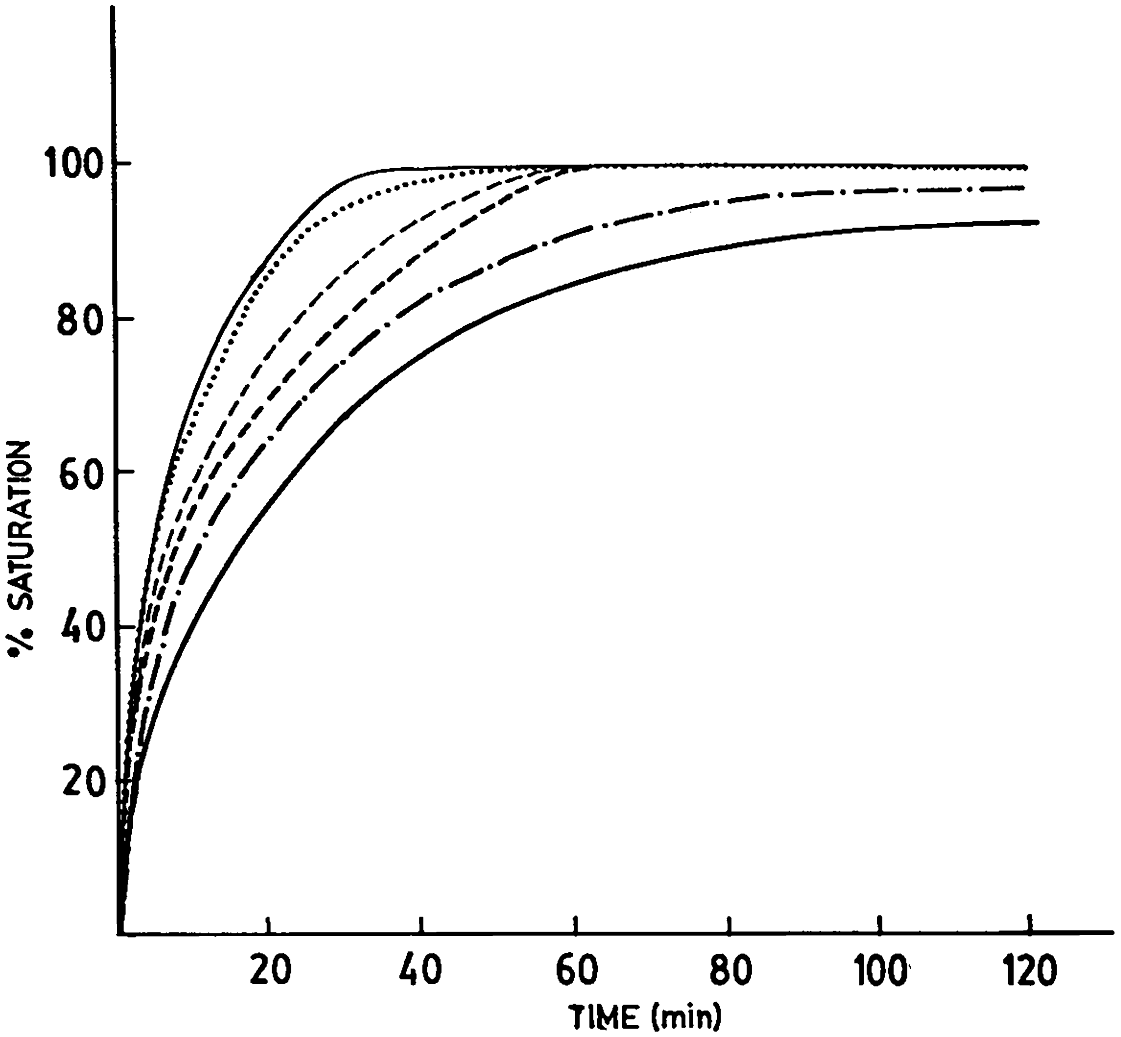


Fig. 2.3 Kinetics of sorption of metal ions on ST-3 resin

Amount of resin 0.1g, volume of solution 10 ml, amount of metal ion 4.0 mg, pH of solutions - Hg(II) 2.0, Cu(II)4.0, Pb(II) 5.0, Cd(II) 6.0, Ag(I) 3.0 and Zn(II) 5.5, temperature 28 ± 1°C. (—·—) Hg(II), (– – –) Cu(II), (·······) Pb(II), (——) Cd(II) (——) Ag(I), (– – –) Zn(II).

are capable of coordinating with Ag(I) ions. Thus the capacity for Ag(I) ion above pH 2 may be the sum of those due to $-NH_2$ groups and -SH groups.

Time for half saturation is less than 10 minutes as can be seen from the time-dependent sorption curve (Fig.2.3). When the resin loaded with silver ions is exposed to light over a prolonged period, the brownish yellow material changes its colour to black. This is perhaps due to the light-induced decomposition of the silver complex formed.

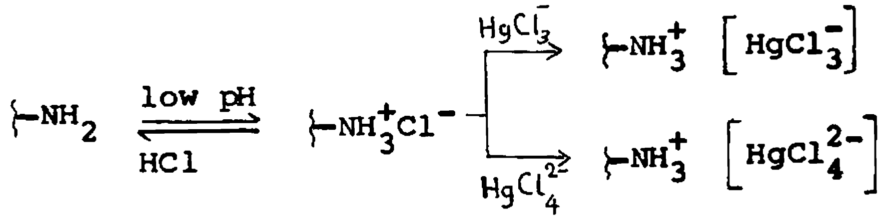
(b) Sorption of mercury (II) ions

It is well known that sulfur and sulfur-nitrogen functions are highly selective towards mercury (II) ions. Here also, it is found that the resin binds mercury very strongly in the pH range below 7. Studies were carried out only in the pH range below 7 since mercury (II) forms the hydroxide (oxide) at higher pH. The percentage sorption of mercury (II) decreases as pH increases and reaches a minimum at around pH 4.

This is perhaps due to the two types of functional groups present, namely, free amino groups, which has not been converted to the desired functional group, and the sulfur function which is a good binder for mercury. The situation may be explained as follows. At low pH, in hydrochloric acid medium, $-NH_2$ is converted to $-NH_3^+$ and $HgCl_2$ is converted to $HgCl_3^-$ and $HgCl_4^{2-}$. Anion exchange occurs on the ammonium function leading to the enhanced uptake of mercury.

$$HgCl_2 + HCl \rightleftharpoons HgCl_3^- + H^+$$

$$HgCl_2 + 2HCl \rightleftharpoons HgCl_4^{2-} + 2H^+$$



$$\vdash NH_2 \underset{HCl}{\overset{\text{low pH}}{\rightleftharpoons}} \vdash NH_3^+Cl^- \left\{ \begin{array}{l} \xrightarrow{HgCl_3^-} \vdash NH_3^+ \left[HgCl_3^-\right] \\ \xrightarrow[HgCl_4^{2-}]{} \vdash NH_3^+ \left[HgCl_4^{2-}\right] \end{array} \right.$$

This type of anion exchange decreases with increase in pH and perhaps becomes negligible after pH 4 and at higher pH the sorption may be exclusively by the sulfur function. Mercury loaded resin is coloured light brown and further darkening of colour does not occur even if it is exposed to diffused light for a longer period. The overall sorption capacity is high at low pH for reasons explained above. The maximum sorption capacity for mercury is 0.37 m $molg^{-1}$ at pH 1 and reaches a minimum value of 0.25 m $molg^{-1}$ at pH 4.1. The half time for saturation is around 10 minutes.

(c) Sorption of lead (II) ions

The sorption capacity for lead (II) was studied in the pH range below 6. pH was adjusted using dilute nitric acid/sodium hydroxide. Sorption shows a steady increase with increase in pH and a large inflection is observed between pH 4.5 and 5.2. This may be due to the fact that the formation of anionic species and its exchange with the ammonium form is negligible. Reversible lead (II) ion binding occurs at intermediate pH range and a clear influence of pH typical of a reverse equilibrium is observed. Decreased sorption at low pH may be due to the influence of H^+ ion concentration on the ion-exchange reaction.

$$RH + 1/2\ Pb^{2+} \rightleftharpoons RPb^{2+}_{1/2} + H^{+}$$

Capacity for lead (II) reaches a maximum value of 0.23 $mmolg^{-1}$ above pH 5.6. The time for half saturation is around 6 minutes.

(d) Sorption of copper (II) ions

Sorption of Cu(II) was studied in the pH range 2-6. HCl/NaOH or acetic acid/sodium acetate was used for adjusting pH. Sorption increases with increase in pH, reaches a maximum at around pH 5 and then decreases. Increase in sorption with increase in pH may be due to the effect of H^+ ions in ion-exchange equilibrium. At higher pH, Cu(II) may exist as the acetate complex which is likely to affect the ion-exchange equilibrium.

$$2RH + Cu^{2+} \rightleftharpoons R_2Cu + 2H^+$$

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

$$2Cu^{2+} + 4\ CH_3COO^- \rightleftharpoons Cu_2(CH_3COO^-)_4$$

(Binuclear)

(e) Sorption of cadmium (II) ion

Sorption capacity for cadmium is very low and increases with increase in pH upto 7. Higher pH were not studied since cadmium chloride undergoes hydrolysis. A sorption capacity of 0.16 $mmolg^{-1}$ is observed at pH 7. Time for half saturation is around 25 minutes and is much larger than the values observed for lead, mercury and copper.

(f) Sorption of zinc (II) ions

The sorption capacity for zinc ion is also small. (0.16 mmol/g at pH 7). It shows a slight decrease and reaches a minimum at pH 4.5 and then increases and reaches a maximum above pH 6.5.

(g) Sorption of nickel (II) ions

Nickel ions are sorbed only to a negligible extent and it may be assumed that it does remain virtually unretained over the whole pH range studied.

The sorption behaviour of Cu(II), Hg(II), Ag(I), Pb(II), Zn(II), Cd(II) and Ni(II) ions are presented in Fig.2.2 and the pH values at which maximum sorption is observed are given in Table 2.8. Time dependence of sorption is indicated in Fig.2.3 and the time for half saturation is given in Table 2.15. The dependence of distribution coefficient (K_D) on pH is indicated in Fig.2.4.

The K_D values at pH of maximum sorption are in the order Ag(I) $>$ Hg(II) $>$ Cu(II) $>$ Pb(II) $>$ Zn(II) $>$ Ni(II). It is seen that the K_D values of Ag(I) and Hg(II) are extremely high and hence these metal ions can be preferentially sorbed in presence of other metal ions. Others can also be sorbed on the resin to some extent but they are displaced when excess of Hg(II) or Ag(I) ions come in contact with the resin. For example:

$$R - Cu^{2+} + Hg^{2+} \rightleftharpoons R - Hg^{2+} + Cu^{2+}$$

Even though the capacities of Cu(II), Cd(II), Zn(II) and Pb(II) are low, the pH dependence varies widely. Thus these metal ions can be separated on the resin using eluents of different pH. The high values of K_D for Ag(I) and Hg(II) also point to the fact that the two metal ions can be pre-concentrated on the resin. However, separation of Ag(I) and Hg(II) from each other is difficult due to the close values of their K_D. It is also evident that in the absence of silver, mercury can be separated and pre-concentrated in presence of Cu(II), Pb(II), Ni(II), Cd(II) and Zn(II) ions most of which usually co-occur in natural and industrial materials.

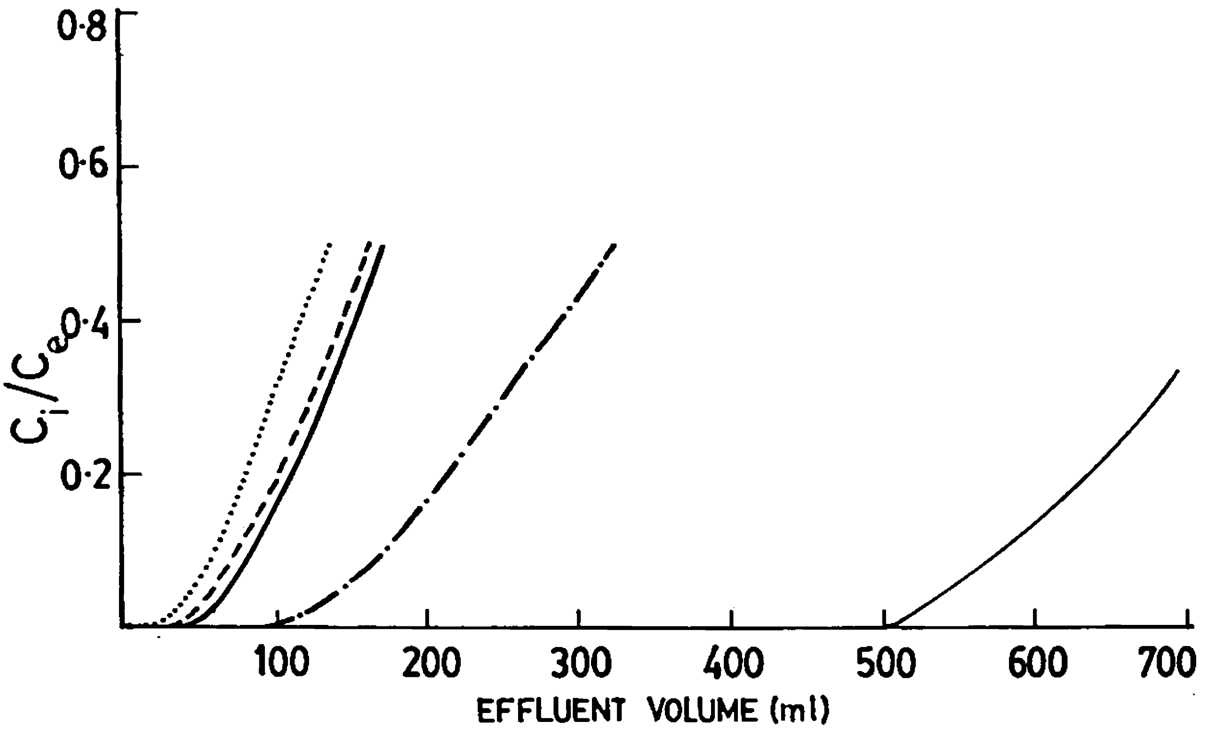


Fig. 2.5 Breakthrough curves of metal ions on ST-3 resin.

Column dimension 0.5 x 10 cm, particle size 100-200 mesh, concentration of metal ion solutions 100 μg/ml, pH of solutions Ag(I) 2.0, Hg(II) 2.0, Cd(II) 5.7, Cu(II) 4.0 and Pb(II) 5.0, flow rate 0.5 ml/min, volume of fractions 5 ml, (——) Ag(I), (—·—)Hg(II), (——)Cd(II), (- - -)Cu(II), (·······) Pb(II).

C_i = conc. of metal ion in influent,
C_e = conc. of metal ion in effluent.

The breakthrough curves for these metal ions are in conformity with the corresponding capacity and K_D values (Fig.2.5). Thus Pb(II), Cd(II) and Cu(II) breakthough very fast on a column of ST-3 resin. Hg(II) breakthrough afterwards with sufficient separation from the other three. Ag(I) is characterized by a high value of dynamic capacity as seen from the curve.

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CHAPTER - III

PRE-CONCENTRATION OF MERCURY FROM SEA-WATER

3.1 INTRODUCTION

Mercury pollution of the aquatic environment is a very serious problem due to the acute toxicity of mercury compounds. Mercury compounds selectively bind with sulfhydril groups of protein and enzyme structures, thereby disrupting their normal biological functions. Accumulation of mercury in the human body affects the nervous system leading to the paralysis of central nervous system.[141]

3.1.1 Sources of mercury in the aquatic environment

Mercury comes into the aquatic environment from natural as well as anthropogenic sources. Weathering of igneous rock releases about 800 tonnes of mercury per year, mostly to fresh water and eventually to the oceans.[142] Mercury release from anthropogenic sources far outweigh natural sources. Vapour released from fossil fuelled power plants and other combustion processes is the largest anthropogenic source. Atmospheric fallout by rain brings it to rivers and lakes. Other anthropogenic sources include agricultural uses of mercury bearing fungicides, effluents from mining and smelting process, chlor-alkali plants, paper mills, leather tanning, paints and electrical apparatus.

Chemical speciation of mercury in the environment is important. The toxicity of mercury depends on the chemical form in which it enters into the living body. Elemental mercury has significant vapour pressure (at 25°C mercury has a vapour pressure of 19.7×10^{-4} mm). Mercury vapour leads to severe physiological effects if inhaled. The Environmental Protection Agency (USA) has prescribed a permissible level of 1 $\mu g/m^3$ in air for long-term exposure,[143] and 2 $\mu g/l$ in drinking water.

More than 90% of the total mercury present as inorganic species in the aquatic environment may be located in the sediments, a major portion of the rest being associated with suspended particles.[144,145] Inorganic and organic mercury species are fairly strongly sorbed on organic particles especially those with high sulfur content. The sedimented mercury, especially when associated with organic particles, undergoes anaerobic fermentation, (e.g., by methano bacterium amelanskis) giving alkyl mercury species.[146] The organic mercury species, being more soluble in biological fluids, undergo bio-amplification in the food chain. The enrichment factor from water to fish may exceed 10^3.[147] The classical methods used for fixing mercury as inorganic precipitates are not recommended since it is ultimately converted into soluble organic species.[148]

The fatal nature of methyl mercury compounds was brought to lime light by the Minamata episode in Japan which was caused by the extensive poisoning of the consumers of mercury contaminated fish harvested from the Minamata bay. The patients progressively suffered from a weakening of muscles, loss of vision, impairment of cerebral function and paralysis which ultimately resulted in coma and death. The source of methyl mercury was the effluents from the plants of Chisso Chemical Company manufacturing plastics. Methyl mercury formed from acetaldehyde and inorganic mercury (used as catalyst) was discharged into the drainage channels which lead into the Minamata bay. Later many cases of Minamata disease were reported in Japan and in other countries.[149]

3.1.2 Analysis of mercury in environmental samples

Mercury occurs in sea-water and fresh water to the tune of about 0.01 μg/l and 0.1 μg/l respectively.[150] Such low levels necessitate a pre-concentration step for analysis since the lower limit for analysis by cold vapour AAS (0.5 μg/l) and spectrophotometry (1mg/l using SCN^- method) are much higher than the levels available in the samples. More sensitive methods such as atomic fluorescence spectroscopy can be employed but they are more expensive. Thermal volatilisation and amalgamation of mercury vapour with copper, silver or gold are also recommended for pre-concentration. Pre-concentration by extraction with chelating agents[151] or absorption in acidified potassium permanganate solution are also employed.[152]

Recent developments in chelating ion-exchange resins have led to a convenient pre-concentration method for traces of mercury in environmental samples. The method is marked by operational convenience compared to solvent extraction. Since the formation constant of resin-mercury complex is greater than that of the corresponding ligand complex in solution,[153] a large volume of the sample solution can be run over the resin. The mercury thus pre-concentrated in the resin can be washed free of other metal ions and eluted from the resin phase into a small volume of the eluent using a strong displacing ligand and then quantitated using a suitable method. Generation of mercury vapour with stannous chloride followed by sweeping it into the sample cell of a cold vapour AAS is very popular.

3.2 EXPERIMENTAL

Studies on the sorption of mercury were carried out from synthetic sea-water and from naturally occurring sea-water with a view to develop pre-concentration method using ST-3 resin.

3.2.1 Preparation of synthetic sea-water

Synthetic sea-water was prepared by the method suggested by Muroi and Hamaguzhi.[154] The composition of synthetic sea-water used in this study is given below:

Salt	Concentration (g/l)
NaCl	23.476
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.066
$NaHCO_3$	0.192
KBr	0.096
H_3BO_3	0.026
$SrCl_2$	0.024
NaF	0.003

The salts were dissolved in distilled water and diluted to 1 litre. The overall chloride concentration was 18.7 g/l. The sea-water was spiked with mercuric chloride so as to get a Hg(II) concentration of 100 μg/ml.

3.2.2 Natural sea-water

Natural sea-water was collected from the Arabian sea, off Cochin shore. Sampling of water was done at a depth of 1 m. This was also spiked with mercuric chloride to get a concentration of 100 μg/ml of Hg(II).

3.2.3 Mercury stripping studies

Sea-water had a pH of 6.5. It was not necessary to adjust the pH of the solution. Sea-water spiked with Hg(II) was allowed to run on a column of ST-3 resin. The set up used had the exact configuration as in the breakthrough studies. Sample was run over the loaded column at a flow rate of 0.5 ml/min. Fractions were collected in 5 ml lots and mercury concentration measured in each fraction. A blank determination was done using the sea-water sample.

3.2.4 Elution and determination of mercury

The elution of mercury (II) from the resin is very slow and incomplete even with 1M HCl. Hence it was eluted using 5% thiourea in 0.1M HCl. This possess some difficulty in generating mercury vapour required for measurement by AAS.

For the determination of mercury in the eluate, a suitable aliquot of the sample was taken in a reaction vessel, 10 ml of 30% (w/v) potassium hydroxide solution was added and diluted to 50 ml.

To this was added 5 ml of 10% (w/v) tin (II) chloride solution in 5M HCl. Air flow was started immediately. The mercury vapour formed was passed through the quartz cell and the peak height was used for measurement. A blank was also determined using the same procedure.

3.3 RESULTS AND DISCUSSION

The selectivity of the resin for silver and mercury points to the advantage of using it for pre-concentration of these metals from lean sources. The pre-concentration of mercury from sea-water and its analysis have been carried out as described in the experimental section. 100 μg/ml Hg(II) solution percolated through a packed column at the rate of 0.5 ml/min gave curve-A in Fig.3.1. Even at this moderately large flow rate mercury is retained on the column. The influence of large concentration of chloride ion on the uptake of mercury was investigated using samples of synthetic sea-water spiked with Hg(II). The solution contains 18.7g/l of Cl^- (i.e., 0.52 molar solution). The concentration of Hg(II) in this solution was

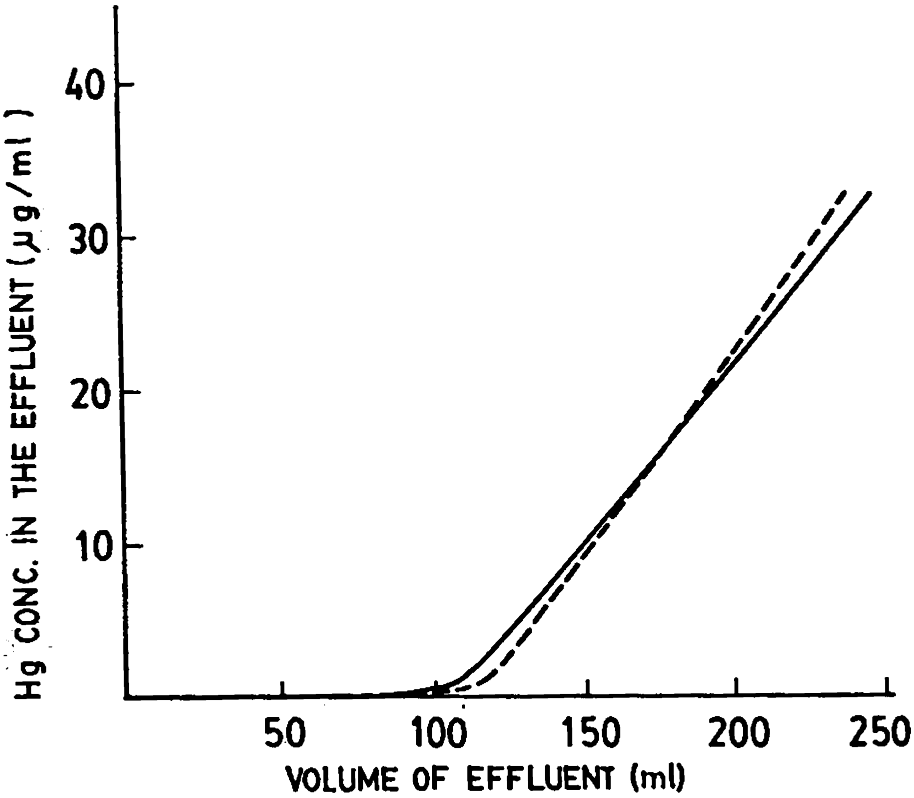

Fig. 3.1 Breakthrough curve of mercury-spiked sea-water on ST-3 resin.

Column dimension 0.5 x 10 cm, particle size 100-200 mesh, A, (----) standard solution of Hg(II), concentration of Hg(II) 100 μg/ml, B, (——) Hg(II)-spiked sea-water, concentration of Hg(II) 100 μg/ml, flow rate 0.5 ml/min, volume of fraction 5 ml, pH of solution 6.5.

100 μg/ml (i.e. 0.5 x 10^{-3} molar). Here, Cl^- is 1000 fold excess in terms of molar concentrations, hence the complex formation reaction,

$$HgCl_2 + Cl^- \rightarrow HgCl_3^-$$
$$HgCl_2 + 2Cl^- \rightarrow HgCl_4^{2-}$$

is largely shifted to the right. However, the large K_D value for Hg(II) sorption makes it possible to extract Hg(II) from this solution of high Cl^- concentration.

$$2RSH + Hg^{2+} \rightleftharpoons RSHgSR + 2H^+$$
$$RSH + HgCl_2 \rightleftharpoons RSHgCl + H^+Cl^-$$
$$RSH + HgCl_3 \rightleftharpoons RSHgCl + 2Cl^- + H^+$$
$$RSH + HgCl_4^{2-} \rightleftharpoons RSHgCl + 3Cl^- + H^+.$$

Selectivity of the resin for Hg(II) was also studied from solution containing 10 mg/l each of Hg(II), Cu(II), Pb(II) and Cd(II). The breakthrough curve obtained indicates that the presence of Cu(II), Pb(II) and Cd(II) exerts very little influence on the breakthrough of Hg(II), Cu(II), Pb(II) and Cd(II) ions initially sorbed on the resin are displaced by Hg(II) in competition (see fig.3.2) as given below:

Table - 3.1 Mercury enrichment from sea-water*

Sample	Hg(II) added (μg)	Hg(II) recovered (μg)**	Recovery %
1^a	100	98.6	98.6
2^b	100	95.2	95.2
3^c	100	97.1	97.1

*Total volume run 100 ml

**Each result represents the mean of three values after correction for the blank.

(a) Standard mercury (II) solution

(b) Synthetic sea-water

(c) Natural sea-water.

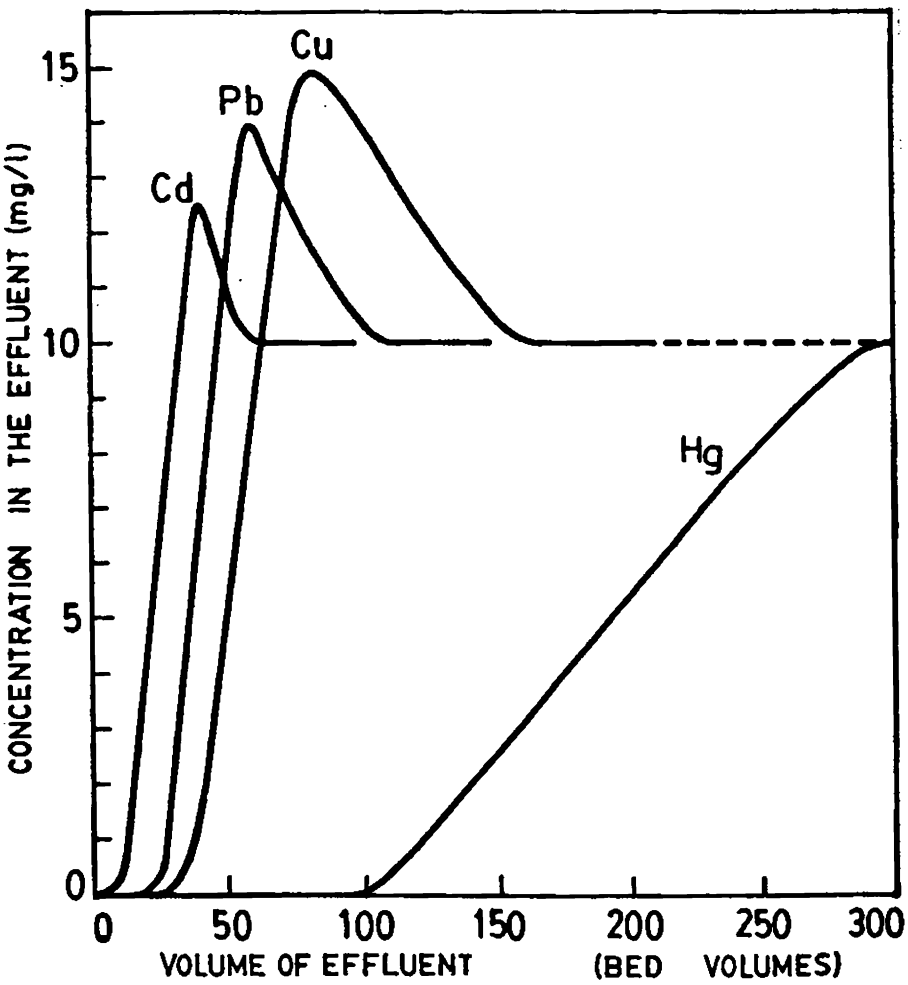

Fig. 3.2 Replacement of Cd(II), Pb(II) and Cu(II) ions by Hg(II) ions.

Concentration of feed 10 mg/l each of Cd(II), Pb(II), Cu(II) and Hg(II), flow rate 1 ml/min., bed volume 1.6 ml.

$$2RS\text{-}H + M^{2+} \rightleftharpoons RS\text{-}M\text{-}SR \overset{Hg^{2+}}{\rightleftharpoons} RS\text{-}Hg\text{-}SR + M^{2+}$$

The results of the analysis using synthetic sea-water and actual sea-water spiked with Hg(II) are given in Table 3.1. This method has very clear advantage over the previously reported methods of analytical pre-concentration involving thermal volatilisation and adsorption on gold, extraction with dithizone and absorption in acidified potassium permanganate solution. Also, this gives marked operational convenience compared to solvent extraction.

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CHAPTER - IV

REMOVAL OF MERCURY FROM CHLOR-ALKALI PLANT EFFLUENT

4.1 INTRODUCTION

Discharge from chlor-alkali industry is one of the major sources of mercury pollution. There are about 35 chlor-alkali plants in India of which 24 plants use mercury cell process.[155] The installed capacity of the chlor-alkali industry in India for the manufacture of sodium hydroxide is 7.8 lakh tonnes per year. In a properly supervised and maintained plant mercury loss is about 70-80 g/tonne of caustic soda produced. This loss reaches about 250-300 g/tonne in old and badly maintained plants.[155] Thus it can be seen that the total amount of mercury discharged from chlor-alkali industry is substantial.

4.2 CURRENT TECHNIQUES USED IN THE REMOVAL OF MERCURY

In recent years great efforts were made to reduce mercury discharge from chlor-alkali plant effluents. The following methods which use redox reaction and physical separation or ion-exchange are popular.[149]

(1) Treatment of mercury-bearing waste with inorganic sulfides followed by sedimentation of mercuric sulfide. The effluent containing Hg(II) is freed from oxidants and pH is adjusted <7. It is then treated with sodium sulfide.

$$\mathrm{Hg} \xrightarrow{\text{Oxidant}} \mathrm{Hg}^{2+} \xrightarrow{\mathrm{Na_2S}} \mathrm{HgS}$$

(2) Ferrous chloride was later used for reduction and precipitation as metallic mercury. This method could bring down the residual concentration of mercury to 0.1 to 0.93 mg/l.

$$\mathrm{Hg}^{2+} + 2\mathrm{Fe}^{2+} \longrightarrow \mathrm{Hg} + 2\mathrm{Fe}^{3+}$$

Both these treatment techniques lead to serious secondary pollution problems arising from the bacterial action on the sedimented mercury.

(3) Mercury recovery from brine has been accomplished by a strong base anion exchange resin by which mercury concentration was brought down to 0.1 mg/l and to a few ng/ml after passing through an adsorption tower.

(4) In the Ventron process, $NaBH_4$ was used as a reducing agent. The effluent concentration is claimed to be below 10 ng/ml and almost all the elemental mercury is recovered by cyclone and polishing filter.

(5) In the Osaka Soda process, ion-exchange stripping recovers mercury which is reduced using sodium amalgam. An effluent concentration of 5 ng/ml is reported.

(6) Fairly selective removal of mercury has also been done using ferrosilicon alloy without significant iron contamination of the water.[156]

(7) One of the latest developments is the use of starchxanthate cationic polymer,[157] where the mercury concentration is brought down from 100 µg/ml to 3.8 ng/ml.

(8) The process developed by Akzo-Zout Chemie of Netherlands,[159] based on a thiol containing chelating exchanger is among the most successful and commercially exploited ones. It involves a three step pre-treatment process of the effluent. (1) Oxidation of metallic

mercury using chlorine after adjusting pH to about 3. (2) Filtration of the solution to prevent clogging of the column, and (3) dechlorination with a special activated carbon column in order to protect the thiol groups of the resin against oxidation. The resin developed by them removed mercury down to about 5 ng/ml.

Ion-exchange process, if used, has two advantages, viz., low secondary pollution and possibility of recycling of the mercury. However, the resin must be selective towards mercury and capable of competing with Cl^- ion which is present in high concentration in the brine effluent.

4.3 EXPERIMENTAL

There are two major sources of mercury in the aquatic environment from chlor-alkali effluent, cell house effluent and general effluent. Cell house effluent is rich in mercury (2.5 mg/l) in conjection with a high concentration of chloride and alkali. General effluent is a diluted form of the above. Typical compositions of these effluents are given in the Results and Discussion section. Since these effluents contain fine droplets of elemental mercury, direct sorption on exchanger does not take place. Hence the effluent was given a pre-treatment to convert the elemental mercury into ionic mercury. Excess of oxidising species (chlorine and hypochlorite) were removed by suitable processing so that the functional groups which are sensitive to oxidising agents are not lost.

4.3.1 Oxidative pre-treatment of effluent

The effluent had a pH of 11. No further adjustment in pH was done. It was treated with chlorine so that the chlorine content was about 2-3g/l and left overnight to ensure complete oxidation of elemental mercury.

4.3.2 Removal of excess chlorine

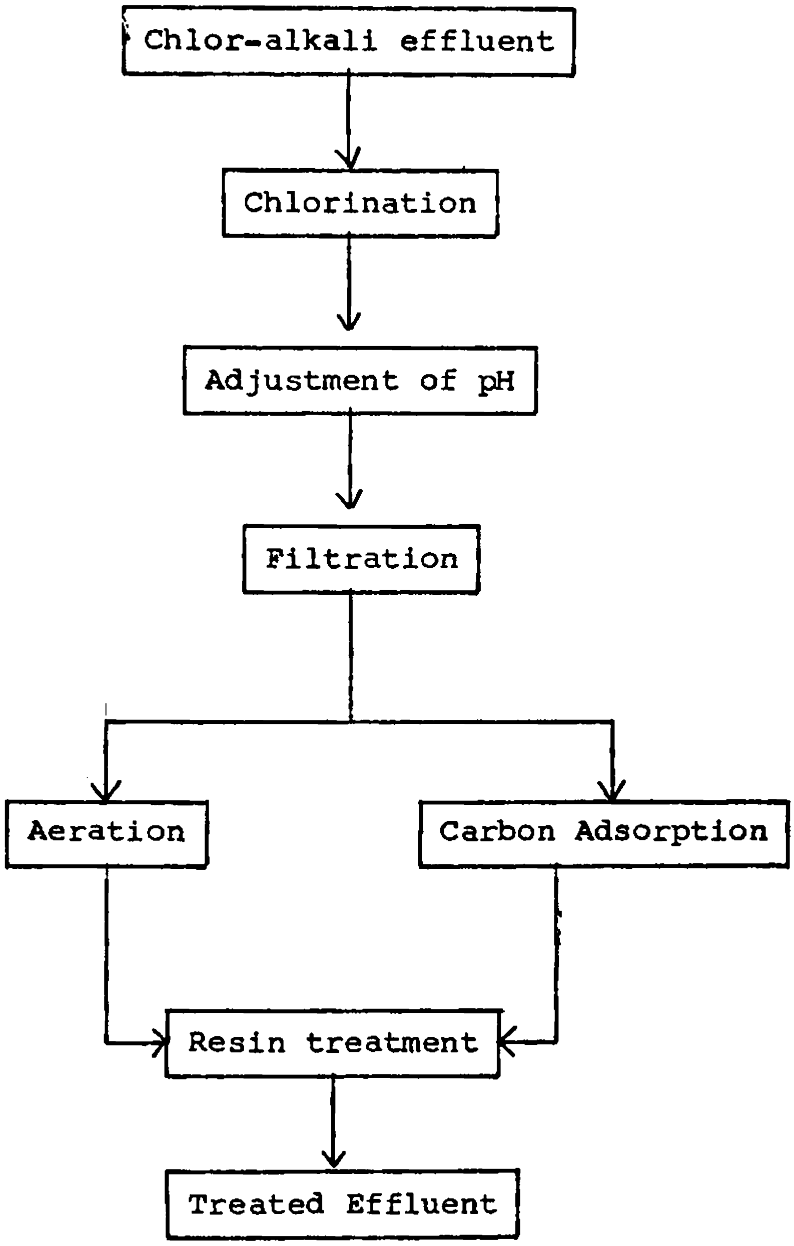
Chlorine in the effluent is detrimental to the performance of the resin since the functional group is liable to be oxidised by strong oxidants. Removal of chlorine was done by two parallel techniques, to evaluate their relative merits.

(a) The solution was acidified using hydrochloric acid to a pH of 3 and filtered to remove suspended particles. Chlorine set free in the solution was swept out by blowing air for 3 hours.

(b) The acidified solution was allowed to percolate through a bed of activated carbon prepared from readily available carbonacious source. The filtrate was analysed for chlorine as well as for mercury concentration.

4.3.3 Stripping of mercury

The chlorine - oxidised effluent was checked for the presence of residual chlorine. The chlorine-free effluent was allowed to pass through a packed column of ST-3 resin. Operating conditions and analysis techniques were as in section - 3.2.


Chlor-alkali effluent
Chlorination
Adjustment of pH
Filtration
Aeration
Carbon Adsorption
Resin treatment
Treated Effluent

4.4 RESULTS AND DISCUSSION

Chlor-alkali effluent contains mercury, mostly in elemental form and as finely dispersed droplets. Ion-exchange methods employ its conversion to Hg(II) and subsequent stripping using the resin. Mercury is easily oxidized using Cl_2 which is a product of chlor-alkali industry. Cell-house effluent has a pH of $\approx$11 and under this condition chlorine used for oxidation is fixed as hypochlorite and volatilisation does not occur.

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

A chlorine concentration of 2-3g/l was maintained and left overnight. Complete oxidation of mercury was shown by the reproducability of Hg(II) ion content. Since the ST-3 resin is sensitive to strong oxidants, solutions containing chlorine and hypochlorite cannot be fed directly on to the column. Removal of excess chlorine is essential for the life of the resin. Before dechlorination, pH is brought down to 3 by the addition of hydrochloric acid, which is again a byproduct of chlor-alkali industry. At pH 3 hypochlorite is converted to

Cl_2 and is rendered volatile. In one case air was flushed through the solution which carried away chlorine. On industrial scale this procedure has two advantages. The flushed out chlorine can be recycled into the oxidizing tank thus preventing its release into the atmosphere. Aeration is economical since no other medium is involved. However, recycling can be achieved only in a closed tank.

Second method was based on activated carbon granules obtained from coconut shell by pyrolysis under controlled conditions. This charcoal had a chlorine uptake capacity of 6.6 meq/g. The charcoal is effective in the complete removal of chlorine and partial removal of mercury. However, the use of activated carbon necessitates periodic regeneration which is a drawback.

Subsequent passage of the solution through a column loaded with ST-3 resin reduces the mercury level to below 5 μg/l which is actually the sensitivity limit of the instrument used. The flow rate was 0.4 ml/min. The resin could be regenerated using 5% thiourea in 0.1N hydrochloric acid. The results obtained are given in Fig.4.1 and Table 4.1.

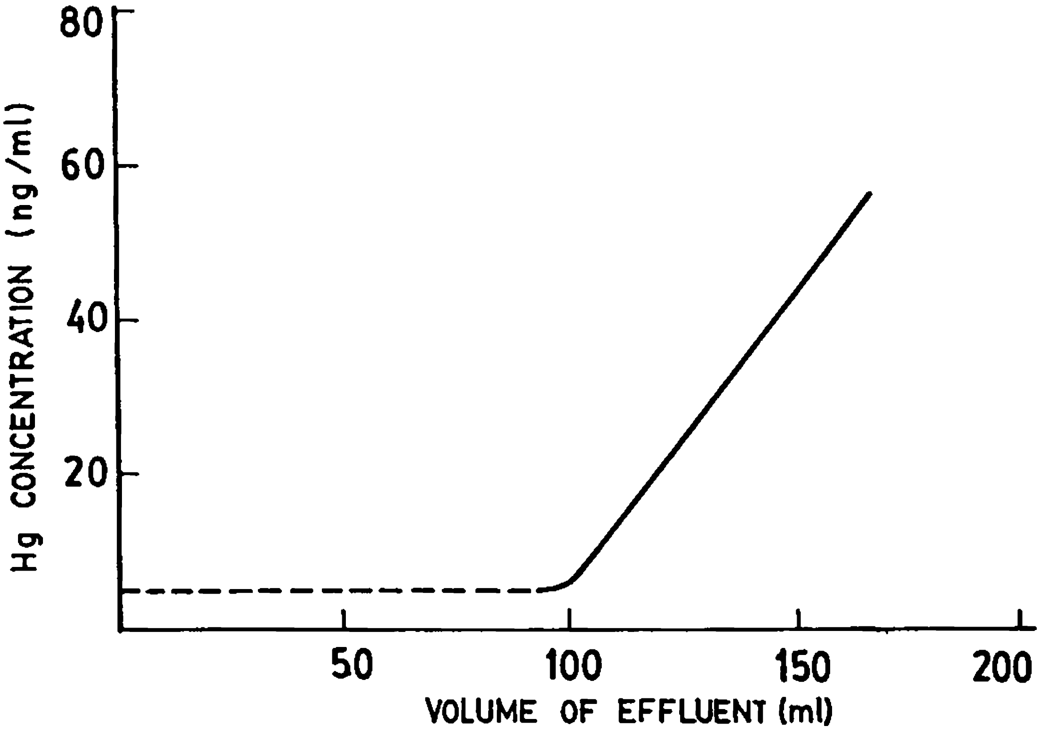


Fig. 4.1 Breakthrough curve of pretreated chlor-alkali effluent on ST-3 resin.

Column dimension 0.5 x 10 cm, Hg(II) concentration in feed solution 2.75 mg/l, pH of feed solution 3.0, flow rate 0.5 ml/min, volume of fraction 10 ml.

Table - 4.1 Concentration of Hg in the chlor-alkali effluent after different treatments

Nature of sample	Concentration of Hg(II) (μg/ml)
1. Oxidized effluent[a]	2.75
2. Dechlorinated effluent I[b]	2.75
3. Dechlorinated effluent II[c]	0.02
4. Effluent from ST-3 resin column[d]	0.005

a) Chlor-alkali effluent oxidized using chlorine.

b) Excess chlorine removed by aeration

c) Excess chlorine removed by percolation through charcoal filter

d) 100 ml of the sample run over the column.

Thus it is observed in the analytical scale that mercury can be removed to environmentally acceptable level using ST-3 resin. However, conversion of elemental mercury to Hg(II) is essential. Chlorine can be used for this purpose. But removal of excess chlorine is also necessary which can be achieved by blowing air or by using an activated carbon filter.

Previous workers have also used the same technique of pre-treatment but they were depending on the tedious activated carbon stripping of chlorine. Here, we suggest aeration and recycling of chlorine as a practicable solution to the problem of chlorine removal.

Since the study was concentrated on the analytical scale, details regarding its application in the real industrial situation could not be assessed. The stripping of chlorine was done on an empirical scale, flushing rate of air and the optimum time required for blowing out chlorine could not be obtained. However, a negative pressure aspirator based on a water pump required a maximum time of 3 hours to remove 2-3gl^{-1} of chlorine from a solution at pH 3.

REFERENCES PART I

1. Helfferich, F. "Ion Exchange", McGraw-Hill, New York, 1962, P.2.

2. Rieman, W.III.; Walton, H.F. "Ion Exchange in Analytical Chemistry", Pergamon Press Inc: New York, 1970, P.2.

3. Adams, B.A.; Holmes, E.L. J. Soc. Chem. Ind. 1935, 54T, 1.

4. Walton, H.F. "Ion Exchange Chromatography", (Benchmark Papers in Analytical Chemistry V.1), Halsted Press, Dowden, Hutchinson; Ross Inc: New York, 1976, P.5.

5. Efendiev, A.A.; Kabanov, V.A. Pure. Appl. Chem. 1982, 54(11), 2077.

6. Tomkins, F.R. Anal. Chem. 1950, 22, 1352.

7. Benefield, L.D.; Judkins, J.F.; Weand, B.L. "Process Chemistry for Water and Wastewater Treatment", Prentice-Hall Inc: New Jersey, 1982, P.315.

8. Helfferich, F. "Ion Exchange", J.A. Marinsky ed., Marcel Dekker, Vol.1, 1966, P.86.

9. Janaver, G.E.; Gibbons, R.E. JR. "Ion Exchange", J.A. Marinsky ed., Marcel Dekker, Vol.1, 1966, P.56.

10. Janaver, G.E.; Gibbons, R.E. JR. "Ion Exchange", J.A. Marinsky ed., Marcel Dekker, Vol.1, 1966, p.63.

11. Loewenschuss, H.; Schmukler, G. *Talanta* 1964, *12*, 1399.

12. Eger, C.,; Anspach, W.M.; Marinski, J.A. *J. Inorg. Nucl. Chem.* 1968, *30*, 1911.

13. Marton-Schmidt, E.; Inczedy, J.; Laki, Z.; Szabadka, O. *J. Chrom.* 1980, *201*, 73.

14. Erlenmeyer, H.; Dahn, H. *Helv. Chim. Acta* 1939, *22*, 1369. (C.A. 1940, *34*, 1269^{7}.)

15. Griesbach, R. *Z. Angew Chem*. 1939, 215. (C.A. 1939, *33*, 4746^{5}.)

16. Skogseid, A. *Norv. Pat*. 72583. (C.A. 1948, *42*, 1682_{a}.)

17. Mellor, D.P. *Aust. J. Sci*. 1950, *12*, 183. (C.A. 1950, *44*, 10445_{b}.)

18. Gregor, H.P.; Taifer, M.; Citarel, L.; Becker, E.I. *Ind. Eng. Chem.* 1952, *44*, 2834.

19. Parrish, J.R. *Chem. Ind.* 1955, 386.

20. Parrish, J.R. *Chem. Ind.* 1956, 137.

21. Davies, R.V.; Kennedy, J.; Lane, E.S.; Williams, J.L. *J. Appl. Chem.* 1959, *9*, 368.

22. Bayer, E. *Angew. Chem.* 1964, *76*, 76.

23. Millar, J.R. *Chem. Ind.* 1957, 606.

24. Loewnsenschuss H.; Schmuckler G. *Talanta*, 1964, *11*, 1399.

25. Hirsch, H.F.; Gancher, E.; Russo, F.R. *Talanta* 1970, *17*, 483.

26. Vernon, F.; Eccles, H. *Anal. Chim. Acta* 1973, *63*, 403.

27. Griesbach, M.; Lieser, K.H. *Fresenius Z. Anal.* 1980, *109*, 149.

28. Sturgeon, R.E.; Berman, S.S. *Anal. Chem.* 1981, *53*, 2387.

29. Ryan, D.K.; Weber, J.H. *Talanta* 1985, *32*(9), 859.

30. Eccles, H .; Vernon, F. *Anal. Chim. Acta* 1973, *66*, 231.

31. Philips, R.J.; Fritz, J.S. Anal. Chim. Acta 1982, 139, 237.

32. Philips, R.J.; Fritz, J.S. Anal. Chim. Acta 1980, 121, 225.

33. Winston, A.; Mazza, E.T. J. Polym. Sci. 1975, 13, 2019.

34. Vernon, F. Pure Appl. Chem. 1982, 54 (11), 2077.

35. Shah, A.; Surekhadevi. Analyst 1985, 110, 1501.

36. Gregor, H.P.; Dolar, D.; Guenther, K.M. J. Am. Chem. Soc. 1955, 77, 3675.

37. Maeda, H.; Egawa, H. Nippon Kgaku Kaishi 1983, 4, 578.

38. Trader, K.; Matsumoto, K.; Inaba, T. Anal. Chim. Acta 1985, 170, 225.

39. Deratani, A.; Sebille, B. Anal. Chem. 1981, 53, 1742.

40. Slovak, Z.; Smrz, M.; Docekal, B.; Slovakova, S. Anal. Chim. Acta 1979, 111, 243.

41. Slovak, Z.; Docekal, B. Anal. Chim. Acta 1980, 117, 293.

42. Deratani, A.; Sebille, B. Macromol. Chem. 1981, 182(7), 1875.

43. Hudson, M.J. C.A. 1986, 104(10), 72204.

44. Liesser, K.H.; Rober, H.M.; Burba, P. Z.Anal.Chem.

45. Gruber, H. Monatsh. Chem. 1981, 112, 747.

46. Sidhanta, S.; Das, H.R. Talanta 1985, 32(6), 457.

47. Sugii, A.; Ogawa, N.; Hagiwara, H. Talanta 1984, 31(12), 1079.

48. Ryan, D.K.; Weber, J.H. Talanta 1985, 32(4), 854.

49. Muzarelli, A.A.; Tanfani, F. Pure Appl. Chem. 1982, 54(11), 2141.

50. Hitratani, K.; Onishi, Y.; Nakasawa, T. Appl. Polym. Sci. 1981, 26(5), 1475.

51. Moyers, E.M.; Fritz, J.S. Anal. Chem. 1976, 48, 1117.

52. Kostler, G.; Schmuckler, G. Anal. Chim. Acta 1967, 38, 179.

53. Bauman, A.J.; Weetall, H.H.; Weliky, N. Anal. Chem. 1967, 39, 932.

54. Dhandukia, M.M.; Indusekhar, V.K.; Govindan, K.P. Ind. J. Tech. 1982, 20, 203.

55. Samara, C.; Kauimtzis, TH.A. Anal. Chim. Acta 1985, 174, 305.

56. Suzuki, T.M.; Yokoyama; Matsunaga, H.; Kimura, T. Chem. Letters 1985, 41.

57. Terada, K.; Nakamura, K. Talanta 1981, 28, 123.

58. Ghosh, J.P.; Das, H.R. Talanta 1981, 28, 274.

59. Warshawsky, A. Talanta 1974, 21, 624.

60. Warshawsky, A. Talanta 1974, 21, 962.

61. Orf, G.M.; Fritz, J.S. Anal. Chem. 1978, 50, 1328.

62. Myasoedova, G.V.; Bolshakova, L.I. Zh. Anal. Khim. 1968, 23, 504.

63. Sykova, V.; Dubsky, F. Collect. Czech. Chem. Communs. 1972, 37(33), 1504.

64. Grote, M.; Kettrup, A. Anal. Chim. Acta 1985, 172, 223.

65. Shepherol, E.J.; Kitchener, J.A. J. Chem. Soc. 1957, 86.

66. Gold, D.H.; Gregor, H.P. J. Phys. Chem. 1959, 64, 1458, 1464.

67. Yokoyama, T.; Kikuchi, A.; Kimura, T.; Suzuki, T.M. Bull. Chem. Soc. Jpn. 1983, 56, 463.

68. Card, R.J.; Neckers, D.C. J. Am.Chem.Soc. 1977, 99, 7733.

69. Blasius, E.; Bock, I. J. Chrom. 1964, 14, 244.

70. Schmuckler, G. Talanta 1965, 12, 281.

71. Wolf, L.; Hering, R. Chem. Technol. 1958, 10, 663.

72. Kaeriyama, K.; Shimura, Y. Makromol. Chem. 1979, 180, 2499.

73. Blasius, E.; Brozio J. Chrom. 1965, 18, 572.

74. Moyers, E.M.; Fritz, J.S. Anal. Chem. 1977, 49, 418.

75. Oslen, R.L.; Diehl, H.; Collins, P.E.; Ellested, R.B. Talanta, 1961, 7, 187.

76. Turse, R.; Rieman, W. III. Anal. Chim. Acta 1961, 24, 202.

77. Parrish, J.R. Anal. Chem. 1982, 54, 1890.

78. Cornaz, J.P.; Deuel, H. Experientia 1954, 10, 137.

79. Cornaz, J.P.; Hutschneker, K.; Deuel, H. Helv. Chim. Acta 1957, 40, 2015. (C.A. 1958, 52, 6892e).

80. Deuel, H.; Hutschneker, K. Chimia 1955, 9, 49. (C.A. 1955, 49, 8526.)

81. Vernon, F. Pure Appl. Chem. 1982, 54, 2151.

82. Vernon, F.; Eccles, H. Anal. Chim. Acta 1976, 82, 369.

83. Vernon, F.; Eccles, H. Anal. Chim. Acta 1976, 83, 187.

84. Wan Yunus, W.M.Z.B. Ph.D. Thesis (Salford, U.K.) 1981.

85. Philips, R.J.; Fritz, J.S. Anal. Chim. Acta 1980, 121, 225.

86. Philips, R.J.; Fritz, J.S. Anal. Chim. Acta 1982, 139, 237.

87. Stamberg, J.; Seidl, J.; Rahm, J.R. J. Polym. Sci. 1958, 31, 15.

88. Blasius, E.; Laser, M. J.Chrom. 1963, 11, 81.

89. De Geiso, R.C.; Donaruma, K.G.; Tomic, E.A. J. Org. Chem. 1962, 27, 1424.

90. Nickless, G.; Marshall, G.R. Chrom. Rev. 1964, 6, 154.

91. Pennigton, L.D.; Williams, M.B. Ind. Eng. Chem. 1959, 51, 1959.

92. Lumbroso, R.; Conderc.R. Fr.Pat. 1964, 1360169. (C.A. 1965, 63, 3135_b)

93. Mikes. J.A. Hung. Pat 1963, 1360169. (C.A. 1963, 59, 10312_c.)

PART I

94. De Geisso, R.C.; Donaruma, L.G.; Tomic, E.A. J. Appl. Polym. Sci. 1963, 7, 1515.

95. Sahni, S.K.; Reedijk, J. Co-ordination Chem. Rev. 1984, 59, 87.

96. Blasius, E.; Janzen, K.P. Pure Appl. Chem. 1982, 54, 2115.

97. Sahni, S.K.; Reedijk, J. "Co-ordination Chem. Rev." Elsevier Science Publishers B.V. Amsterdam, 1984, 59, 110.

98. Gramain, P.; Frere, Y. Ind. Eng. Chem. Prod. Dev. 1981, 20, 524.

99. Warshawsky, A.; Kalir, R.; Patchornik, A. J. Org. Chem. 1978, 43, 3151.

100. Tabushi, I., Kobuke, Y.; Nishiya, T. Nature 1979, 280, 665.

101. Nyssen, G.A.; Jones, M.M.; Jeringam, J.D.; Harbison, R.D.; Macdonald, J.S. J. Inorg. Nucl. Chem. 1977, 39, 1889.

102. Overberger, C.G.; Lebovits, A. J. Am. Chem. Soc. 1955, 77, 6618.

103. Magee, R.J. Rev. Anal. Chem. 1973, 1, 333.

104. Okawara, M.; Sumitomo, Y. Kogyo Kayaku Zasshi 1958, 61, 1508.

105. Murthy, R.S.S.; Ryan, D.E. Anal. Chim. Acta 1982, 140, 163.

106. Suzuki, T.M.; Yokoyama, T. Polyhedron 1983, 2, 127.

107. Chikuma, M.; Nakayama, M.; Tanaka, T.; Tanaka, H. Talanta 1979, 26, 911.

108. Kemula, W.; Brajter, K. Chem. Anal. (Warsaw) 1968, 13 (2), 305.

109. Mathur, N.K.; Williams, R.E. J. Macromol. Sci. Rev. Macro Chem. 1976, C15, 117.

110. Akelah, A.; Sherrington, D.C. Chem. Rev. 1981, 81, 557.

111. Sahni, S.K.; Reedijk, J. "Co-ordination Chem. Rev." Elsevier Science Publishers, B.V. Amsterdam 1984, 59, 14.

112. Maeda, H.; Egawa, H. J. Appl. Poly. Sci. 1984, 29, 2281.

113. Egawa, H.; Nonaka, T. J. Appl. Poly. Sci. 1986, 31, 1677.

114. Blasius, E.; Brazio, B. in "Chelates in Analytical Chemistry", Flaschka, H.A.; Barnard, A.J. Jr. eds. 1967, Vol.1, P.55.

115. Vernon, F. Chem. Ind. 1977, 634.

116. Hodgkin, J.H. Chem. Ind. 1979, 153.

117. Pepper, K.W.; Paisely, H.M.; Young, M.A. J. Chem. Soc. 1953, 4097.

118. Griesbach, M.; Lieser, K.H. Die Angew. Macromol. Chemie 1980, 90, 143.

119. Melby, L.R. J. Am. Chem. Soc. 1975, 97, 4044.

120. D'Alelio, G.F.; Monacelli, W.J. U.S. Pat. 1968, 3395134 & 3395197.
(C.A. 1968, 69, 107366_a, 107365_z)

121. VonLillin, H. Angew. Chem. 1954, 66, 649.

122. Yoshioka, T.; Shimamura, M. Bull. Chem. Soc. Jpn. 1983, 56, 3726.

123. Yoshioka, T.; Shimamura, M. Bull. Chem. Soc. Jpn. 1984, 57, 334.

124. Yoshioka, T. Bull. Chem. Soc. Jpn. 1985, 58, 2618.

125. Green, B.R.; Jaskulla, E. in "Ion Exchange Technology", Nuden, D.; Street, M. eds. 1984, P.490.

PART I

126. Permutit, Co. Ltd.; Holmes, E.L.; Holmes, L.E.; Prescot, W.G. Brit. Patent 1939, 506, 291. (C.A. 1939, 33, 9490^7)

127. Sahni, S.K.; Reedijk, J. "Coordination Chemistry Reviews" Elsevier Science Publishers B.V., Amsterdam 1984, 59, P.6.

128. Seymour, M.D.; Fritz, J.S. Anal. Chem. 1973, 45, 1632.

129. Fritz, J.S.; Goodkin, L. Anal. Chem. 1974, 46, 959.

130. Small, H.; Stevens, T.S.; Bauman, W.C. Anal. Chem. 1975, 47, 1801.

131. Fritz, J.S.; Gjerde, D.T.; Pohlandt, C. "Ion Chromatography", Dr. Alfred Hüthig Verlag Heidelberg Basel: New York, 1982, P.2.

132. Fritz, J.S.; Gjerde, D.T.; Pohlandt, C. "Ion Chromatography" Dr. Alfred Hüthig Verlag Heidelberg Basel: New York, 1982, P.24.

133. Schoniger, W. Mikrochim. Acta. 1955, 123.

134. Schoniger, W. Mikrochim. Acta. 1956, 869.

135. Bradstreet, R.B. Anal. Chem. 1957, 29, 944.

136. Meites, L. "Handbook of Analytical Chemistry", McGraw-Hill Book Company, New York, 1st edn., 1963, P.6-27.

137. Meites, L. "Handbook of Analytical Chemistry", McGraw-Hill Book Company, New York, 1st edn., 1963, P.6-21.

138. Vogel, A.I. "A Textbook of Quantitative Inorganic Analysis", Longman Group Ltd. England, 4th edn., 1985, P.744.

139. Meites, L. "Handbook of Analytical Chemistry", McGraw-Hill Book Company, New York, 1st edn., 1963, P.6-23.

140. Meites, L. "Handbook of Analytical Chemistry", McGraw-Hill Book Company, New York, 1st edn., 1963, P.6-24.

141. Hampel, C.A. "The Encyclopaedia of the Chemical Elements", Reinhold Book Corp., New York, 1976, P.410.

142. Moore, J.W.; Moore, E.A. "Environmental Chemistry", Academic Press Inc; New York, 1976, P. 397.

143. Fortsner, U.; Wittman, G.T. "Metal Pollution in the Aquatic Environment", Springer-Verlag Berlin,Heidelberg, 2nd Revised edn. 1981, P.30.

144. Jernelov, A. Nord. Hyg. Tidskar 1969, 50, 174.

145. Jernelov, A. in "The Changing Chemistry of the Oceans", Dyressan, D.; Jagner, D. eds., Wiley, New York, 1972.

146. Moore, J.W.; Moore, E.A. "Environmental Chemistry", Academic Press Inc: New York, 1976, P.404.

147. Moore, J.W.; Moore, E.A. "Environmental Chemistry", Academic Press Inc: New York, 1976, P.401.

148. Thanabalasingam, P.; Pickering, W.F. Environmetnal Pollution (B) 1985, 9, 267.

149. Fortsner, U.; Wittmann, G.T. "Metal Pollution in the Aquatic Environment", Springer-Verlag Berlin, Heidelberg, 2nd revised edn., 1981, P.20.

150. Natusch, D.F.S.; Hopke, P.K. "Analytical Aspects of Environmental Chemistry", John Wiley and Sons, New York, 1983, P.40.

151. Gardner, D.; Riley, J.P. Nature (London) 1973, 241, 526.

152. Harsanyi, E.; Polos, J.; Pungor, E. Anal. Chim. Acta 1973, 67, 229.

153. Ashurstk.G. in "Ion Exchange Technology", Naden D.; Streat M., Eds., Ellis Horwood Limited, West Sussex, 1984, P.189.

154. Muroi, M.; Imai, S.; Hamaguchi, A. Analyst 1985, 110, 1083.

155. Taquikhan, M.M. National Science Day Supplement C.S.I.R. New Delhi, 1987, P.163.

156. Mckaverey, J.P.; Fassinger, W.P.; Stiven, D.A. Environ. Sci. Technol. 1972, 6, 1109.

157. Swanson, C.; Wing, R.E.; Donae, W.M.; Russel, C.R. Environ. Sci. Technol. 1973, 7, 614.

158. DeJong, G.J.; Rekers, C.J.N. J. Chrom. 1974, 102, 443.

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PART - II

CHAPTER - I

CHELATING RESINS WITH IONICALLY ANCHORED FUNCTIONAL GROUPS

1.1 INTRODUCTION

Enhancing the selectivity of ion-exchange resins for metal ions by using complexing agents either in solution or in the resin phase had been contemplated.[1] The two well-known basic methods for the synthesis of chelating resins, polycondensation and polymer transformations, have their inherent limitations.

Polycondensation has been accepted as the simplest method and it gives maximum incorporation of the chelating group. However, the resistance of such resins to physical and chemical stress is low. Another disadvantage is that the cross-linking phenol introduces additional functional groups which may decrease the selectivity. In polymer transformation, the functional groups are introduced by chemical reactions of the polymer matrix. The availability of polymers with desirable characteristics for use as starting material is an advantage, but this method gives low yield in functionalisation.

Moreover, each subsequent reaction will progressively clog the pores of the cross-linked polymer and in some cases intramolecular reactions within the dense resin gel may lead to undesirable results. Polymerization of vinyl compounds containing chelating groups is also used widely which gives resins with high capacity. The synthesis of vinyl monomers with chelating groups is rather difficult and hence this method is used only rarely.

Thus the use of chelating resins is limited by difficulties in the synthesis of materials with desired properties and also due to the relatively high cost of the material produced.

Recent studies have shown that the selectivity of chelating agents and operating convenience of ion-exchange resins can be exploited by a different approach.[2-4] The steric limitations imposed by the rigidity imparted to the chelating group by covalent anchoring on the polymeric matrix can also be overcome by the new approach which can be accomplished in two ways:

(1) An ionic group is introduced into the chelating agent, the reagent is now allowed to

complex the metal ion in solution. The resulting ionic chelate is exchanged on the ion-exchange resin. If we represent the chelating agent as HL and the ionic group as X^-, then,

$$HL + X^- \longrightarrow (HLX)^-$$

$$M^{n+} + n(HLX)^- \rightleftharpoons [M(LX)_n]^{n-} + nH^+$$

$$\overline{nR^+} + [M(LX)_n]^{n-} \rightleftharpoons \overline{R^{n+}[M(LX)_n]^{n-}}$$

where X^- is usually $-SO_3^-$ or $-COO^-$.

(2) The ionic chelating agent may be exchanged on an ion-exchange resin. The chelating agent thus becomes electrostatically anchored to the resin matrix. Such a reagent - loaded resin may be used as the medium for the pre-concentration and separation of metal ions.

$$\overline{R^{n+}} + n(HLX)^- \rightleftharpoons \overline{R^{n+}(HLX)^{n-}}$$

$$\overline{R^{n+}\ (HLX)^{n-}} + M^{n+} \rightleftharpoons \overline{R^{n+}(MLX)^{n-}} + nH^+$$

This technique is simple and the loaded resin is inexpensive compared to the co-valently anchored resin. The selectivity of the loaded resin towards metal ions is sometimes further enhanced by the freedom in spatial orientation of the chelating group. The loaded resin shows properties associated with ion-exchangers, chelating agents and also of a physical sorbent. Leaching of the loaded reagent by strong electrolytes is a major drawback of this approach.

For the convenience of synthesis, usually a strongly ionised functional group like sulphonic acid is introduced into the chelating agent thus yielding an anionic species. The chelate formed with metal may be uncharged in the co-ordination sphere but since there is an overall negative charge associated with the functional group introduced, anion exchange occurs. In the case of metals with a tendency to form anionic complexes with common anions such as chloride, these complex anions may also compete with the chelate anion, thus limiting the selectivity.

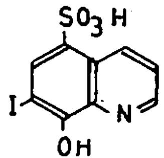
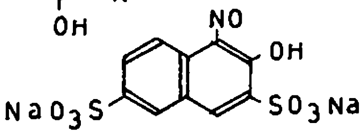
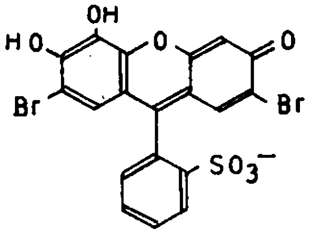
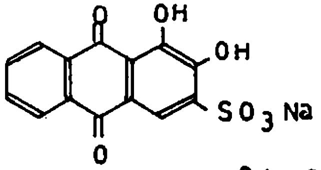
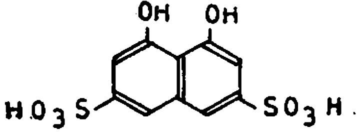
1.2 AN OVERVIEW OF DEVELOPMENTS IN IONICALLY ANCHORED CHELATING AGENTS

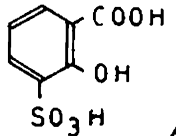
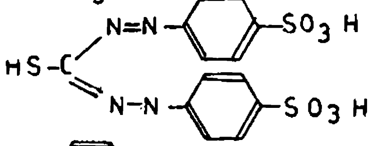
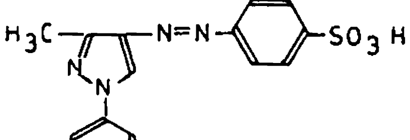
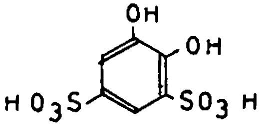
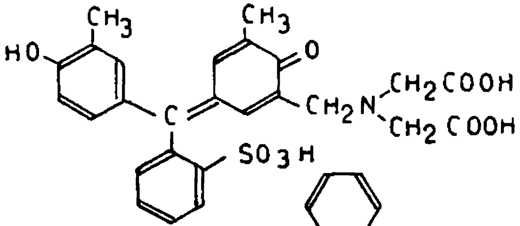
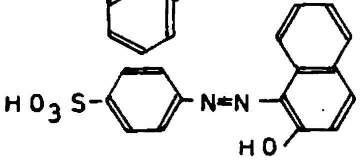
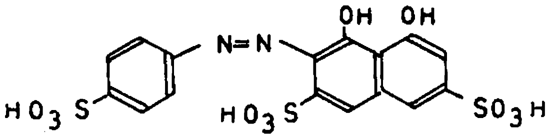
The anion exchange separation of very similar metal ions such as ziroconium and hafnium was extensively worked out by Kraus et al. [5,6]

The method is useful in preparative scale anion exchange chromatographic separation. It loses its advantage as far as pre-concentration of traces of metals is concerned. A fairly concentrated acid solution is used as eluent, thus suppressing the distribution coefficient. A large K_D value is an essential prerequisite for any system used in analytical pre-concentration. Hence anion exchange of metal found little use as a pre-concentration technique. The potential of anionic chelating agents loaded on an anion-exchange resin as a pre-concentration medium was realised by Brajter et al. In a series of publications, they have demonstrated the applications of this medium (Table-1.1).

Ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) was the first of the reagents studied by them.[14] Ferron forms soluble chelates with many metals and photometric methods have been developed for the determination of Al(III), Ca(II), Fe(III), Mo(VI), Nb(V), U(VI) and V(V). Even though the reagent is of limited selectivity, when it is loaded

Table - 1.1 **Ionically Anchored Chelating Agents**

Sl. No.	Reagent		Support Resin	Pre-concentration/ Separation	Ref.
	Name	Structure			
1.	Ferron		Anion exchange resin (Dowex 1-X8)	Cu, Pb, Zn, Cd	7,8
2.	Nitroso-R-Salt		Amberlite IRA-400	Co, Cu, Ni, Fe,Cr	2
3.	Bromopyrogallol red		Amberlite IRA-400	Ti, Co, Cu, Cr,Fe	3
4.	Alizarin red		Amberlite IRA-400	Zr, Al	3
5.	Chromotropic acid		Amberlite IRA-400 (Dowex 1-X8)	Ti, Fe, Cu, Cr	3,8

Sl. No.	Reagent Name	 Structure	Support Resin	Pre-concentration/ Separation	Ref.
6.	5-Sulfosalicylic acid		Dowex 1-X8	Fe, Cu	8
7.	Dithizone sulfonic acid		Amberlite IRA-400	Cu, Hg	9
8.	Azothiopyrine-disulfonic acid		Amberlite IRA-400	Se, Hg	10,11
9.	Tiron		Amberlite IRA-400	Pb, Al, Ga, In, Ti	12
10.	Xylenol orange		Amberlyst A-26 (macroreticular anion exchange resin)	Al, Ga, In, Zn,Cu,Mn	13
11.	Orange II		Amberlyst A-26	Bi, Cd	4
12.	SPADNS		Amberlyst A-26	Bi, Cd	4

on an anion exchange resin, it was very effective in the separation of Zn(II) and Cd(II) ions.

Nitroso-R-salt selectively forms a soluble chelate with Co(II). It has been widely used in the estimation of Co(II). Brajter used this reagent for the separation of mixtures of Co with Cu, Ni, Fe and Cr on the anion exchange resin Amberlite IRA - 400.[2] Iron(III) was eluted with 0.4N H_3PO_4, Cr(III) with 0.5N HCl, Cu(II) with 2N HCl and Ni(II) with 5N $HClO_4$. The method was useful in the colorimetric determination of Co in Cu and Ni alloys.

Bromopyrogallol Red, alizarin-S, chromotropic acid, SPADNS and orange-II were also used in ionically immobilized form for the separation of metal ions.[3,4] The separation shown is excellent and is readily adopted for pre-concentration. A general observation is that chelating agents bearing a naphthalene ring shows higher affinity towards anion exchange resins than those having a benzene ring.

Later, more selective reagents have been investigated. Going et al have shown that

2-(3'-sulfobenzoyl) pyridine-2-pyridyl hydrazone is effective in the pre-concentration and separation of Fe, Co,Ni,Cu,Zn,Cd,Hg and Pd for estimation by AAS.[15] Chromotropic acid, 5-sulfosalicyclic acid and 7-iodo-8-hydroxyquinoline-5-sulfonic acid were investigated by Lee et al again for pre-concentration of metal ions prior to determination by AAS.[8] The versatility of dithizone as an extractant prompted Chikuma et al to synthesize sulfonic acid derivative of dithizone (DzS) and study the pre-concentration of copper and mercury.[9] They also investigated tetraphenyl porphine trisulfonic acid, sulfonazo III, arsenazo III, thiosalicyclic acid and 2-mercaptobenzene sulfonic acid for the pre-concentration of mercury. Of these, the resin loaded with DzS, tetraphenylporphinetrisulphonic acid or zincon were stable in 1M sodium chloride whereas sulphonazo III, arsenazo III, thiosalicyclic acid and p-mercaptobenzenesulphonic acid were found to be labile in the same medium.

Tiron (1,2-dihydroxy benzene-3, 5-disulfonic acid disodium salt) forms strong complexes (log $K_{ML} >$ 10) in acid medium with Al(III), Be(II), Cu(II) and Zr(IV). All these metal ions are known to form complexes with chelating agents having two oxygen donors. Tiron has been used as a photometric reagent in the determination of a large number of metal ions. The reagent immobilized on an anion exchange resin was investigated by Brajter and Złotorzynska.[12] The uptake of the reagent on the resin could be improved by using macroporous anion exchange resin Amberlyst A-26. Separation could be achieved for Pb(II), Al(III), In(III) and Ti(VI), Ga(III).

Chikuma et al have reported the synthesis of azothiopyrine disulfonic acid (ATPS) loaded anion exchange resin which showed selectivity towards mercury.[10,16] ATPS sorbed on the resin does not bleed into solution even in 0.5M sodium chloride. The thiol group was resistant to oxidation even in 10M hydrochloric acid. Mercury could be eluted with 100% recovery using 10% thiourea in 0.1M perchloric acid. ATPS loaded on anion exchange resin was also used in the pre-concentration of Se(IV).[11]

Selenium could be eluted with 13M nitric acid and could be determined fluorometrically. Slight leakage of ATPS from the loaded resin is observed when the hydrochloric acid concentration exceeded 1M. Cadmium and copper do not interfere with this pre-concentration method unless present in large excess.

These studies have clearly shown the following loading and separation characteristics of ionic chelating agents anchored on an anion exchange resin.

(1) The loading capacity of the reagent on the resin is higher when the reagent contains a fused ring system in its structure.

(2) The strength of anchoring of the reagent depends on the number of ionic groups on the reagent molecule.

(3) The reagent-loaded resin is suitable for pre-concentration and separation of metal ions to which the reagent is selective.

(4) The degree of selectivity is not the same as that observed in solution.

These observations point to the fact that it is worth investigating the exchange behaviour of each and every reagent towards selected sets of metal ions.

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CHAPTER - II

PREPARATION AND CHARACTERISATION OF R-PGS

2.1 INTRODUCTION

Recent studies have shown that aromatic complexing agents containing sulfonic acid groups when anchored to anion exchange resins are particularly useful in the separation of metal ions.[2-4,8,9] Pyrogallol sulfonic acid (PGS) shows interesting chelating properties similar to those of tiron and provides useful separations of those metal ions which differ sufficiently in their affinity for the donor oxygen atoms of the ligand, when anchored to a strong base anion exchange resin. The reagent-loaded resin (R-PGS) shows high affinity towards Mo(VI),V(V) and Fe(III). The synthesis , characterisation and metal sorption studies of R-PGS are described in this chapter.

2.2 EXPERIMENTAL

2.2.1 Sulfonation of pyrogallol

Pyrogallol was sulfonated using chlorosulfonic acid by slightly modifying the procedure given by Pollak and Fulnegg.[17] Pyrogallol (5g) was taken in a dry round bottomed flask and chlorosulfonic acid (25 ml) was added in drops from a dropping funnel fitted with a guard tube. The mixture was refluxed on a boiling water bath for 2 h. The reaction mixture was cooled and water was added slowly followed by excess of 20% sodium hydroxide solution refluxed on a boiling water bath for half an hour, cooled, filtered and sodium pyrogallol sulphonate precipitated from water by adding ethanol. The sample was recrystallized from water-ethanol mixture.

2.2.2 Preparation of pyrogallol sulfonic acid-loaded resin (R-PGS)

Seralite SRA-400 (SISCO Research Laboratories, Bombay) with 8% cross-linking in the chloride form, was powdered, sieved and particles of 100-200 mesh size was used as the anion exchange resin. The exchange capacity of the resin was determined by dynamic method.

The chelating agent-loaded resin was prepared by keeping the resin soaked in aqueous solution of pyrogallol sulfonic acid (PGS) for 8 h. with occasional stirring. The resin was filtered, washed with 0.1N HCl and then with water and dried at 60°C for 24 h. and kept in a descicator. The resin was allowed to swell and then conditioned in appropriate buffers before sorbing the metal ions.

2.2.3 Estimation of PGS by spectrophotometry

Since PGS gives highly coloured solution, it can be determined spectrophotometrically. The visible spectrum of PGS was recorded at various pH. Concentrations were measured spectrophotometrically in the pH range 5-7. The absorption band of λmax occurs at 438 nm and the absorbance remains steady in this pH range. Hence the band with λmax 438 nm was used for the spectrophotometric determination.

A sample of purified PGS (0.1g) was dissolved in distilled water and diluted to 100 ml in a standard flask. Different aliquots (5 ml, 10 ml, 15 ml, etc.) were diluted to get concentrations of 0.002 to 0.02% and the absorbance of the solution at 438 nm were measured. A calibration curve of absorbance vs concentration was drawn which gave a straight line.

2.2.4 Kinetics of uptake of PGS on the resin

Aliquots (20 ml) of a 2% solution of PGS were kept shaken with 0.5g - samples of resin in stoppered 25 ml flasks for different intervals of time. Residual concentration of PGS was measured spectrophotometrically.

2.2.5 pH-dependent sorption of PGS on the resin

A weighed amount of the resin (0.1g) was kept shaken with 20 ml of 0.5% solution of PGS at different concentrations of HCl. Residual concentration of the reagent was measured spectrophotometrically after adjusting the pH to 5 by adding dilute NaOH.

2.2.6 Determination of the reagent eluted with sodium chloride solution

The stability of R-PGS towards leaching of the loaded reagent by electrolytes was studied using sodium chloride solutions of different concentrations. The reagent-loaded resin was slurry-packed in a column (0.5 x 10 cm) and 100 ml of sodium chloride solution was passed through it at a flow rate of 2 ml/min. The amount of reagent leached out was determined spectrophotometrically.

2.2.7 Procedures used in sorption studies

Stock solutions of Fe(III), Cu(II) and Ni(II), were prepared using their salts as given in Part I, Section 2.2.6. Mn(II), Mo(VI), V(V) and Be(II) solutions were prepared using manganese sulfate ($MnSO_4.H_2O$) (E. Merck (India) Ltd., Bombay), ammonium heptamolybdate $(NH_4)_6 MO_7O_{24}.4H_2O)$ (E.Merck (India) Ltd., Bombay), and beryllium sulfate ($BeSO_4.4H_2O$) (CDH, Bombay) respectively.

All chemicals used were of guaranteed purity and solutions were prepared in doubly distilled water. Stock solutions of 2000 mg/l were prepared and were standardised by recommended procedures.

pH of experimental solutions were adjusted using 0.1N sodium hydroxide and 0.1N hydrochloric acid unless otherwise specified. Details are given under Results and Discussion.

The sorption characteristics of R-PGS for Fe(III), Cu(II), Ni(II), Mn(II), Mo(VI), V(V) and Be(II) were studied by batch and column methods.

(a) Batch technique

Aliquots of metal ion solutions (400 μg/ml) at different pH were kept shaken with 0.1g of the reagent-loaded resin at 28 ± 1°C. pH of the solution was checked after equilibration also. After shaking for 24 h the residual concentrations of metal ion in the solution phase weredetermined by withdrawing the supernatant liquid. The amount of metal ion sorbed by the resin was taken in terms of the difference between the original and residual concentration in the solution. The sorption capacities and K_D values for the metal ions at various pH were calculated.

Kinetics of sorption of various metal ions were studied at the pH of maximum sorption by keeping R-PGS shaken with aliquots of metal ion solution for different intervals of time. Residual concentration of metal ion in the solution phase was determined.

(b) Column operations

The breakthrough studies of Mo(VI), V(V), Cu(II), Mn(II), Fe(III) and Ni(II) were done using the column technique. A glass column of 0.5 cm i.d., and 10 cm length was slurry-packed with R-PGS resin of particle size 100-200 mesh by applying suction at a water pump. It was pre-conditioned by running 100 ml of 0.1N HCl followed by 100 ml of doubly distilled water at a flow rate of 1 ml/min.

(i) Molybdenum (VI)

Molybdenum (VI) solution (100 μg/ml) was prepared at pH 3 by adding dil. HCl/dil.NaOH and allowed to pass through the column at a flow rate of 0.5 ml/min. Fractions were collected in 5 ml lots and the concentration of molybdenum (VI) in each fraction was determined spectrophotometrically using gallic acid.[18]

(ii) Vanadium (V)

Through the column conditioned using 0.001N HCl a solution of V(V) (100 μg/ml) was run at a flow rate of 0.5 ml/min. Fractions were collected in 5 ml lots and the concentration of vanadium(V) in each fraction was determined spectrophotometrically using sodium tungstate and phosphoric acid.[19]

(iii) Iron (III)

The column was preconditioned using doubly distilled water of which the pH was adjusted to 4 using sodium citrate/citric acid buffer. Iron (III) solution (100 μg/ml) at pH 4 in the same buffer was run through the column at a flow rate of 0.5 ml/min. Fractions were collected in 5 ml portions and concentration of Fe(III) in each fraction was determined spectrophotometrically using 1,10-phenanthroline after reduction with hydroxylamine.[20]

(iv) Nickel (II), Manganese (II) and Copper (II)

Breakthrough of Ni(II), Mn(II) and Cu(II) were studied using solutions of 100 g/ml of each metal. The pH of the solutions were adjusted to 4 using acetate buffer and each sample was run through the column at a flow rate of 1 ml/min. fractions were collected in 5 ml portions and concentration of metal ion in each fraction was determined spectrophotometrically.[21-23]

2.3 RESULTS AND DISCUSSION

2.3.1 Nature of Seralite SRA-400

This is an anion exchange resin of the quarternary ammonium type in the chloride form. The backbone structure is DVB-styrene copolymer. Its anion exchange capacity determined by dynamic elution procedure is 1.5 meq/g of dry resin and its water regain is 44%.

2.3.2 Nature of PGS

Sodium salt of pyrogalloldisulfonic acid is soluble in water and the solution is bluish green in colour. In acid medium it is yellow in colour. It is easily dissolved in 0.1N acetic acid. The compound is sensitive to air oxidation and may be partially converted to quinone form, as indicated by the carbonyl bands in the IR spectrum.[24] The FT-IR spectrum of R-PGS shows the characteristic bands of PGS. The band assignments are: 3441 cm^{-1} (phenolic OH), 1624 cm^{-1} (C = O), 1168 cm^{-1}, 1203 cm^{-1}(SO_3^-).

PGS absorbs in the visible region and it has a λ max at 438 nm. In the pH range 5-9, the spectrum in the visible region is insensitive to

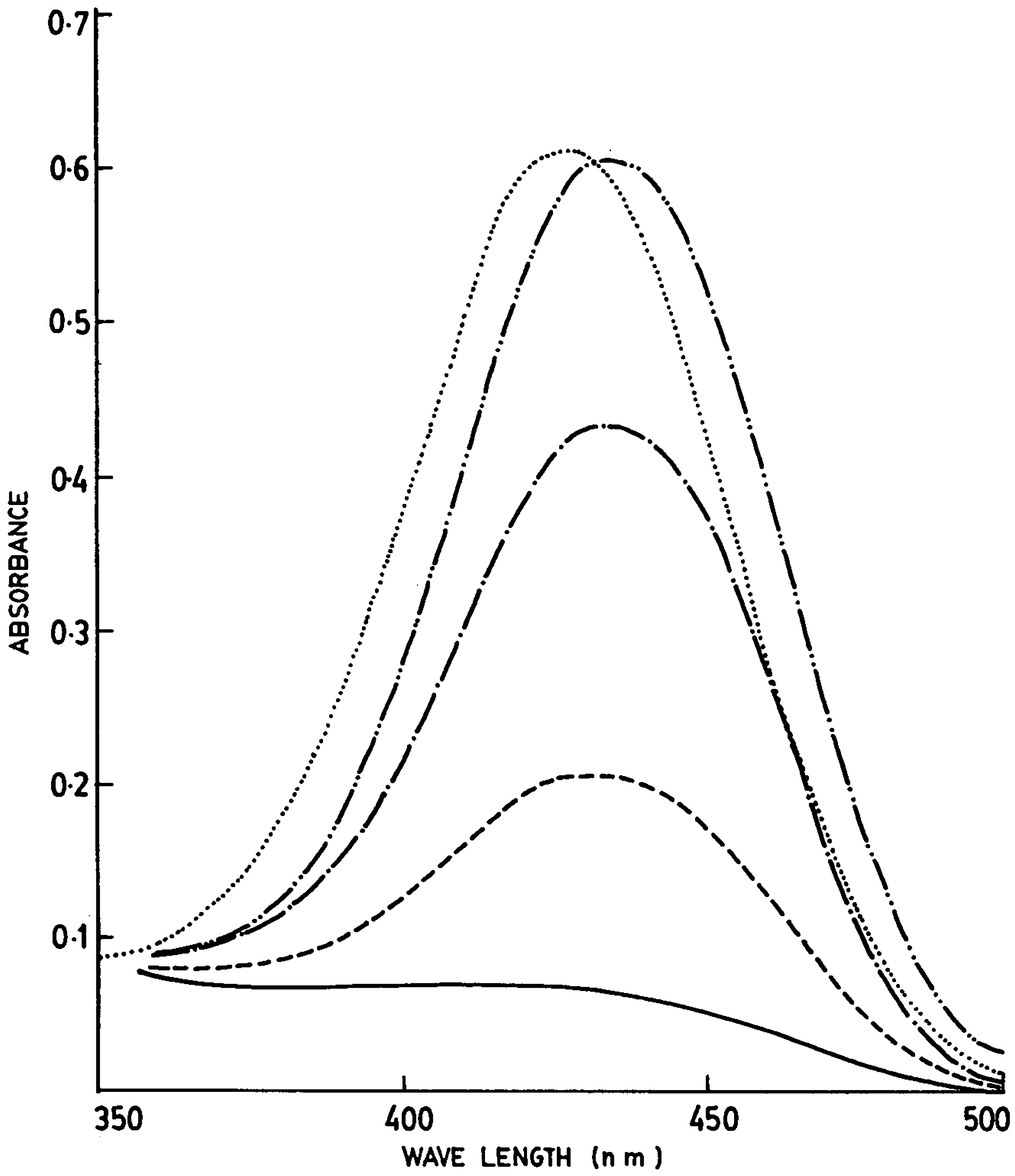

Fig. 2.1 pH dependence of absorption spectrum of PGS.

Concentration of PGS 0.01%, scan rate 120 nm/min., slit width 2 nm, (——) pH 1, (----) pH 2, (—·—) pH 3, (—··—) pH 5-9, (·········) pH 11.

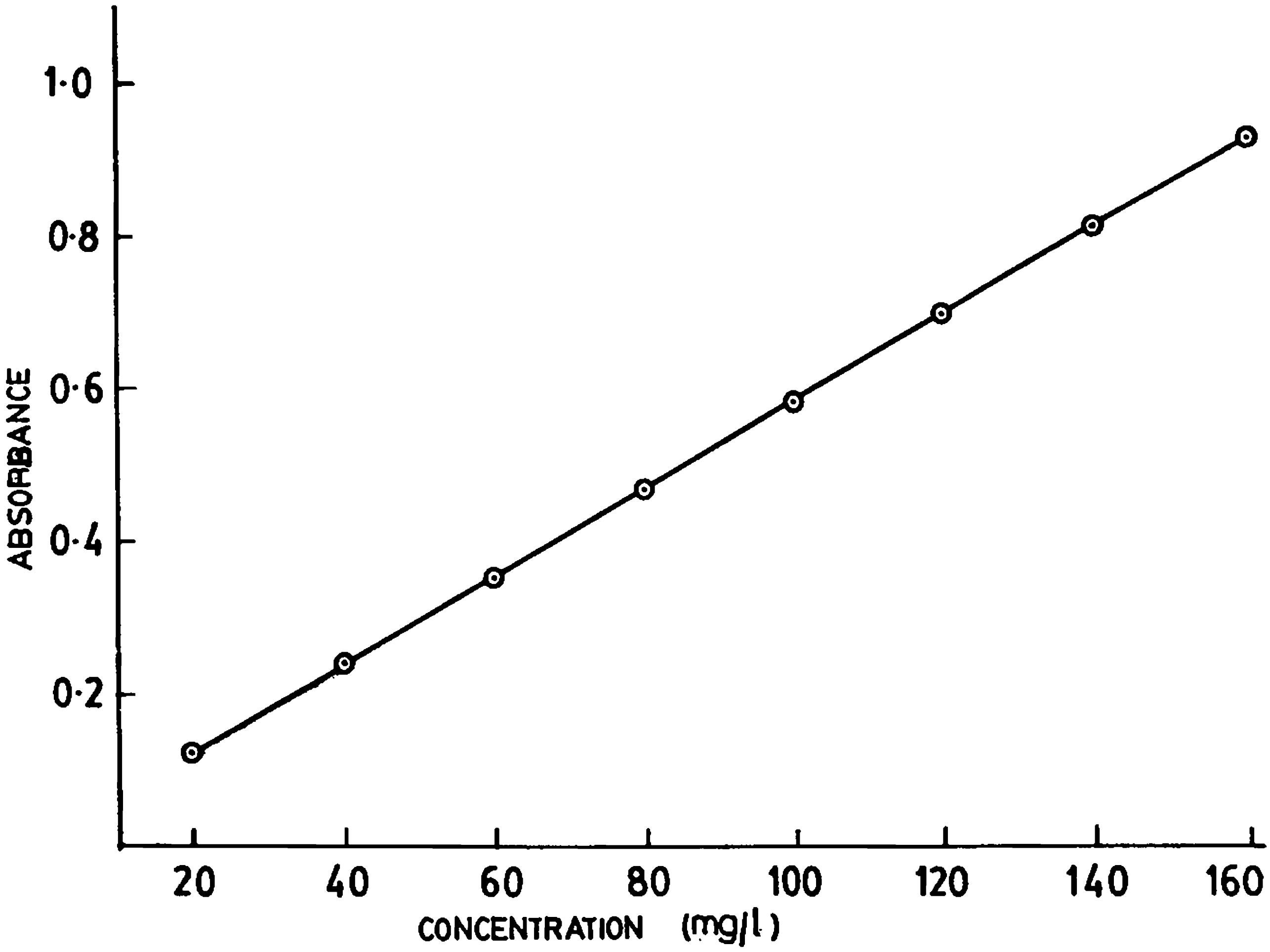

Fig. 2.2 Spectrophotometric calibration curve for PGS at 438 nm.
pH of solution 6.0.

variation in pH (Fig.2.1) and has a specific absorbance of 12.4 $lg^{-1}cm^{-1}$ at 438 nm. Hence the quantitation of PGS has been carried out spectrophotometrically after adjusting the pH of the solution to neutral. (calibration curve Fig.2.2).

2.3.3 Loading of PGS on Seralite SRA-400

The uptake capacity of Seralite SRA-400 resin for PGS in 0.5M to 0.001M hydrochloric acid was studied. The capacity increases with decrease in concentration of acid and reaches saturation in 0.1M hydrochloric acid. The sorption experiments carried out in batches have shown that the uptake of PGS on the resin is very fast. Half-saturation occurs in 3 minutes from aqueous solution(Fig.2.3). The tenacity of sorption of PGS on the resin was tested by eluting it with 0.1M hydrochloric acid. It is found that the elution is negligible. In 0.1M sodium chloride also elution of PGS from the loaded resin (R-PGS) is negligible. However, as the concentration of the electrolyte increases, the elution of PGS occurs and more than 80% of PGS is leached out by 30 bed volumes of 1M sodium chloride.

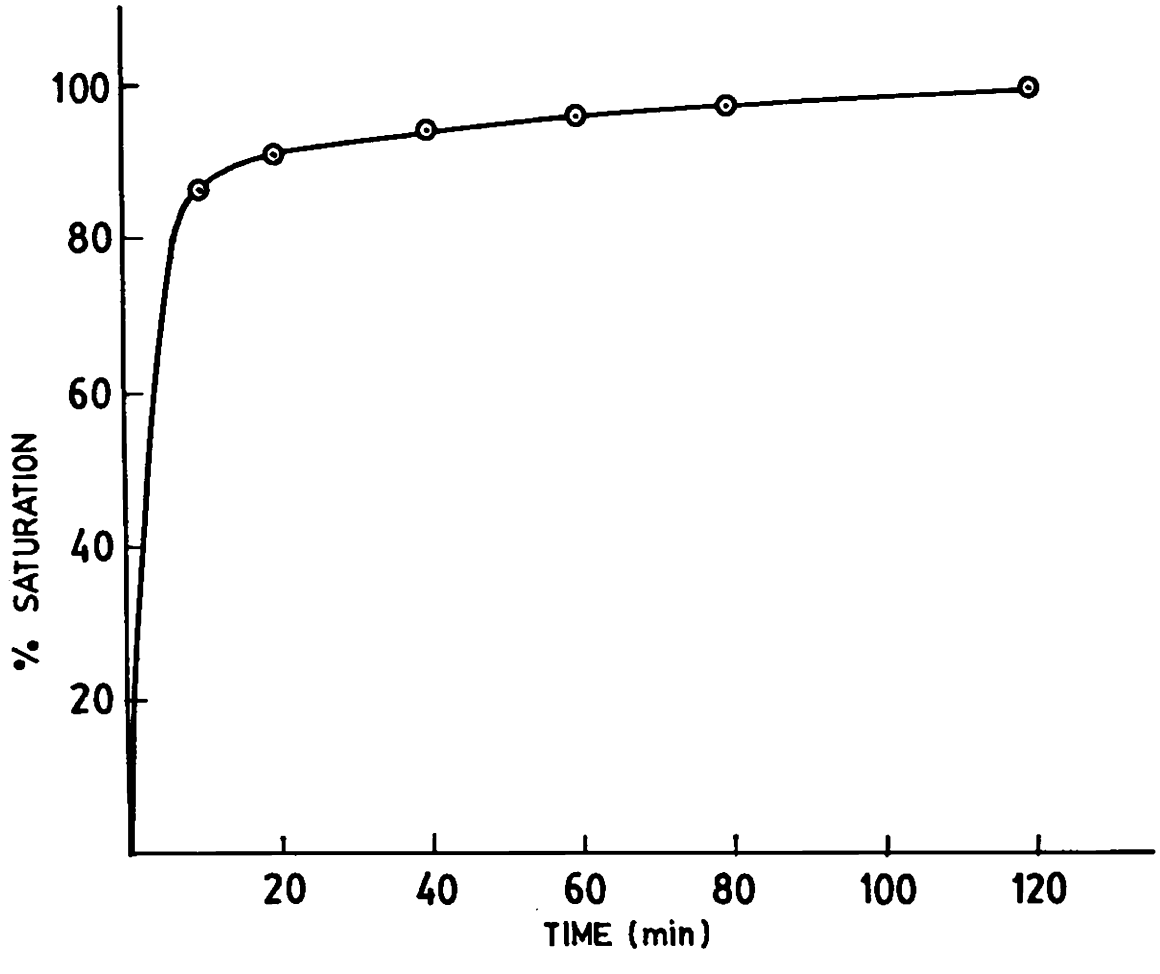

Fig. 2.3 Kinetics of sorption of PGS on Seralite SRA-400.

Amount of resin 0.5g, aliquots of PGS solution (2%) 20 ml, temperature 28 ± 1°C

2.3.4 Sorption characteristics of metal ions on R-PGS

There are two possibilities for the sorption of metal ions on R-PGS: (1) the oxygen atoms of PGS coordinate with metal ions thus keeping it on the resin, and (2) the metal may form an anionic complex which in turn may exchange at the cationic sites of the resin by displacing PGS, which of the two dominates is determined by the relative stability of the metal-PGS complex and the anionic complex normally requires either a strongly complexing anion such as CN^- or F^-, or high concentration of a weakly complexing anion. Since we are dealing with only solutions of low ionic concentration, the latter situation does not exist. Most of the studies were carried out in the pH range 2-6 and also only in Cl^- NO_3^-, SO_4^{2-}, ClO_4^-, acetate or citrate media. Whenever solution of high ionic strength was used, experiments were conducted to see the elution pattern of PGS by these solutions. Results are mentioned under appropriate individual cases (Tables 2.1-2.14, Figs. 2.4-2.6).

The resin used in this study showed a reagent loading capacity of 0.8mmol/g. From the M:L ratio shown in Table 2.8, in the case of Mo(VI), Fe(III), V(V) and Be(II), the metal to ligand ratio varies from

1:1.95 for Mo(VI) to 1:0.78 for Be(II). These metals are known to form strong complexes with O,O-donors. This means that the ligand, even though available in excess satisfies only part of the co-ordination sites of the metal, rest of the sites being occupied by water. The restricted mobility of the ligand prevents it from taking orientation around the metal ion. In the case of Ni(II), Cu(II), and Mn(II), the low capacity is a consequence of their lack of affinity for oxygen donors.

(a) Sorption of iron (III)

It was found that 0.1M citrate buffer does not leach PGS under the conditions used in this study. At higher concentrations of Fe(III), slow elution of reagent took place. The sorption capacity increases with pH and reaches a maximum of 0.69 mmol/g at about pH 4 (Fig. 2.4).

(b) Sorption of vanadium (V)

The capacity for V(V) is low at low pH. At around pH 2 it suddenly increases and reaches a maximum of 0.75mmol/g at pH 3 and then remains steady (Fig.2.4,Table 2.6). In fact, V(V) shows maximum

Table 2.1-2.7 Sorption of metal ions on R-PGS as a function of pH

Amount of resin 0.1g, particle size 100-200 mesh, volume of solution 10 ml, amount of metal ion 4.0 mg, shaking time 24 h, temperature 28 ± 1°C.

Table - 2.1 Molybdenum (VI)

Equilibrium pH	Capacity (mmol/g)	Log K_D
1.3	0.27	2.27
2.1	0.41	3.73
3.1	0.41	3.78
4.0	0.40	3.60
4.9	0.29	2.36
6.0	0.28	2.32

Table - 2.2 Iron (III)

Equilibrium pH	Capacity (mmol/g)	Log K_D
1.4	0.04	0.77
2.1	0.29	1.83
3.0	0.49	2.33
4.1	0.69	3.35
4.5	0.62	2.79
5.6	0.55	2.51

capacity among various metal ions studied on R-PGS. Since V(V) is a fairly strong oxidant, PGS which is a polyhydroxy phenol, is easily oxidised. However, no leaching was observed under this condition.

(c) Sorption of molybdenum (VI)

The capacity for Mo(VI) increases with pH, reaches a maximum of about 0.4 mmol/g at pH 2-4 and then slightly decreases. (Fig.2.4,Table 2.1). In the case of Mo(VI) also it is known that in acid medium it oxidises polyhydroxy phenols. This may be the reason for the low capacity of Mo(VI) observed at low pH.

(d) Sorption of copper (II)

The sorption capacity for Cu(II) increases with increasing pH and reaches a maximum of 0.2 mmol/g at around pH 5. (Fig.2.4, Table 2.4).

(e) Sorption of Ni(II) and Mn(II)

The sorption capacity of Ni(II) and Mn(II) are very low on R-PGS. However, the capacities are pH dependent. The results are given in Fig. 2.4, Table 2.3, 2.6. This is as expected since these metal ions have a low affinity for oxygen donors.

Table - 2.3 Manganese (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.0	0.002	-0.69
3.1	0.03	0.61
4.2	0.03	0.64
5.2	0.05	0.88
5.8	0.06	0.94

Table - 2.4 Copper (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.1	0.09	1.18
3.1	0.09	1.18
4.0	0.13	1.33
4.6	0.09	1.18
5.1	0.20	1.51

Table - 2.5 Nickel (II)

Equilibrium pH	Capacity (mmol/g)	Log K_D
2.0	0.025	0.57
3.0	0.09	1.12
4.2	0.08	1.09
5.1	0.055	0.91
6.1	0.04	0.75
7.0	0.104	1.18

Table - 2.6 Vanadium (V)

Equilibrium pH	Capacity (mmol/g)	Log K_D
1.0	0.025	0.51
1.9	0.019	0.98
3.0	0.75	3.37
4.1	0.77	3.62
5.1	0.78	4.01
6.1	0.78	4.09

Table - 2.7 Beryllium (II)

Equilibrium pH	Capacity* (mmol/g)	Log K_D
1.1	0.52	1.12
2.2	0.57	1.17
3.0	0.66	1.24
3.9	0.61	1.20
5.0	0.83	1.36
5.8	1.02	1.48

*The large values of capacity in contrast to the low values of log K_D is due to:

(a) the atomic weight of Be is only 9

(b) low sensitivity of the method for quantitation, higher concentrations were employed.

Table - 2.8 Sorption capacities of metal ions on R-PGS at optimum pH*

Sl. No.	Metal Ion	Capacity (mmol/g)	M:L Ratio	Log K_D
1.	Mo(VI)	0.41	1:1.95	3.78
2.	Fe(III)	0.69	1:1.16	3.35
3.	V(V)	0.78	1:1.03	4.09
4.	Be(II)	1.02	1:0.78	1.48
5.	Ni(II)	0.10	1:8.0	1.18
6.	Cu(II)	0.20	1:4.0	1.51
7.	Mn(II)	0.06	1:13.3	0.94

*PGS loading of the resin 0.8 mmol/g.

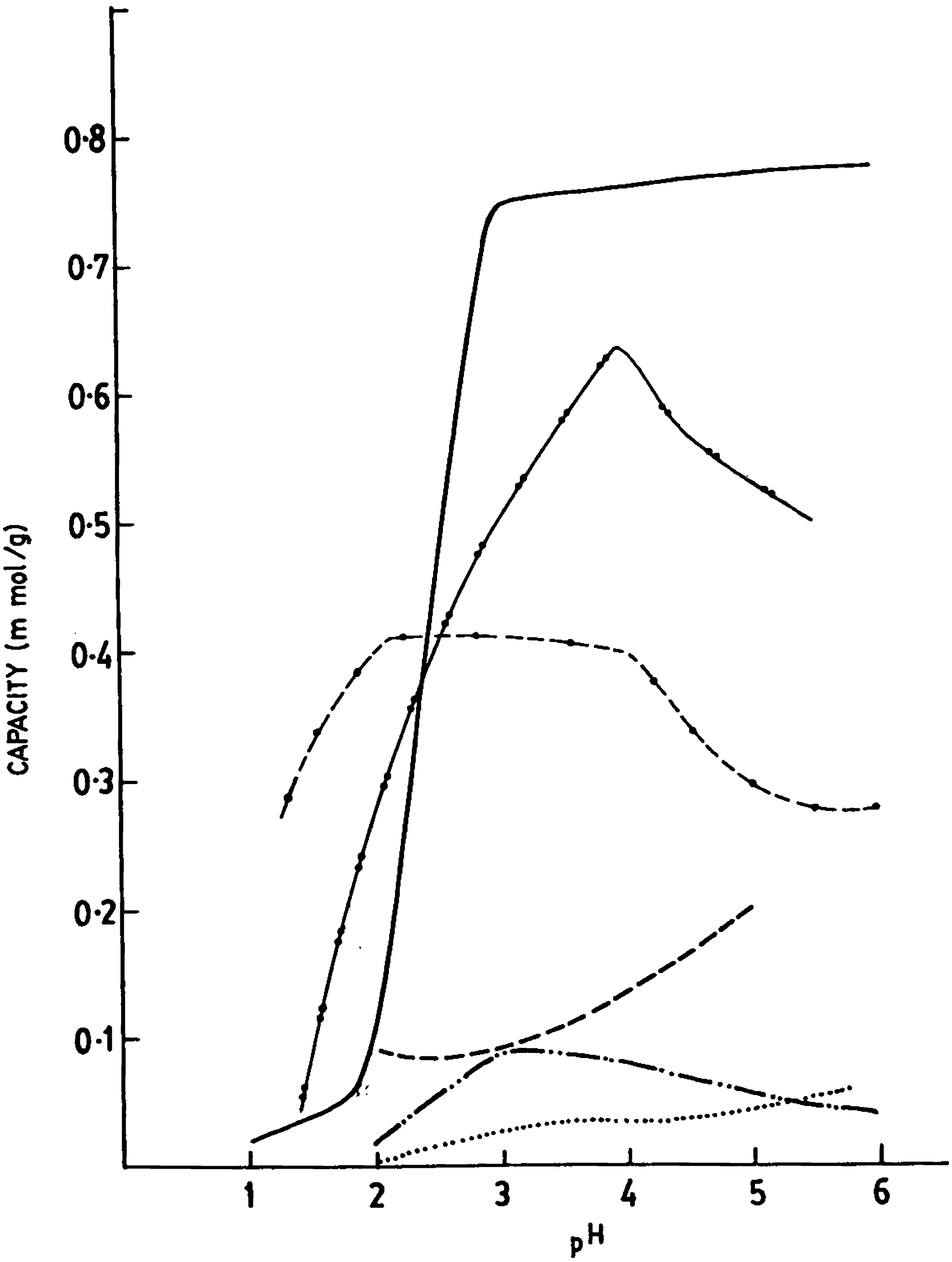

Fig. 2.4 Effect of pH on the sorption of metal ions on R-PGS.

Amount of resin 0.1g, particle size 100-200 mesh, reagent loading on the resin 0.8 mmol/g, volume of solution 10 ml, amount of metal ion 4.0 mg, shaking time 24 h. (——) V(V) (•—•) Fe(III), (•- - -•) Mo(VI), (- - -) Cu(II), (—··—) Ni(II), (·······) Mn(II).

(f) Sorption of beryllium (II)

The sorption capacity for Be(II) remains almost steady in the pH range studied. It has a maximum capacity of 1.02 mmol/g at about pH 6. Beryllium (II) has an affinity for oxygen donors, especially for vicinal dihydroxy compounds and the result is in accordance with that.

Kinetics of sorption

The dynamic sorption of metal ions become favourable for separation in a column only when the metal ion diffuses fast into the sorption medium and chelation occurs rapidly. In all the cases of the metal ions studied namely, Fe(III), Cu(II), Ni(II), Mn(II), Mo(VI), V(V) and Be(II), the sorption was fast and saturation of capacity reached within 2 h. In fact, the half-saturation time in all cases were less than 10 minutes (Table 2.14). This points to the fact that R-PGS is suitable for the ion chromatographic separation of the metal ions studied.

Table - 2.9-2.13 Kinetics of sorption of metal ions on R-PGS

Amount of resin 0.1g, particle size 100-200 mesh, volume of solution 10 ml, amount of metal ion 4.0 mg, temperature 28 ± 1°C.

Table - 2.9 Iron (III)

Time (min.)	% Saturation of Capacity*
5	50.6
15	70.0
30	86.6
60	94.5
80	98.5
100	99.2
120	100
240	100

*pH of solution 3.

Table - 2.10 Copper (II)

Time (min.)	% Saturation of Capacity*
5	47.0
15	60.0
30	71.0
60	80.0
80	84.5
100	87.6
120	90.2
240	100

*pH of solution 5.

Table - 2.11 Beryllium (II)

Time (min.)	% Saturation of Capacity*
5	53.5
15	64.3
30	85.7
60	96.0
120	98.5
240	100

*pH of solution 5.5

Table - 2.12 Molybdenum (VI)

Time (min.)	% Saturation of Capacity*
10	41.6
20	78.3
40	89.7
60	93.0
80	95.5
120	98.3
240	100

*pH of solution 3.

Table - 2.13 Vanadium (V)

Time (min.)	% Saturation of Capacity*
5	42.0
10	53.7
20	74.7
40	83.2
60	89.0
80	92.6
120	94.5
240	100

*pH of solution 3.

Table - 2.14 Time for 50% saturation

Metal ion	pH	$t_{1/2}$ saturation (min.)
Fe(III)	4.0	10
Mo(VI)	3.0	5
V(V)	6.0	< 10
Be(II)	5.7	< 5
Cu(II)	5.1	< 10

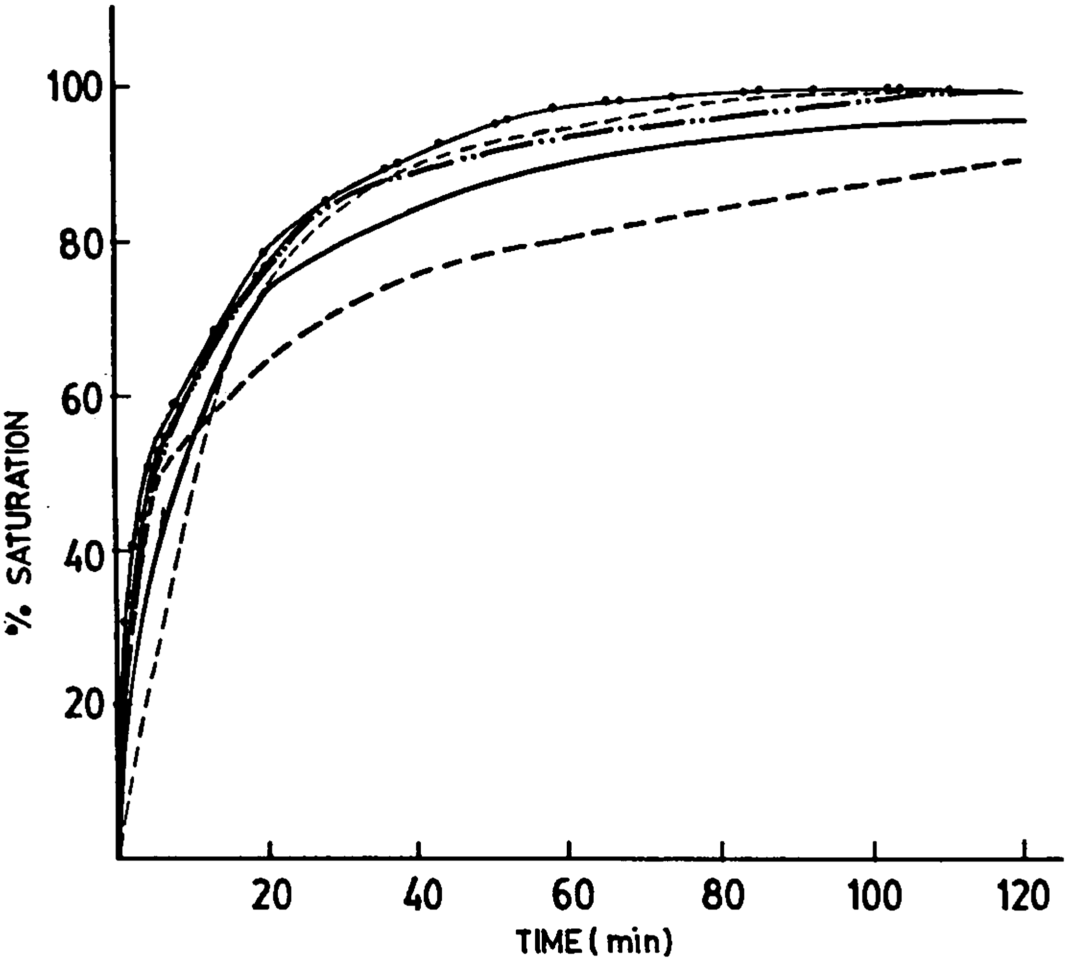

Fig. 2.5 Kinetics of sorption of metal ions on R-PGS.

Amount of resin 0.1g, particle size 100-200 mesh, reagent loading on the resin 0.8 mmol/g, volume of solution 10 ml, amount of metal ion 4.0 mg, temperature 28 + 1 °C.

(- - -) Be(II), (—··—) Fe(III), (•—•—)Mo(VI),
(——) V(V), (– – –) Cu(II).

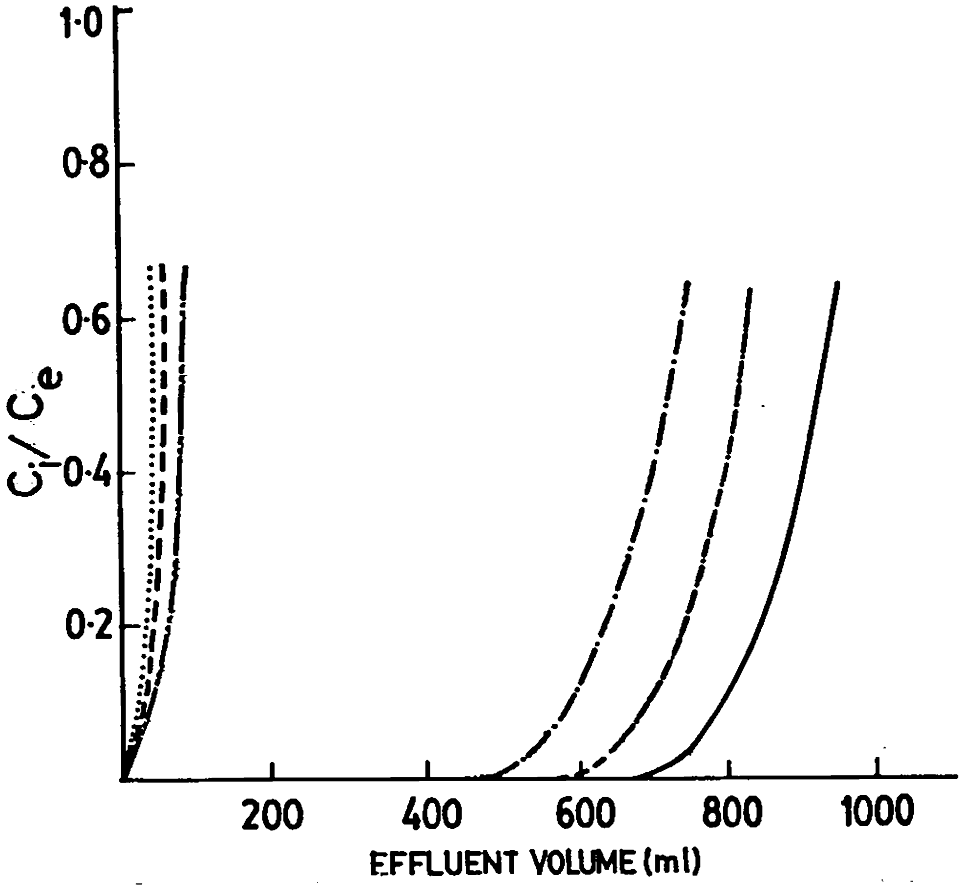

Fig. 2.6 Breakthrough curves of metal ions on R-PGS.

Column dimension 0.5 x 10 cm, particle size 100-200 mesh, concentration of metal ion solutions 100 μg/ml, pH of solutions V(V) and Mo(VI) 3, Fe(III), Ni(II), Cu(II) and Mn(II) 4.

(——) V(V), (–·–·–) Mo(VI), (—·—·—) Fe(III), (–·–·) Ni(II), (– – –) Cu(II), (·······) Mn(II). C_i = concentration of metal ions in the influent, C_e = concentration of metal ions in the effluent.

2.3.5 Breakthrough studies

Even though the kinetics of sorption and capacities give a clue to the possibility of separating metal ions on column, the dynamic breakthrough capacities will give direct hint on actual separations possible. Accordingly the breakthrough studies of Fe(III), Cu(II), Ni(II), Mn(II), V(V) and Mo(VI) were carried out in the appropriate pH range. Mn(II), Cu(II) and Ni(II) breakthrough the column almost simultaneously with very low retention whereas, Fe(III), Mo(VI) and V(V) breakthrough at various bed volumes. The inflections of the breakthrough curves are sufficiently sharp and well separated indicating that mixtures of the combinations of these metal ions can be easily separated on R-PGS column. Fig.2.6 shows the breakthrough curves for the various metal ions.

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CHAPTER - III

APPLICATIONS OF R-PGS

A. SEPARATION OF METAL IONS

Studies on the pH-dependent sorption of metal ions and breakthrough studies have indicated the possibility of separating a large number of binary mixtures of metal ions on R-PGS by ion-exchange chromatography. Accordingly the following metal ions were separated and quantitated. Molybdenum was preconcentrated from very dilute solutions using R-PGS and the recovery is reported.

3.1 EXPERIMENTAL

3.1.1 Copper (II)-Iron (III) separation

Solutions containing various amounts of Cu(II) and Fe(III) were prepared. The pH of the solution was adjusted to 3 using sodium citrate/citric acid buffer. The column packed with R-PGS (100-200 mesh) was preconditioned at pH 3 using the same buffer and 1 ml of the mixture was introduced into the column through a calibrated sample loop. Copper (II) was eluted using citrate buffer (pH 3) at a flow rate of 0.3 ml/min and fractions were collected in 10 ml lots. Concentration of Cu(II) in each fraction was determined spectrophotometrically after extraction into chloroform as diethyldithiocarbamate complex. Fe(III) was eluted using 2% ascorbic acid in 0.1N HCl using the same procedure and concentration was determined spectrophotometrically using 1,10-phenanthroline. The experiment was replicated.

3.1.2 Nickel (II)-Iron (III) separation

Solutions containing various proportions of Ni(II) and Fe(III) were prepared, the pH of which was adjusted to 4 using citrate buffer. The column of R-PGS was conditioned at pH 4 using the same buffer and 1 ml of the mixture was introduced into the column. Ni(II) was eluted using the citrate buffer (pH 4) at a flow rate of 0.5 ml/min , fractions were collected in 10 ml lots and concentration was determined spectrophotometrically using dimethylglyoxime. Fe(III) was eluted subsequently using 2% ascorbic acid in 0.1N HCl and concentration in each fraction was determined spectrophotometrically using 1,10-phenanthroline.

3.1.3 Manganese (II)-Iron (III) separation

Solutions containing various proportions of Mn(II) and Fe(III) were prepared, the pH of which was adjusted to 4 using citrate buffer. After conditioning the column at pH 4 using the same buffer, 1 ml of the mixture was introduced followed by elution of Mn(II) using the citrate buffer (pH 4). The eluate was collected in 10 ml fractions and concentration of Mn(II) was determined spectrophotometrically. Elution of Fe(III) was also done as before using 2% ascorbic acid in 0.1N HCl and the concentration was determined.

3.1.4 Iron (III)-Molybdenum (VI) separation

Mixtures of Fe(III) and Mo(VI) were prepared and their pH was adjusted to 3 using citrate buffer. The mixture (1 ml) was introduced into the column conditioned at pH 3 using the same buffer. Fe(III) was eluted using 2% ascorbic acid in 0.1N HCl, collected in 10 ml lots, and estimated. Mo (VI) was eluted subsequently with 1M $HClO_4$ and concentration was measured using ICP-AES.

3.1.5 Manganese (II)-Vanadium (V) separation

Solutions containing various amounts of Mn(II) and V(V) were prepared, the pH of which was adjusted to 4 using acetate buffer and 1 ml of the mixture was introduced into the column conditioned at pH 4 using the same buffer. Mn(II) was eluted using the same buffer and collected in 10 ml fractions. The concentrations of Mn(II) in the fractions were determined spectrophotometrically. V(V) was eluted subsequently with 2% ascorbic acid in 0.1N HCl and the concentration of V(V), collected in 10 ml lots was determined using ICP-AES.

3.1.6 Vanadium (V)-Molybdenum (VI) separation

Mixtures of V(V) and Mo(VI) were prepared in 0.001N HCl and 1 ml of the mixture was introduced into the column conditioned at pH 3 using dilute HCl. V(V) was eluted with 2% ascorbic acid in 0.1N HCl. Mo(VI) was eluted subsequently with 1M $HClO_4$. Eluate was collected in 10 ml lots and V(V) and Mo(VI) were quantitated using ICP-AES.

3.1.7 Separation of Manganese (II)-Copper (II)-Iron (III)

Solutionscontaining various amounts of Mn(II), Cu(II) and Fe(III) were prepared, the pH of which was adjusted to 4 using citrate buffer and 1 ml of the mixture was introduced into the column conditioned at pH 4. Mn(II) was eluted using the citrate buffer (pH 4) followed by elution of Cu(II) and Fe(III) using citrate buffer (pH 2.5) and 2% ascorbic acid in 0.1N HCl respectively. The fractions were collected in 10 ml lots and concentrations of metal ions measured spectrophotometrically.

3.2 RESULTS AND DISCUSSION

Mixtures of metal ions commonly encountered in analysis were separated using the column technique and quantitated. Separation of a number of binary mixtures were found to be possible. Only a few typical separations have been described here. These mixtures include Cu(II)-Fe(III), Ni(II)-Fe(III), Mn(II)-Fe(III), Fe(III)-Mo(VI), Mn(II)-V(V) and V(V)-Mo(VI). Separation of a ternary mixture containing Mn(II), Cu(II) and Fe(III) was also studied.

In all these cases synthetic mixtures were prepared by appropriate combinations. Different amounts were also tried to check the validity of separation at different ranges of concentration. Analyses were replicated and standard deviations were calculated. Metal ion to loaded ligand ratio was kept below 1:50. Higher ratios were not studied in detail since the immobilised reagent is slowly dislodged at higher concentrations of the electrolyte.

3.2.1 Copper (II)-Iron (III)

From the capacity-pH curves (Fig.2.4) and the breakthrough curves (Fig.2.6), it is clear that Cu(II) and Fe(III) can be separated in acid medium. The medium used in this study was 0.1M citrate buffer of pH 3. Citrate was used to suppress hydrolysis of Fe(III) and to keep it in solution. Mixtures of the following compositions were tried. (1) Cu(II) 100µg- Fe(III) 100 µg, (2) Cu(II) 200µg- Fe(III) 100 µg, (3) Cu(II) 100µg- Fe(III) 200 µg. Cu(II) was eluted first using the citrate buffer (pH 2.5). The eluted Cu(II) is quantitated by extraction into chloroform as diethyldithiocarbamate complex after rendering the medium to pH 8.5 by addition of ammonia. Fe(III) retained on the column was eluted using ascorbic acid in 0.1N HCl. In this process Fe(III) is reduced to Fe(II) which can be quantitated directly using 1,10 phenanthroline. The elution curve for the chromatographic separation is given in Fig.3.1. The separation is clear and the two peaks are well separated thus facilitating quantitation. Relative standard deviations of the order of about 0.37 to 0.80% are comparable with the values obtained by other standard analytical methods.

3.2.2 Nickel (II)-Iron (III)

It is evident from the breakthrough curve (Fig.2.6) that Ni(II) and Fe(III) can be separated from their mixtures in acid medium. Citrate buffer of pH 4 was used as the medium. Mixtures of the following compositions were studied - (1) Ni(II) 100 μg-Fe(III) 100 μg, (2) Ni(II) 200 μg - Fe(III) 100 μg, (3) Ni(II) 100 μg - Fe(III) 200 μg. Ni(II) was eluted first using the citrate buffer of pH 4 and estimated using dimethyl glyoxime after oxidation

Table - 3.1 <u>Copper(II)-Iron(III) Separation</u>

Amount loaded (μg)		Amount recovered (μg)	Amount recovered (μg) (Mean value)	Error of mean value (%)	Relative standard deviation (%)
1. Cu(II)	100.0	97.4			
		98.3			
		98.0	98.2	-1.8	0.84
		97.9			
		99.6			
Cu(III)	100.0	103.5			
		101.8			
		102.7	102.7	2.7	0.86
		103.7			
		101.9			
2. Cu(II)	200.0		197.2	-2.8	0.37
Fe(III)	100.0		101.7	1.7	0.84
3. Cu(II)	100.0		99.0	-1.0	0.76
Fe(III)	200.0		204.3	4.3	0.44

Column dimension 0.6 x 15 cm; flow rate 0.3 ml/min; volume of fraction 10 ml; eluent for Cu(II)-citrate buffer (pH 2.5); eluent for Fe(III) - 2% ascorbic acid in 0.1N HCl, volume of eluate 50 ml; number of determination 5.

Table - 3.2 Nickel(II) - Iron(III) Separation

	Amount loaded (μg)		Amount recovered (μg) (Mean value)	Error of mean value (%)	Relative standard deviation (%)
1.	Ni(II)	100.0	99.7	-0.3	0.38
	Fe(III)	100.0	101.4	1.4	0.75
2.	Ni(II)	200.0	199.5	-0.5	0.27
	Fe(III)	100.0	101.7	1.7	0.72
3.	Ni(II)	100.0	99.4	-0.6	0.32
	Fe(III)	200.0	200.8	0.8	0.40

Column dimension 0.6 x 15 cm; flow rate 0.3 ml/min. volume of fraction 10 ml, eluent for Ni(II)-citrate buffer (pH 4), eluent for Fe(III) - 2% ascorbic acid in 0.1N HCl, volume of eluate 50 ml, number of determination 5.

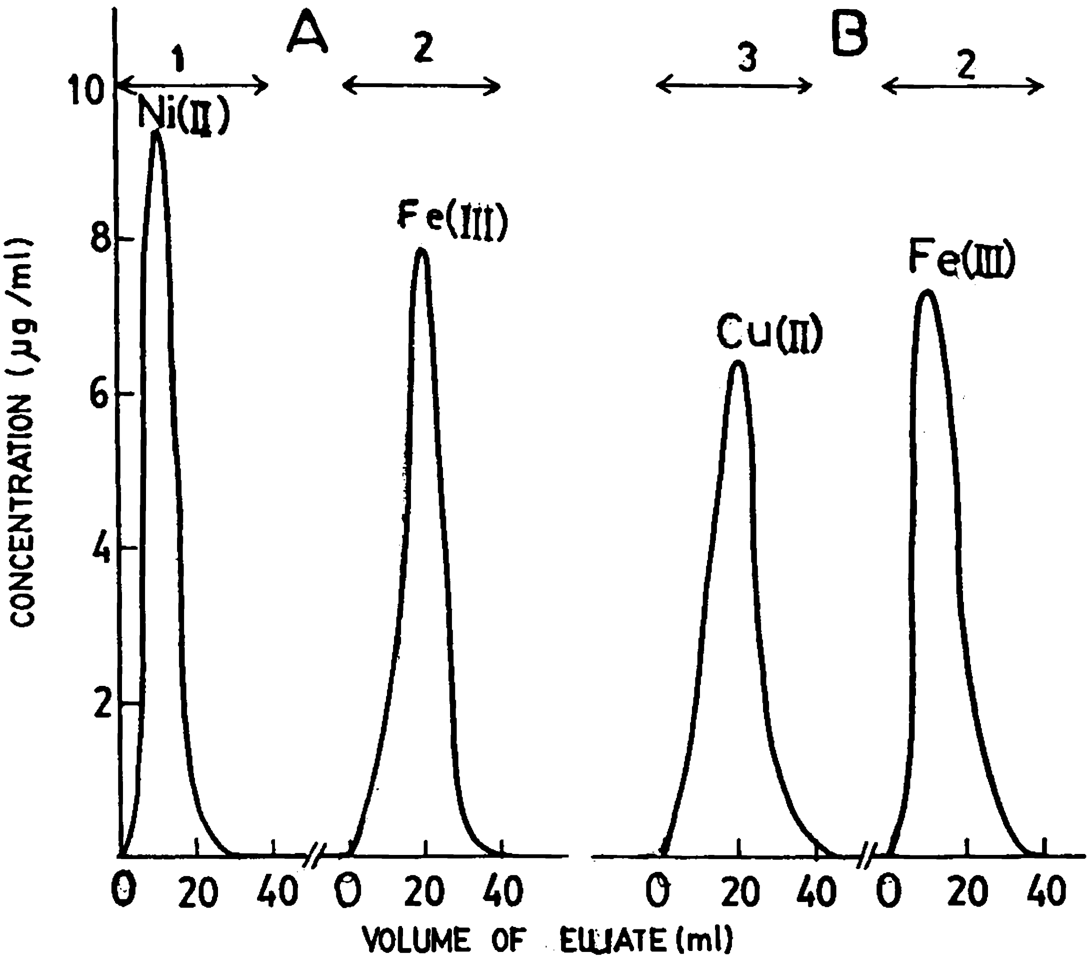


Fig. 3.1 Elution curves for

A. Ni(II)-Fe(III)
B. Cu(II)-Fe(III)
1, Citrate buffer (pH 3), 2, 2% ascorbic acid in 0.1N HCl, 3, citrate buffer (pH 2.5)

with bromine water. Fe(III) was eluted subsequently with ascorbic acid in 0.1N HCl. The elution curve for the chromatographic separation (Fig. 3.1) gives two well separated peaks. Relative standard deviations for the recovery are given in Table 3.2.

3.2.3 Manganese (II)-Iron (III)

As in the case of Ni(II)-Fe(III)separation, citrate buffer of pH 4 was used as the medium and Mn(II) was eluted with the same buffer. The quantitation of Mn(II) was done after oxidation with permanganate which required a large amount of periodate. Elution and quantitation of Fe(III) was done as in the previous two cases and the two peaks in the elution curve are well separated indicating the feasibility of separation.

3.2.4. Iron (III)-Molybdenum (VI)

The capacities of Fe(III) and Mo(VI) on R.PGS are comparable. The medium used in this study was citrate buffer of pH 3. Both Fe(III) and Mo(VI) are sorbed strongly on the column. Fe(III) was first eluted using ascorbic acid in 0.1N HCl

Table - 3.3 <u>Manganese(II) - Iron(III) Separation</u>

	Amount loaded (μg)		Amount recovered (μg) (Mean value)	Error of mean value (%)	Relative standard deviation (%)
1.	Mn(II)	100	99.3	0.7	0.55
	Fe(III)	100	103.5	3.5	0.40
2.	Mn(II)	200	201.2	1.2	0.22
	Fe(III)	100	102.7	2.7	0.37
3.	Mn(II)	100	98.9	-1.1	0.52
	Fe(III)	200	203.0	3.0	0.21

Column dimension 0.6 x 15 cm, flow rate 0.3 ml/min., volume of fraction 10 ml, eluent for Mn(II)-citrate buffer (pH 4), eluent for Fe(III) - 2% ascorbic acid in 0.1N HCl, volume of eluate 50 ml, number of determinations 5.

Table - 3.4 <u>Iron(III) - Molybdenum(VI) Separation</u>

	Amount loaded (μg)		Amount recovered (μg) (Mean value)	Error of mean value (%)	Relative standard deviation (%)
1.	Fe(III)	100.0	100.7	0.7	0.69
	Mo(VI)	100.0	98.2	-1.8	0.77
2.	Fe(III)	200.	201.5	1.5	0.44
	Mo(VI)	100.0	97.7	-2.3	0.82
3.	Fe(III)	100.0	102.9	2.9	0.79
	Mo(VI)	200.0	198.1	-1.9	0.26

Column dimension 0.6 x 15 cm; flow rate 0.3 ml/min. volume of fraction 10 ml, eluent for Fe(III) - 2% ascorbic acid in 0.1N HCl, eluent for Mo(VI)-1M $HClO_4$, volume of eluate 50 ml, number of determinations 5.

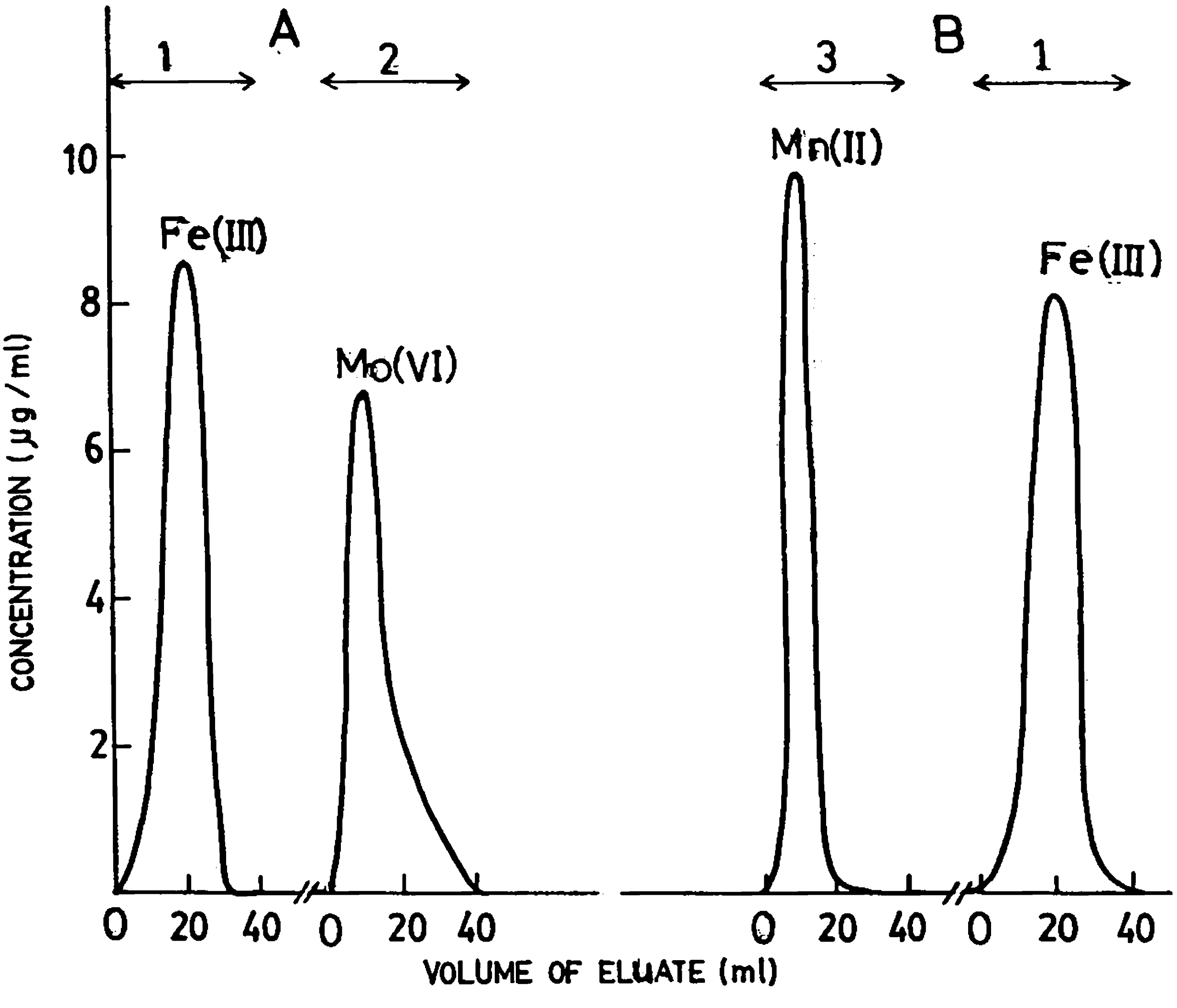


Fig. 3.2 Elution curves for

A. Fe(III)-Mo(VI)
B. Mn(II)-Fe(III)
1, 2% asorbic acid in 0.1N HCl,
2, 1M $HClO_4$, 3, citrate buffer (pH 4)

as before. Since Mo(VI) is strongly retained, it was eluted using 1M $HClO_4$. As Mo(VI) is eluted, the reagent is also dislodged from the resin and comes in the eluate. Here Mo(VI) cannot be determined spectrophotometrically since the leached out reagent interferes with the measurement. Hence AAS or ICP emission spectroscopy is recommended for its quantitation.

3.2.5 Manganese (II)-Vanadium (V)

It is clear from the capacity-pH curves and breakthrough curves that Fe(III) and V(V) also can be separated from their mixtures with Mn(II), Cu(II), Ni(II) or Mo(VI). As a typical case Mn(II)/V(V) mixtures in the following combinations were studied. (1) Mn(II) 100 μg- V(V) 100 μg, (2) Mn(II) 200 μg- V(V) 100 μg and (3) Mn(II)100 μg-V(V) 200 μg. Very dilute hydrochloric acid was used as the medium. Mn(II) was eluted first using very dilute HCl and quantitated. V(V) was subsequently eluted with ascorbic acid in 0.1N HCl. The spectrophotometric determination of vanadium as phosphotungstate is not possible due to the presence of ascorbic acid. Hence either AAS or ICP emission spectroscopy is recommended.

Table - 3.5 Manganese(II) - Vanadium(V) Separation

	Amount loaded (μg)		Amount recovered (μg) (Mean value)	Error of mean value (%)	Relative standard deviation (%)
1.	Mn(II)	100.0	99.3	-0.7	0.25
	V(V)	100.0	98.9	-1.1	0.43
2.	Mn(II)	200.0	198.0	-2.0	0.19
	V(V)	100.0	99.2	-0.8	0.39
3.	Mn(II)	100.0	98.8	-1.2	0.52
	V(V)	200.0	197.5	-2.5	0.16

Column dimension 0.6 x 15 cm, flow rate 0.5 ml/min., volume of fraction 10 ml, eluent for Mn(II)-very dil. HCl (pH 4); eluent for V(V)-2% ascorbic acid in 0.1N HCl, volume of eluate 50 ml, number of determinations 5.

3.2.6 Vanadium (V)-Molybdenum (VI)

Separation of V(V) and Mo(VI) from their mixture is also possible because when ascorbic acid in 0.1N HCl is used as the eluent, vanadium will come out and molybdenum will remain in the column. Elution of Mo(VI) is possible using 1M $HClO_4$(Fig.3.3).As mentioned earlier AAS or ICP emission spectroscopy can be used for their quantitation.

3.2.7 Manganese (II)-Copper (II)-Iron (III)

Separation of Mn(II), Cu(II) and Fe(III) from their ternary mixture is also found to be possible on R-PGS column. Citrate buffer of pH 4 was used as the medium. The three metal ions were taken in different ratios and the results of the separations achieved are given in Table 3.7. Mn(II) and Cu(II) were completely eluted with the citrate buffers of pH 4 and pH 2.5 respectively. Finally Fe(III) was eluted using ascorbic acid in 0.1N HCl. The elution curve for the separation is given in Fig. 3.4 . The peaks are well separated and standard deviation is in the order of about 0.21 to 0.84 (Table 3.7)

Table - 3.6 Vanadium(V) - Molybdenum(VI) Separation

	Amount loaded (μg)		Amount recovered (μg)	Error of mean value (%)	Relative standard deviation (%)
1.	V(V)	100.0	99.5	-0.5	0.22
	Mo(VI)	100.0	98.7	-1.3	0.37
2.	V(V)	200.0	198.4	-1.6	0.09
	Mo(VI)	100.0	98.4	-1.6	0.37
3.	V(V)	100.0	99.3	-0.7	0.28
	Mo(VI)	200.0	198.0	-2.0	0.17

Column dimension 0.6 x 15 cm, flow rate 0.5 ml/min., volume of fraction 10 ml, eluent for V(V) - 2% ascorbic acid in 0.1N HCl, eluent for Mo(VI) - 1M $HClO_4$, volume of eluate 50 ml, number of determinations 5.

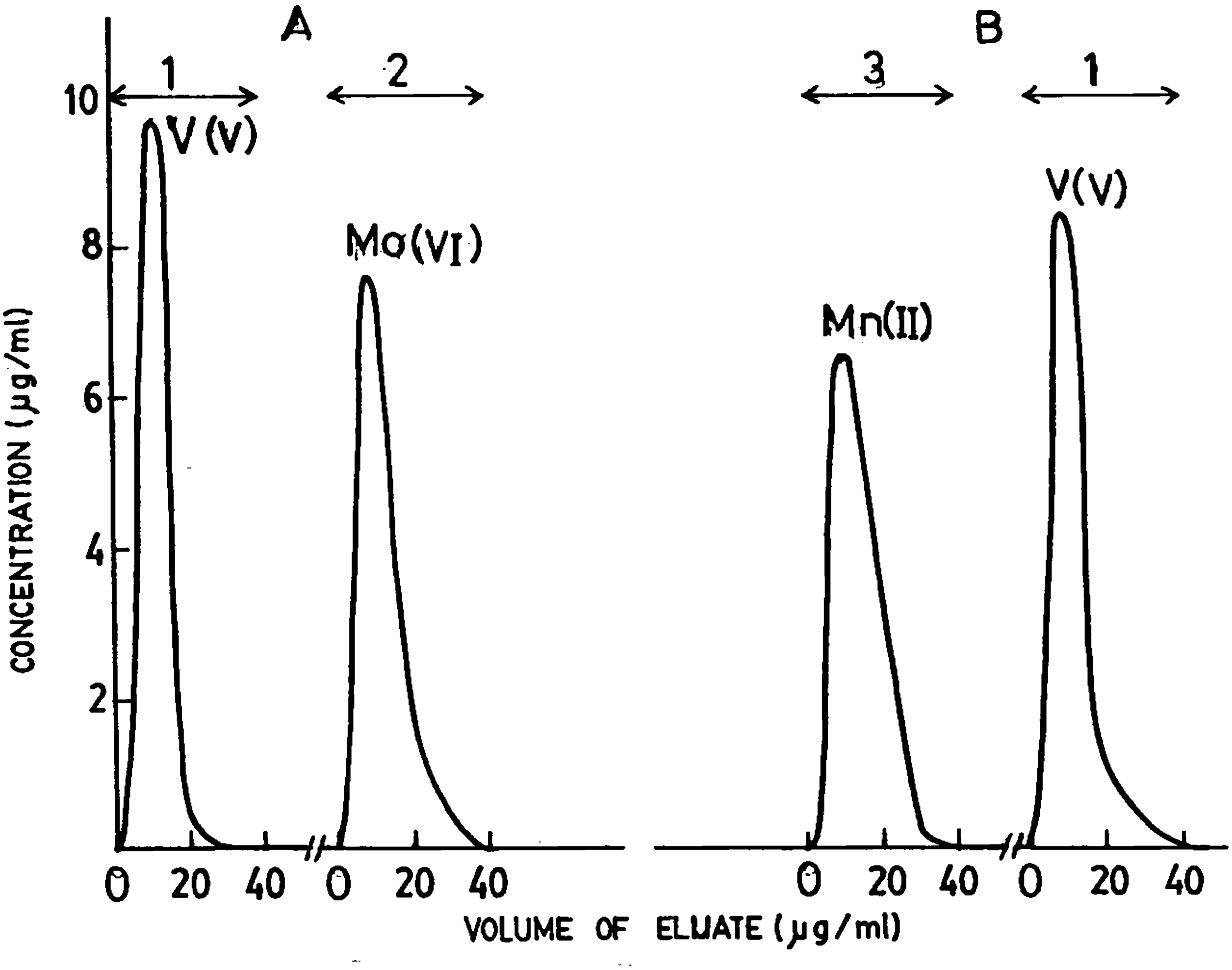


Fig. 3.3 Elution curves for

A. V(V)-Mo(VI)
B. Mn(II)-V(V)
1, 2% ascorbic acid in 0.1N HCl,
2, 1M $HClO_4$, 3, citrate buffer (pH 4).

Table - 3.7 Manganese(II) - Copper(II) - Iron(III) Separation

Amount loaded (µg)		Amount recovered(µg) (Mean value)	Error of mean value (%)	Relative standard deviation (%)
Mn(II)	100.0	99.7	-0.3	0.52
1.Cu(II)	100.0	98.5	-1.5	0.84
Fe(III)	100.0	102.0	2.0	0.60
Mn(II)	200.0	200.6	0.6	0.30
2.Cu(II)	200.0	198.7	-1.3	0.39
Fe(III)	100.0	101.5	1.5	0.47
Mn(II)	100.0	100.2	0.2	0.34
Cu(II)	100.0	99.2	-0.8	0.69
Fe(III)	200.0	201.6	1.6	0.21

Column dimension 0.5 x 15 cm; flow rate 0.5 ml/min., volume of fraction 10 ml, eluent for Mn(II)-citrate buffer (pH 4), eluent for Cu(II)-citrate buffer (pH 2.5), eluent for Fe(III) - 2% ascorbic acid in 0.1N HCl, volume of eluate 50 ml, number of determinations 5.

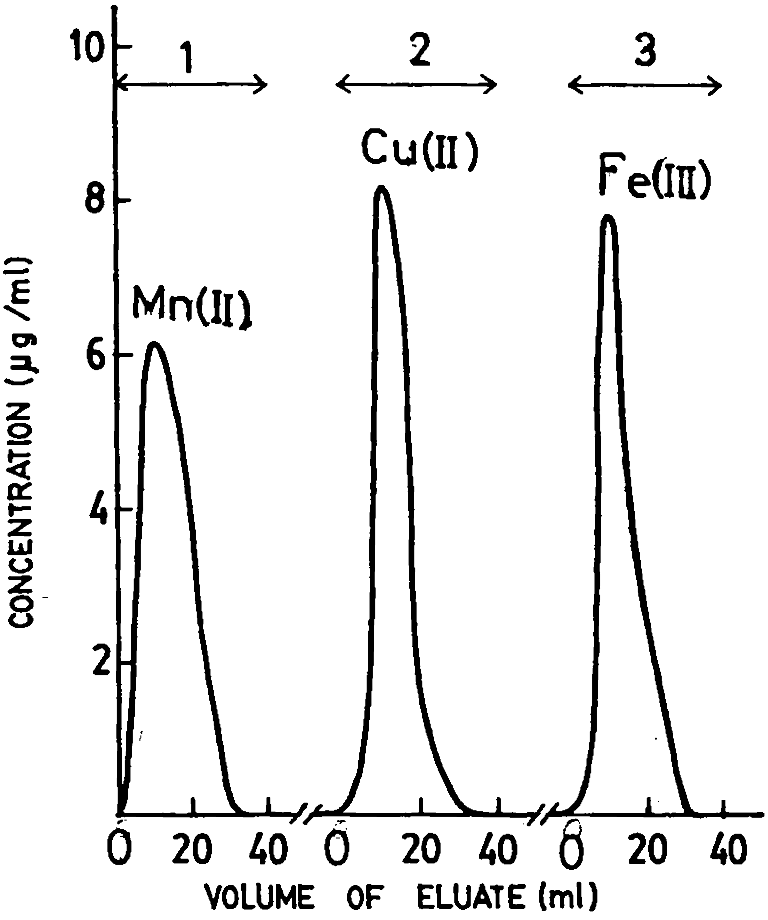


Fig. 3.4 Elution curves for Mn(II)-Cu(II)-Fe(III)

1, citrate buffer (pH 4), 2, citrate buffer (pH 2.5), 3, 2% ascorbic acid in 0.1N HCl.

B. PRE-CONCENTRATION OF MOLYBDENUM FOR ATOMIC ABSORPTION OR EMISSION SPECTROPHOTOMETRY

3.3 INTRODUCTION

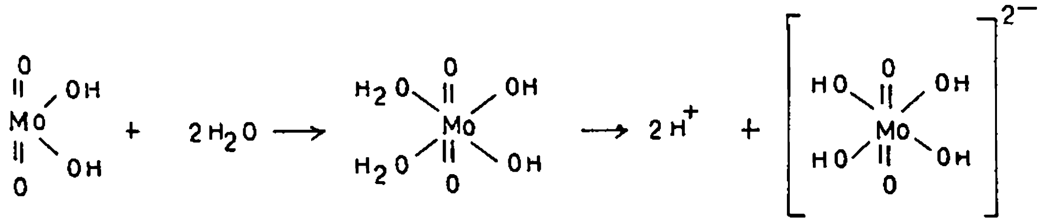
The use of molybdenum has increased rapidly in various fields. The major uses are in ferrous metallurgy, in cemented carbides, in refractory materials and in catalysts. Molybdenum enters the aquatic environment from process effluents related to these industries. Its occurrence in river-water from mining wastes is more widespread. The toxicity of molybdenum is mainly due to its competition with copper for binding sites in enzymes.

The analytical chemistry of molybdenum has also expanded parallel to its widespread use. Among the various methods used for the quantitation of molybdenum, those based on chelate formation and absorption spectrophotometry are more popular due to simplicity. However, the limits of sensitivity of this method (> 0.5 mg/l) are not favourable for the quantitation of low levels of molybdenum that occur in natural sources (less than 10 μg/l). The other method of choice is AAS in nitrous oxide flame. This method is also limited by its low sensitivity thus requiring preconcentration. Emission spectroscopy and neutron activation analysis also demand preconcentration of molybdenum. Use of modern techniques such as graphite furnace AAS, anodic-stripping voltametry, electron paramagnetic resonance spectrometry and oscillography also introduces problems in achieving the desired accuracy of analysis due to prevalence of matrix interference.

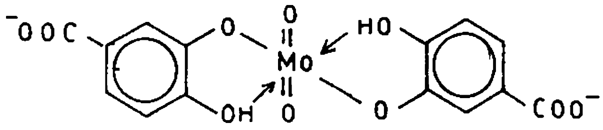
The preconcentration methods used for the recovery of molybdenum from low levelaquatic sources include coprecipitation,[25,26] cocrystallisation,[27] extraction,[28,29] ion-exchange[30-32] and adsorption on activated charcoal.[33] The determination is completed using uv-vis absorption spectrophotometry or by AAS.

The systems developed so far for the preconcentration of molybdenum for determination by uv-vis spectrophotometry or AAS are mainly based on solvent extraction. This procedure enhances the sensitivity and eliminates interferences from cations. Of these 8-quinolinol/isobutyl-methyl ketone (IBMK),[34] 8-quinolinol/n-amylmethyl ketone[35], Ammonium tetramethylene dithiocarbamate/IBMK[36], dithiol/IBMK[37] and thiocyanate/IBMK[38] are simple and applicable for the determination of molybdenum in water. Ternero and Gracia have developed a method in which molybdenum is preconcentrated on Chelex-100 resin.[38] The preconcentrated molybdenum is eluted with ammonia and extracted with 1,4-dihydroxyphthalimide dithiosemicarbazone in dimethyl formamide/iso-amylalcohol mixture and then determined by AAS. Addition of ascorbic acid prior to extraction was found to eliminate interference from several cations. A sensitivity of 0.3μg/l has been achieved.

In aqueous solution molybdenum commonly occurs in hexavalent state. It can be reduced to the pentavalent state by suitable reductant in acid medium. Both Mo(VI) and Mo(V) show strong tendency to coordinate with oxygen donors leading to the formation of hydroxomolybdenyl complexes.[39] Molybdenum trioxide monohydrate when dissolved in water is acidic. The process has been presented in scheme 3.1.



The final product in this equation is the tetrahydroxo complex of the molybdenyl (VI) cation which is an appropriate formulation of "monomolybdate" ion.[39] The chelate formation of molybdate with phenolic chelating agents can be represented as:



Due to the oxygen co-ordinating tendency of molybdenum, a large number of polyphenols have been studied for their reaction with Mo(V) and Mo(VI). These compounds include hydroquinone[40], pyrocatechol[41-48], pyrogallol[44,47,48], gallic acid,[44,46-49] pyrocatechuic acid[44,47,48], tiron[47,50,51], 3,4,5-trihydroxybenzene sulfonic acid,[52] 4,5,6-trihydroxy-m-benzene disulfonic acid,[47] napththalenediols,[47,48] and hydroxynapththalene sulfonic acids,[47,48]. Of these ortho-dihydroxy compounds form stable chelates. Additional substitution of the ring can enhance stability of the chelates.[53] The chelate formation of molybdenum with polyphenols has been reviwed by Halmekoski.[54]

The studies presented herein shows that R-PGS is highly selective for Mo(VI). Hence the preconcentration of molybdenum from water was studied using R-PGS.

3.4. EXPERIMENTAL

Standard Mo(VI) solution was prepared using ammonium heptamolybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ and diluted to get a concentration of 1 μg/ml of Mo(VI) after adjusting the pH to 3 using dil. HCl. The column (0.5 x 10 cm) was packed with R-PGS resin (100-200 mesh) and pre-conditioned with 0.001N HCl. Mo(VI) solution (1 μg/ml) was allowed to run through the column at a flow rate of 1.5 ml/min. After running 500 ml, Mo(VI) sorbed on the resin was eluted using 1M $HClO_4$. The eluate was collected in 20 ml fractions and concentration of Mo(VI) in each fraction was determined using ICP-AES, at a wavelength of 202.034 nm, with an integration time of 0.2 seconds.

3.5 RESULTS AND DISCUSSION

The chelation properties of Mo(VI) shows that the K_{ML} value is fairly high for polyphenols. The observed K_{MR} value is also in accordance with that. The problem of analytical preconcentration of Mo(VI) by chelating resin has been worked out by combined ion-exchange-solvent extraction.[38]

Here the method described is a simple preconcentration on the resin followed by elution into a small volume of 1M $HClO_4$. The pH can go down to 2 as seen in the capacity - pH curves (Fig.2.4) Mo(VI) to immobilized reagent ratio upto 1:3 can be handled in the column (Fig.2.6). The recovery after elution decreases with increasing quantity of Mo(VI) loaded and for that reason, for rapid preconcentration and elution, amounts less than 100 μg are ideally suited. The method gives the recovery ratios comparable with other methods (Table 3.8) which is reasonably good for a multi-step analytical process involving preconcentration.

Table - 3.8 Enrichment of molybdenum (VI) on R-PGS*

Amount of Mo(VI) Added	Amount of Mo(VI) Recovered (μg)**	Recovery (%)
100	96.5	96.50
250	238.2	95.28
500	466.8	93.36

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*Each spike was added to 500 ml of water.

**Each result represents the mean of three values

Column dimension 0.5 x 10 cm, loading of reagent on the resin 0.8 mmol/g, eluent 1M $HClO_4$, flow rate 1.5 ml/min., volume of fraction 20 ml.

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CHAPTER - IV

CONCLUSIONS

CONCLUSIONS

During the last fifty years ion-exchange method has evolved as a major technique in analytical chemistry as well as in process technology. This is mainly due to the operational convenience and versatility of the technique in achieving preconcentration and separation of anions and cations. The quest for achieving better selectivity for ion-exchange resins led to the development of resins bearing chelating functional groups. The ultimate aim was to synthesize resins specific for each kind of metal ion. Inspite of the extensive investigations, chelating exchangers are still insufficiently used in the practice of analytical chemistry due to the complexity of their synthesis and high cost.

Our study outlined in this thesis, was concentrated on preparing chelating resins with improved selectivity. Starting from polystyrene, a new chelating resin, ST-3 was synthesized. It is a sulfur and nitrogen containing resin prepared by a simple three-step procedure. The thiol group is protected from oxidation by a prosthetic group. The resin is stable in 2M HCl, 0.1M NaOH and 0.1M HNO_3. Sorption studies of metal ions on the resin revealed its high selectivity towards mercury (II) (K_D = 1500) and silver (I) (K_D = 4600). The resin is very effective in the enrichment and recovery of mercury at ppb levels prior to determination. Results of mercury stripping studies from chlor-alkali effluents on the analytical scale are given. The resin shows promising properties in this application and reduces mercury in the effluent to an environmentally acceptable level of $< 5\ \mu g/l$. Investigation on the scale up aspects of the resin is being carried out. The resin is capable of competing with chloride ions present in high concentration in the brine effluent and the sorbed mercury can be eluted using thiourea in dil. HCl, thus effecting the recovery of the resin.

The commercially available sulfur-bearing resins are also capable of removing mercury from aqueous effluents after pretreatment to the environmentally acceptable level. Of these resins IMAC

TMR and Duolite ES 465 (Diamond Shamrock) are stable in acid medium, but are sensitive to oxidants. MISSO ALM-525 (Nippon Soda) and Sumichelate Q-IOR (Sumitomo) are also capable of stripping mercury at trace levels. These being dithiocarbamates deteriorate in acid medium and are sensitive to oxidation even by mild oxidizing agents. ST-3 resin has similar sorption characteristics to IMAC TMR and Duolite ES 465 resins. It has a definite advantage that it is prepared by simple procedure and has a higher stability due to the thiol group being protected from oxidation by (mild oxidants) by an additional functional group.

Another chelating resin was prepared by electrostatically anchoring pyrogallol disulfonic acid to the commercially available strong base anion-exchange resin, Seralite SRA 400. The reagent loaded resin, R-PGS, is stable towards 0.1M HCl and shows high degree of selectivity towards Fe(III), Mo(VI) and V(V). Exchange behaviour of several metal ions were studied and a comparison of K_D values for various metal ions showed that R-PGS is an excellent medium for the preconcentration and separation of a number of metal ions. Thus separations of Fe(III)-Mn(II), Fe(III)-Cu(II), Fe(III)-Ni(II), Fe(III)-Mo(VI), V(V)-Mn(II), V(V)-Mo(VI) and Mn(II)-Cu(II)-Fe(III) were carried out successfully and recovery and standard deviations are reported. Elution of Cu(II), Ni(II) and Mn(II) were possible with very dil. HCl. Fe(II) and V(V) could be eluted with ascorbic acid in dil. HCl. Elution of Mo(VI) from the column was achieved using 1M $HClO_4$. The reagent loaded resin can be prepared by running the reagent solution through the anion exchange column. This is a definite practical advantage of R-PGS over chelating resins with covalently-bound functional group. Preconcentration and recovery of Mo(VI) from lean sources are also reported.

It is hoped that the studies presented in the two sections of this thesis add to the present knowledge of preconcentration and separation of metal ions using chelating polymers. In that respect, this is a modest contribution to the rapidly expanding field of separation science.

Part of the outcome of these studies has been presented/published in the following forms:

1. V.N. Sivasankara Pillai and Lucy Joseph "Ion-Exchange Characteristics of a Novel Polystyrene thiol Resin (ST-3) and its Application to the Recovery of Mercury (II)", Third National Symposium of Indian Society of Analytical Scientists, January 9-11, 1986, Waltair Abstracts P 5.

2. V.N. Sivasankara Pillai and Lucy Joseph "Removal of Mercury from Chlor-alkali Plant Effluent Using a Chelating Resin" Fourth National Symposium of the Indian Society of Analytical Scientists, January 23-25, 1987, Burdwan Abstracts P 13.

3. V.N. Sivasankara Pillai and Lucy Joseph "Sorption Studies of Heavy Metal Ions on a Novel Chelating Resin and its Application in the Stripping of Mercury (II)", Environmental Pollution, U.K. (in Press).

4. Lucy Joseph & V.N. Sivasankara Pillai "Separation of Metal ions on Pyrogallolsulfonic acid-loaded Anion Exchange Resin", Proceedings of the 24th Annual Convention of Chemists, December, 1987, Kolhapur, Abstracts D 25.

5. Lucy Joseph & V.N. Sivasankara Pillai, "Preconcentration of Molybdenum (VI) for Determination by ICP-AES" (under communication.

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REFERENCES PART II

1. Skogseid, A. Norv. Pat. 1947, 72583.
   (C.A. 1948, 42, 1682_a.)

2. Brajter, K. Chem. Anal. 1973, 18(1), 125.

3. Brajter, K. J. Chrom. 1974, 102, 385.

4. Brajter, K.; Zlotorzynska, E.D. Talanta 1986, 33(2), 149.

5. Kraus, K.A.; Moore, G.E. J. Am. Chem. Soc. 1949, 71, 3263.

6. Kraus, K.A.; Moore, G.E. J. Am. Chem. Soc. 1951, 73, 9.

7. Kemula, W.; Brajter, K. Chem. Anal.(Warsaw) 1968, 13(2), 305.
   (C.A. 1968, 69, 83038.)

8. Lee, K.S.; Lee, D.W. Anal. Chem. 1978, 50(2), 255.

9. Chikuma, M.; Nakayama, M.; Itoh, T.; Tanaka, T. Talanta 1980, 27, 807.

10. Nakayama, M.; Chikuma, M.; Tanaka, H.; Tanaka, T. Talanta 1982, 29, 503.

11. Nakayama, M.; Chikuma, M.; Tanaka, H.; Tanaka, T. Talanta 1983, 30(7), 455.

12. Brajter, K.; Zlotorzynska, E.D. Talanta 1980, 27, 19.

13. Brajter, K.; Sleszynska, E.O. Talanta 1983, 30(5), 355.

14. Kemula, W.; Brajter, K. Chem. Anal. 1968, 13(2), 305.

15. Going, J.E.; Wesenberg, G.; Andrejat, G. Anal. Chem. Acta 1976, 81, 349.

16. Chikuma, M.; Nakayama, M.; Tanaka, T.; Tanaka, H. Talanta 1979, 26, 911.

17. Pollak, J.; Fulneg, G. Monatch. 1927, 47, 537. (C.A. 1927, 21, 2676.)

18. Vogel, A.I. "A Textbook of Quantitative Inorganic Analysis", Longman Group Ltd., England, 4th edn., 1985, P. 160.

19. Idem, ibid., P.753.

20. Idem, ibid., P.742.

21. Idem, ibid., P.747.

22. Idem, ibid., P.746.

23. Idem, ibid., P.155.

24. Dyer, J.R. "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall of India Private Limited, New Delhi, 1984, P.34.

25. Chan, K.M.; Riley, K.P. Anal. Chim. Acta 1966, 36, 220.

26. Kim, Y.S.; Zeitlin, H. Anal. Chim. Acta 1970, 51, 516.

27. Kulathilake, A.I.; Chatt, A. Anal. Chem. 1980, 52, 28.

28. Kim, C.H.; Alexander, P.W.; Smythe, L.E. Talanta 1976, 23, 229.

29. McLeod, C.W.; Otsuki, A.; Okamoto, K.; Haraguchi, H.; Fuwa, K. Analyst 1981, 106, 419.

30. Riley, J.P.; Taylor, D. Anal. Chim. Acta 1968, 41, 175.

31. Kawabuchi, K.; Kuroda, R. Anal. Chim. Acta 1968, 40, 479.

32. Korkish, J.; Krivanec, H. Anal. Chim. Acta 1976, 85, 111.

33. Vandersloot, H.A.; Wals, G.D.; Das, H.A. Anal. Chim. Acta 1977, 90, 193.

34. Chau, Y.; Lum-Shue-Chan, K. Anal. Chim. Acta 1969, 48, 205.

35. Butler, L.R.P.; Mathews, P.M. Anal. Chim. Acta 1966, 36, 310.

36. Mansell, R.E.; Emmel, H.W. At. Absorpt. Newsl. 1965, 4, 365.

PART II

37. Delaughter, B. At. Absorpt. Newsl. 1965, 4, 273.

38. Ternero, M.; Gracia, I. Analyst 1983, 108, 310.

39. Puschel, R.; Lassner, E. in "Chelates in Analytical Chemistry", Falschka, H.A.;Barnard, A.J. Jr. eds.,1967, Vol. 1, P.267.

40. Heyne, G. Z. Angew. Chem. 1931, 44, 237.

41. McGowan, J.C.; Brian, P.W. Nature 1947, 159, 373.

42. Seifter, S.; Novic, B. Anal. Chem. 1951, 23, 188.

43. Buchwald, H.; Richardson, E. Chem. Ind. (London) 1959, 753.

44. Buchwald, H.; Richardson, E. J. Inorg. Nucl. Chem. 1960, 15, 133.

45. Haight, G.P.; Paragamian, V. Anal. Chem. 1960, 32, 642.

46. Sommer, L. Z. Anal. Chem. 1962, 187, 7.

47. Sommer, L. Z. Anal. Chem. 1962, 187, 263.

48. Buchwald, H.; Richardson, E. Talanta 1962, 9, 631.

49. Varde, M.S.; Athavale, V.T. Proc. Indian Acad. Sci. 1956, A44, 223.

50. Will, F.; Yoe, J.H. Anal. Chim. Acta 1953, 8, 546.

51. Fujimoto, M.; Fukabori, N.; Nakatsukasa, Y. Anal. Chim. Acta 1963, 29, 335.

52. Horak, J.; Okac, A. *Collection Czech. Chem. Commun*. 1964, *29*, 188.

53. Puschel, R.; Lassner, E. in "Chelates in Analytical Chemistry", Falschka, H.A.; Barnard, A.J. Jr., eds., 1967, Vol.1, P.278.

54. Halmekoski, J. *Ann. Acad. Sci. Fennicae, Ser All*, 1959, *96*, 1.