CHAPTER 1

INTRODUCTION

CHAPTER 1

Page

1.0 INTRODUCTION 1

1.1 History of ion exchange 1

1.2 Scope of ion exchange 1

1.3 Types of ion exchangers 3

1.4 Literature survey 7

- 1.4.1 Chelating resins with amino group 7
- 1.4.2 Chelating resins with azo group 9
- 1.4.3 Chelating resins with imino group 10
- 1.4.4 Chelating resins with oxime group 12
- 1.4.5 Chelating resins with oxine group 12
- 1.4.6 Chelating resins with thio group 13
- 1.4.7 Chelating resins with miscellaneous groups 16
- 1.4.8 Commercial resins 17

1.5 Proposed work 18

References 34

1.0 INTRODUCTION

Separation methods are the backbone of analytical processes. Hence chromatography an important separation technique has gained importance over the period of time. Among the chromatographic methods ion exchange has diverscent applications. Ion exchange is a process in which cations or anions from solution are exchanged with cations or anions in an exchanger, which are water insoluble macromolecular polyelectrolytes with crosslinked porous structure and ionic groups. During ion exchange process electroneutrality is maintained both in the liquid and in the solid phases. The process is reversible without any permanent change in the structure of the ion exchange material.

1.1 History of ion exchange

Though the use of ion exchange processes can be traced to pre-Christian era the real develoonment in this field began only after 1850. In 1850 Thompson[1] and Way[2], two English chemist reported the use of soil as ion exchange material for the separation of potassium and ammonium ions from soil. The significant developments taken place in the history of ion-exchange from then till 1950 are listed in Table 1.1. Thereafter ion exchange became more specialised field of applications. Hence only the developments in the area of chelating ion exchangers are discussed in the following sections.

1.2 Scope of ion exchange

Ion exchange is a well established unit operation and is an extremely valuable aid to other separation techniques such as filteration, distillation and adsorption.

Table 1.1 : Historical review*

Sr. No.	Year	Work done	Reference
1.	1850	Calcium and magnesium of soil exchange for potassium and ammonium ions.	1,2
2.	1858	Ion exchange properties due to zeolites in soil.	3
3.	1903	First synthetic ion exchanger : aluminium silicate	4
4.	1905	Commercial use of ion exchanger developed in Germany.	5
5.	1917	First analytical application developed for the separation of ammonia from urin.	6
6.	1923	Column applied in quantitative analysis.	7
7.	1927	Ion exchange column applied for determination of sulphate ions in water.	8
8.	1931	Application of organic ion exchangers	9
9.	1935	Synthetic ion exchange resin discovered	10
10.	1939	First analytical application of synthetic ion exchanger.	11
11.	1944	First polymerization type ion exchanger.	12
12.	1949	First reduction - oxidation resin.	13
13.	1950	First ion exchange membrane.	14

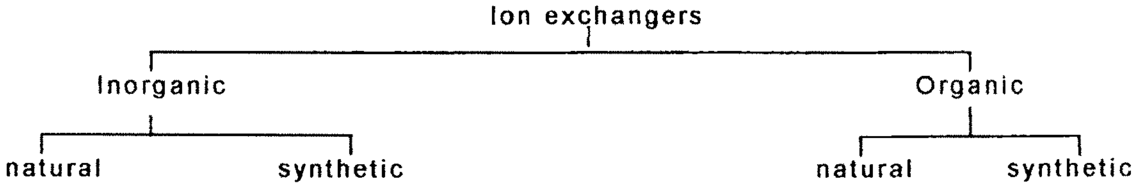
* From `Elements of Ion Exchange' by R. Kunin.

Recent developments in ion exchange have greater importance in preparative and analytical chemistry. Ion exchange is used in water softening and deionization. It also provides a method of separation useful in many chemical processes and analysis. It has a special utility in chemical synthesis, medicinal research, food processing, mining, agriculture, hydrometallurgy and variety of other areas. The use of ion exchanger has given analyst a new tool to meet the requirements of modern laboratories and also has helped in finding solutions to a number of previously unsolved problems. Here it will be appropriate to quote a quotation from Indian Society of Analytical Scientist's News Letter of Dec. 1984 Bombay.

"The chromatographic technique has stimulated revolutionary developments not only in Chemistry but also in several other related disciplines. It appears that any analytical problem, no matter how interactable, can be solved by a proper application of this technique. Hence, it would not be the exaggeration to call chromatography a priceless wonderful lamp readily available to the Alladins of Analytical Sciences".

1.3 Types of ion exchangers

Ion exchangers can be broadly classified as inorganic and organic ion exchangers. They can further be classified as natural and synthetic ion exchangers.



1.3.1 Inorganic ion exchangers

Inorganic ion exchangers include both the naturally occurring materials such as mineral zeolites, the green sands and clays, and synthetic materials such as silicates, gel type zeolite and the hydrous oxides of polyvalent metals. Both natural and synthetic inorganic ion exchangers are less sensitive towards high temperatures and their structures are hard and uniform. Therefore the separation of ions is based on the difference in the cavity size of inorganic ion exchangers. They are also used as ionic and molecular seives. However, even though they have neither high exchange capacity nor good chemical and mechanical resistance, due to high stability towards nuclear radiation they are used in nuclear reactors.

1.3.2 Organic ion exchangers

Organic ion exchangers are also natural and synthetic in origin. Many naturally occurring organic materials have ion exchange properties. Natural organic ion exchangers being highly sensitive to alkalies serve very limited purpose in analytical chemistry. However, cellulose based resins bearing phosphonic acid, sulphonic acid and dimethylamine groups are largely used in chromatography.

Synthetic organic ion exchangers become available in the late 1930s with the introduction of phenolic resins. Styrenic resins appeared in the mid 1940s and acrylic resins about 20 years later.

Here are some of the desirable properties for the ion exchangers.

(i) Good chemical and mechanical resistance,

(ii) Retention of exchange capacity even after prolonged usage,
(iii) Very high exchange rates,
(iv) Hydrophilic gel structure ensuring good accessibility to functional groups and high rate of diffusion of ions, and
(v) Rapid equilibrium.

As natural resins may not have all these properties it is desirable to synthesize a resin with such properties. Hence the advantages of synthetic organic ion exchangers are :

(i) Porosity and particle size can be controlled during polymerization process.
(ii) Physical and chemical stability can be modified.
(iii) Selection of the fixed ionogenic groups according to the desired applications can be achieved.

The synthetic ion exchange resins can further be classified as
(i) cationic
(ii) anionic
(iii) amphoteric and
(iv) chelating

The resinous material used in the present study is of chelating nature and hence this class of resins is discussed here in detail. The chelating resins can be prepared either by introducing the chelating group bearing monomer in the polymeric matrix during polymerization or by anchoring the chelating group to the polymeric matrix after polymerization.

The chelating resins are relatively recent in origin. They have better selectivity, sensitivity and chemical and mechanical stability than the other types of resins.

Chelating resins differ from the ion exchangers in the following aspects :

(i) The strength of the binding forces in a chelating resin is about 60-100 KJ/mole where as in case of ion exchangers it is in the order of 8-12 KJ/mole.

(ii) The ordinary ion exchangers have high exchange rate compared to chelating resins.

(iii) Since in chelating resin, the exchange takes place through chelation the factors affecting the exchange process are different from those governing ion exchange process.

The first chelating resin reported by Skogseid[15] in 1948 contained dipicryl amine group which has a high specificity towards potassium ions. There after various chelating resins have been reported mainly for the preconcentration studies of metal ions. Selected works reported so far have been discussed here after classifying the chelating resins in 8 different groups:

Resins containing,

(i) amino group
(ii) azo group
(iii) imino group
(iv) oxime group
(v) oxine group
(vi) thio group
(vii) miscelleneous group
(viii) commerical resins

1.4 Literature survey

More than 1400 works have been reported earlier in the area of chelating resins. It is not possible to discuss all the references here and hence only some representative works have been discussed just to get the flavour of the diversity involved in this particular topic.

1.4.1 Chelating resins with amino groups

Number of amino derivatives have been used for the synthesis of chelating resins. Some of them are :

A crosslinked polymeric resin of m-phenylene diamine-formaldehyde was prepared by Naumann[16] for the selective sorption of copper. Resin with m and p derivatives of phenylene diamine tetra acetic acid reported by Blasius and Olbrich[17] was found to be useful in the separation of alkali and alkaline earth metals and transition metals such as copper, nickel, cobalt. Where as condensation products of triaminophenol with glyoxal and thioglyoxal were prepared by Bayer[18-20] and were used in the quantitative recovery of copper, uranium, silver, gold and mercury from sea water. A commerical resin Dowex 50 WX-8 with diethylene triamine penta acetic acid was used by Zukriegelova et al[21] for the separation of Ca(II), Mg(II), Zn(II), Pb(II), Co(II), Ni(II), Mn(II), UO_2(II), In(II), Fe(II), Th(IV) and Ti(IV). Where as a commerical XAD-4 resin was converted into 1-3 diamino propane tetra acetic acid derivative by Moyers and Fritz[22] and the resin was characterised for the preconcentration and separation of copper, uranium, thorium, zinc, cadmium, manganese, nickel, cobalt and chromium.

Ethylene diamine-hydroxylamine-maleic anhydride copolymer and anisole-formaldehyde salicylic acid copolymer based resins were used for the separation of various metal ions by Bhatnagar et al[23]. Where as a resin with 2,4,6 triamino-1,3,5 triazine group was synthesized and its exchange and distribution properties for Cu(II), Ag(I), Hg(II), Cd(II) and some anions were studied by Lieser and Thybusch[24]. Polyamine based resins with resorcinol-amino carboxylic acid and resorcinol-formaldehyde were synthesized by Baracco et al[25]. They have used these resins for the extraction of uranium from sea water. Sugii et al[26] synthesized polystyrene based resins with phenyl alanine groups and they did a comparative study of analytical properties of these resins with Dowex A-1 for the recovery of mercury and copper from sea-water.

Other groups incorporated in the polystyrene - DVB copolymer backbone mainly include 2-pyridyl methyl amine[27], N-[2-(2-Pyridyl)ethyl] ethylene diamine[26], salicylamine[27,28], 2-ethenyl amine[27,28] and pyridyl amine[28]. These resins were used for the chelation of Co(II), Ni(II), Cu(II) and Zn(II). A novel resin with α-amino acid bound to hydroxy-ethyl methacrylate gel was synthesized by Hadrabova et al[29] and was used to study its exchange properties for Cu(II), Ni(II) and Zn(II). Maeda and Egawa[30] prepared a macroreticular chelating resin containing triethylene tetraamine side chains. The resin was found to have highest initial adsorption rate and largest break through capacity for zinc. Diethylene triamine functional groups were incorporated in styrene-DVB backbone by Suzuki and Yokoyama[31] and Nishizawa et al[34]. These resins were used for the separation of transition metals, silver and mercury.

Polystyrene based resin with bis (carboxy methyl) amino moiety was found to be selective for In(II), Ga(III) and Au(III) in the column chromatographic studies by Suzuki et al[32] Where as styrene - DVB and methyl methacrylate-DVB resins with amino methyl phosphonic acid groups were synthesized and used by Sahni et al[33] and Maeda and Egawa[35]. They have used them as sorbents for the preconcentration of Cr(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Ca(II) and Mg(II). Chloromethylated styrene - DVB containing diethylene triamine group was reported by Kim et al[36]. They have used this resin for the sorption studies of Cu(II), Ni(II), Pb(II), Cd(II), Zn(II) and Co(II). The stability constants were found in the order of Cu(II) > Ni(II) > Pb(II) > Cd(II) > Zn(II) > Co(II). Maeda and Egawa[37] have reported a resin with aminomethyl phosphonic acid for the removal of Ca(II) and Mg(II) ions from salt solutions. Kumar et al[38] have found an important application of a conducting polymer poly (aniline) as a resin for the separation of Pd(II), Ir(IV), Pt(IV) and Au(III). They have reported that the metal ions were strongly adsorbed at low acidities and the extent of adsorption decreases with increase in acidity. Elution of Pd(II), Pt(IV) and Au(III) was achieved quantitatively with 5 % thiourea in 0.05 M HCl.

A resin Wofatit MK 51 which contains methylamino glucitol group was reported by Schilde et al[39]. This resin was used for the separation of the oxoanions of germanium, tin, arsenic, antimony, tellurium, molybdenum and tungstan. Loading and elution curves as well as break through capacities were also evaluated. Dev and Rao[40] synthesized styrene-DVB crosslinked polymer based resin containing N-hydroxy ethylene thylene diamine. The resin was thoroughly characterised and studied for the sorption of Cu(II), Ni(II), Zn(II), Co(II), Fe(II), Cd(II), Pb(II), Mn(II) and Cr(III). The sorption of metal ion was observed to be pH dependent.

1.4.2 Chelating resins with azo groups

Chelating resins containing azo group are found to be useful in ion exchange and chromatographic studies. Resin containing 4-(2-pyridyl azo) resorcinol functional group was prepared and studied for its exchange properties for Cu(II), Fe(II), Ni(II), UO_2(II), Zn(II), V(V), Al(III) and Co(II) by Eccles and Vernon[41]. Polystyrene based resins containing p-hydroxy benzoic acid and azo salicylic acid were synthesized and their exchange properties were compared by Vernon and Eccles[42]. Where as poly (acrylic acid) triazo/ethyl and acryl thiosemicarbazide resins were synthesized by Sugii et al[43] and were found to have high affinity for Cu(II). Chwastowaska and Mozer[44] introduced 1-(2-pyridylazo) 2-naphthol group in Amberlite XAD-4 and they used this resin for the separation of heavy metals.

Szezepaniak and Kuczynski[45] synthesized styrene-DVB-1,4,8,11-tetra azo-cyclotetradecane resin and they found its affinity order for metal ions as Cu(II) >> Zn(II) > Cd(II) > Ni(II) >> Co(II) >> Ca(II) = Mg(II). Where as Herbert et al[46] synthesized C_{18} based polymeric support loaded with 4-(2-pyridylazo) resorcinol, 1-(2-pyridylazo) 2-naphthol for sorption of Cu(II) and Pb(II). The detection limits using an on-line preconcentration was found to be at ppb level with enhancement factor between 50 to 100.

1.4.3 Chelating resins with imino groups

In this class mainly iminodiacetate or iminodiacetic acid functional groups containing chelating resins were reported. Sykora and Dubsky[47] synthesized chelating reins with 2-hydroxy-imino acetamido functional groups and have studied their exchange behaviour under static and dynamic conditions for Hg(II), Cu(II), Pb(II), Ni(II), Zn(II), Co(II), Ca(II), Mn(II), Ag(I), Fe(II), Al(III), UO_2(II) and Pd(II) at pH < 6. It was observed by Saegusa et al[48] that poly (styrene-g-N-carboxy alkylated ethylene imine) resin forms metal chelates at pH 6 with affinity order Hg(II) > Cu(II) > Cd(II) > Ni(II) > Ca(II). Where as glycidyl methacrylate-ethylene dimethacrylate resin containing iminodiacetic acid group was reported to show chelating affinity order for various metal ions as Ni(II) > Mn(II) > Zn(II) > Pb(II) > UO_2(II) by Kalalova et al[49]. Iminodiacetic acid group was introduced on imidazolyl derivatives[50] and on phenol formaldehyde resins mainly for exchange of transition elements by Tomoshige et al[51].

Polyethylene imine methyolated thiourea resin for water treatment and for the removal of mercury from waste water was reported by Kiyama and Shimura[52]. Iminodiacetic acid group was introduced on cellulose derivatives by Kohovec et al[53] for transition elements mainly for Cu(II) exchange study. Urano et al[54] used phenolic resins with iminodiacetate group and constructed % exchange isotherms for Cu(II), Zn(II), Cd(II) and Pb(II). Similar resins were synthesized by Sato and Taza[56]. They used these resins for the recovery and determination of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II) and Cu(II) from industrial effluents and food materials. Where as polyethylene imine type resins were synthesized and used for retention and separation of copper and iron by Bartulin et al[55].

Iminodiacetic acid on Amberlite IRA 718 resin was reported by Becker and Eldridge[57] for the removal of Hg(II) selectively at pH 1.5 from industrial waste water containing iron, zinc, cadmium and lead. Only 70-80 % desorption of mercury was achieved in the first cycle at pH 7 with 3 M NaCl solution. Amide linkage was incorporated in polyethylene imine based chelating resin and its characteristic properties and metal exchange was studied by Thiagarajan and Subbaiyan[58]. Crosslinked and activated agarose gel with polyethylene imine functionality was prepared by Lone et al[59] and was used for the sorption of Cu(II), Ni(II), Cd(II) and Zn(II). The binding capacity for Cu(II) was found to be 500 μmol cm^{-3} of packed adsorbent. Adsorption capacities, adsorption isotherms, distribution coefficients, % recoveries and relative rates of accumulation of the metal ions were also discussed.

1.4.4 Chelating resins with oxime groups

Poly (hydroxamic acid) and N-methyl poly (hydroxamic acid) resins from XAD-4 were synthesized by Phillips and Fritz[60,64] and they were successfully used for the separation of titanium, iron, thorium and uranium. Acrylonitrile-DVB resin having amidoxime group was synthesized by Collela et al[61] and its chelate forming behaviour with alkali and alkaline earth metals was studied. Vernon and Zin[62] prepared poly (hydroxamic acid) resins which were selective for gold and silver. Vernon[63] has also used these resins for the extraction of uranium from sea water. Whereas Poly (amidoxime)/poly (hydroxamic acid) resins prepared from (acrylonitrile) fibers[65] and polystyrene amidoxime[66] were found suitable for extraction of uranium from natural and sea water. Shah and Devi[67-70,73] synthesized poly (hydroxamic acid) resins from acrylonitrile-DVB cross linked polymer and they were used for the estimation and separation of Cu(II), Zn(II), Cd(II), Pb(II), Cr(II), UO_2(II) and V(V). Motekaitis et al[71] synthesized tris (hydroxamate) cryptand and studied its behaviour towards Fe(III) and Ga(III). Chelating properties of a new cyclic diazo dihydroxamic acid resin were reported by Santos et al[72].

1.4.5 Chelating resins with oxine groups

Vernon and Eccles[75] synthesized oxine containing resin from XAD-2 and used it selectively for the removal of mercury from industrial effluents. Parrish and Stevenson[76] synthesized oxine-formaldehyde-resorcinol resin by modifying the method reported by Pennington and Williams[74]. They observed increased exchange capacities for nickel, cobalt, magnesium, calcium, iron and copper due to the modified synthetic route. Separations from binary mixtures of these metal ions were carried out successfully. Herbert et al[46] reported a sorbent containing quinoline -8-ol reagent on C_{18} based polymeric support.

A macromolecular polystyrene based chelating resin with oxine and diethylamine functional group was synthesized by Sugii et al[77] and its exchange behaviour for copper was studied. Separation of zinc, copper, cadmium, manganese and iron was carried out on a resin containing 8-hydroxy quinoline-5-sulfonic acid group by Zhou and Mao[78]. Where as Janak and Janak[79] studied the sorption behaviour of copper using quinoline-8-ol anchored on porous glycidyl methacrylate matrix. 8-Hydroxy quinoline was surface immobilised on gel type styrene-DVB copolymer by Jonas et al[80]. Fuerst et al[81] have also synthesized 8-hydroxy quinoline based resins for the adsorption of heavy metal ions. Sorption of 8-oxine and 8-oxine-5-sulfonic acid on Amberlite XAD-2 was studied by Abollino et al[82] for the enrichment of trace metal ions like Ca(II), Cd(II), Cu(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II). Purohit and Devi[83-85,87] synthesized a series of chelating resins containing oxine and resorcinol or hydroquinone monomers and different crosslinking agents such as formaldehyde, furfuraldehyde and benzaldehyde. They further used these resins for the preconcentration of copper[83], zinc[84], cadmium[84], lead[85] and nickel[87]. It was found that these resins have variable chelate forming capacities towards metal ions and hence show variation in distribution coefficients. Recovery of Ru(III), Os(IV), Co(II), Rh(III), Ir(III), Ni(II), Pd(II), Pt(IV), Ag(I) and Au(III) in the presence of other metal ions using 7-alkyl-8-hydroxy quinoline containing resin was reported by Gefvert[86].

1.4.6 Chelating resins with thio groups

In the present study, we have used polymeric support anchored with the reagent containing thio group and hence work done earlier on the resins with thio group is discussed here in details.

Poly (sucrose methacrylate) resins with thio glycolic acid group and hexylthioglycolate group on XAD-4 were synthesized and found to be selective for Ag(I), Hg(II), Bi(III) and Au(III) by Moyers and Fritz[88]. Derivative of 2-mercaptobenzothiozole on silica gel for the preconcentration of some heavy metals was reported by Tarada et al[89]. Polystyrene-DVB based resins with thiozole and thiozoline groups were synthesized and used for recovery of mercury from sea water by Sugii et al[90]. Where as thioglycoloyloxy methyl group containing resin was synthesized and used for the separations of Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II), Au(III), Cd(II), Pb(II) and UO_2(II) by Phillips and Fritz[91]. Dithiocarbamate derivatives of cellulose were prepared and exchange capacities of Ag(I), Cr(III), Cu(II), Pb(II) and Se(IV) were measured by Imiai et al[92].

Chelating resins containing poly (dithiocarbamate) groups for the preconcentration of Cd(II), Fe(II), Mo(VI), V(V), Zn(II) and Fe(III), Cr(III), V(V), Ti(IV), Mo(VI), W(VI), Th(IV), Os(IV) were reported by Miyazaki and Barnes[93] and Mianzhi and Barnes[95]. Where as polyacrylamide and poly styrene-DVB resins containing thiosemicarbazide were prepared by Nakazato et al[94] and Siddhanta and Das[96]. These resins were used for the sorption of Pd(II), Pt(IV), Rh(III), Ir(III) and Cu(II), Ni(II), Pb(II) respectively. Liu et al[97] incorporated thiohydroxamate group into Amberlite IRC-50 resin. This resin showed good affinity for Cu(II), Hg(II), Ni(II), Pb(II), Zn(II), Fe(II), Mo(VI) and UO_2(II).

Synthesis of styrene-DVB based resin with 5-chloromethyl 8-mercapto quinoline chlorohydrate group for the preconcentration study of copper, zinc and palladium was reported by Seilkhanov et al[98]. Polystyrene based semithio carbazone for the preconcentration of Cu(II), Ni(II), Fe(II), Co(II), Zn(II), Cd(II), Mo(VI) and UO_2(II) was reported by Syamal and Singh[99]. Where as styrene-DVB copolymer was oxyethylated with dithiocarbamate, methyl thiourea and thiol by Lezzi et al[100] to be used in waste water purification mainly for Hg(II) and Pb(II) removal. Newton et al[101] synthesized 2-mercaptobenzothiozole on clay for the preconcentration of some heavy metal ions.

Dithizone as a chelating reagent for metals was introduced by Fisher[102] in 1925. Whereas Kolthoff and Sandell[103] reported solvent extraction of metals using dithizone as a chelating agent first time in 1941. Irving and Bell[104,105] have reported the new synthetic route for the synthesis of dithizone from 3-chloro-1 : 5-diphenyl formazone and sodium hydrogen sulphide. They also discussed the possibility of its solutions containing the thiol and the thione forms in tautomeric equilibrium based on spectrophotometric studies. However, the first dithizone anchored polystyrene-DVB resin was reported in 1959 by Davies et al[106]. Deposition of dithizone on polyurethane foam was also tried by Braun and Farag[107] for the collection of silver. Again a sorbent was prepared by deposition of dithizone on polyurethane foam[108,109] and polystyrene beads[111] for the preconcentration of mercury from sea water. However, the recovery was not good because of the instability of the sorbent. A chelating resin was prepared by Tanaka et al[110] by treatment of a strongly basic anion exchanger Amberlite IRA 400 with a sulphonic acid derivative of dithizone. Griesbach and Lieser[112] have described the synthesis of fifteen sorbents including one loaded with dithizone, but the products were not analysed and the properties of the sorbents obtained were not discussed.

Polystyrene based dithizone and dehydro dithizone resins were synthesized by Grote and Kettrup[113,114]. They have used these resins for the sorption and desorption of noble and base metal ions. The distribution coefficients of metal ions in different acid strengths were reported. Again polystyrene-DVB based chelating resin containing dithizone was prepared by Chwastowska and Kosiarska[115]. The analytical characteristics of the sorbent were studied and optimum sorption conditions were established for Ag(I), Cu(II), Cd(II), Pd(II), Ni(II), Co(II) and Zn(II) under static and dynamic conditions. Uchiumi et al[116] synthesized porous polymeric resins with thionalide, dithizone or bismuthol-II reagents for removal of heavy metals like As(III), Sb(III) and Cu(II) from industrial waste water. A comparative study of chelating resins containing diethyldithio carbamate, pyrrolidine-1-yldithioformate and dithizone on silica C_{18} sorbent had been carried out for the removal of mercury by Garcia et al[117]. They studied it for the preconcentration of ultratrace amounts of inorganic mercury and methyl mercury. The method was successfully applied to the determination of low level of mercury in sea-water.

1.4.7 Chelating resins with miscelleneous groups

Chelating resins containing any other types of functional groups not discussed earlier are discussed under this section.

Polystyrene based resin containing β-naphthol was reported by Gregor[118] for transition metal ions. Resorcinol-formaldehyde based resin containing anthranilic acid group was reported to be selective for Pd(II), Pt(IV), Rh(III), Ru(III), Os(IV), Au(III), Ag(I) and Cu(II) respectively by Sykora and Dubsky[119]. Other groups incorporated into polystyrene based resins are : nitroresorcinol[120], 3-hydroxy 2-naphthoic acid[121], cysteine[122], 4-hydroxy benzoic acid[42] and phenanthroquinone[130]. All these resins were used for the preconcentration and separation of transition and coinage metal ions and lanthanides.

Pyridine grafted on polystyrene and poly 4 and 2 (vinyl pyridine) was found to be selective for transition metals by Nishide et al[125]. Other polystyrene based resins containing 1-nitroso-2-naphthol[123] and its derivative[124], resorcylic acid[126], 1,3-diketones[127], anthranilic acid hydrazide[128] and piperidine[129] were reported for transition and coinage metal ions and lanthanides.

Polystyrene based resins with 2,4-diformyl pyridine or bis (2'-pyridyl hydrazone) groups for preconcentration of Cu(II), Co(II), Ni(II), Zn(II) were reported by Gavino et al[131]. Where as Fujiwara et al[132] have prepared polystyrene based tris (2,6-dimethoxy phenyl) phosphin resin for noble metal ions. A macroporous cross-linked acrolein-styrene copolymer was synthesized and the aldehyde groups were converted to hydrazone and phenyl hydrazone derivatives by Zhang et al[133]. They studied these resins for the sorption of gold and platinum group metals in acidic solutions. Distribution coefficients as a function of acidity were determined for metal ions under study. Tetradecyl dimethyl benzyl ammonium iodide on naphthalene as an adsorbent for preconcentration of iron, cobalt and copper was used by Puri and Balani[134]. Where as Sharma[135] synthesized acetonaphthene quinone monoxide supported over naphthalene for the preconcentration and separation of Co(II) in vitamines, alloys and ores.

1.4.8 Commercial chelating resins

Commercially available chelating resins such as Dowex 50 X4[136], Chelex-100[137,138,140,145], Dowex A-1[139,142,144], UR-10[141], Zeokarb 226[143], Duolite ES-63[146] were also used for the preconcentration of various metal ions.

1.5 Objectives of the proposed work

The present work has been carried out with the objectives :

(i) To explore the potential of the poly (vinyl pyridine)-DVB copolymer for anchoring of dithizone.

(ii) To study the physicochemical properties of the dithizone anchored poly (vinyl pyridine) resin.

(iii) To explore the potential of this chelating resinous material for the preconcentration and separation of selected metal ions at static and dynamic conditions.

(iv) To develope a continuous flow analyser for online preconcentration of these metal ions.

Table 1.2 : Survey of the selected works on chelating resins.

Sr. No.	Chelating resin and reagents used	Comments	Reference
Resins containing amino groups			
1	m-phenylene diamine - formaldehyde.	Selective sorption of Cu(II).	16
2	Resin containing m and p derivatives of phenylene diamine tetraacetic acid.	Separation of alkali,alkaline earths and transition metals such as Cu(II), Ni(II) and Co(II).	17
3	Condensation products of triaminophenol with glyoxal and thioglyoxal.	Quantitative recovery of Cu(II), UO_2(II), Ag(I), Au(III) and Hg(II) from sea water.	18, 19,20
4	Diethylene triamine pantaacetic acid with Dowex 50 WX-8.	Separation of Tl(IV), Ca(II), Mg(II), Zn(II), UO_2(II), In(II), Fe(II) and Th(IV).	21
5	Commercial XAD-4 resin converted to 1-3 diamino propane tetra acetic acid derivative.	Characterised for exchange and separation of Cu(II), UO_2(II), Th(IV), Mg(II), Zn(II), Cd(II), Mn(II) ,Ni(II), Co(II), Cr(III).	22

6	Ethylene diamine-hydroxyl amine maleic anhydride copolymer and anisol-formaldehyde-salicylic acid copolymer.	Separation of Fe(II) from Fe(III) and preconcentration of Fe(II), Co(II), Ni(II), Zn(II), Cu(II)	23
7	Resin containing 2,4,6-triamino-1,3,5-triazine	Exchange capacity of Cu(II) and Ag(I) and Kd values of Hg(II),Ag(I),Cu(II),Cd(II) and some anions.	24
8	Amino carboxylic acid resorcinol and resorcinol-formaldehyde-polyamine.	Extraction of UO_2(II) from sea water	25
9	Polystyrene based phenyl alanine.	Recovery of Hg(II) and Cu(II) from sea water.	26
10	Styrene-DVB copolymers containing 2-pyridyl methyl amine, N-[2-(2-pyridyl)ethyl] ethylene diamine, salicylamine, 2-ethynyl amine groups.	Chelation of Co(II),Ni(II), Cu(II) and Zn(II). Separation of Cu(II), Ni(II) and Zn(II)	27,28
11	A resin with α-amino acid bound to hydroxyethyl methacrylate gel.	Ion exchange properties for Cu(II), Ni(II) and Zn(II).	29

12	Macroreticular chelating resin containing triethylene tetra-amine	Highest initial adsorption rate and largest break through capacity for Zn(II).	30
13	Styrene-DVB copolymer containing diethylene triamine.	Separation of transition metals and Ag(I) and Hg(II).	31,34
14	Polystyrene containing bis (carboxy methyl) amino moiety	Selective for In(II),Ga(III), Al(III),separation of In(II) and Ga(III) from Al(III).	32
15	Styrene-DVB and methyl methacrylate-DVB copolymers containing amino methyl phosphonic acid.	Preconcentration of Cr(III), Co(II),Ni(II),Cu(II),Zn(II), Ca(II), and Mg(II).	33,35
16	Styrene-DVB copolymer containing diethylene tetra amine	Preconcentration of Cu(II), Ni(II),Pb(II),Cd(II),Zn(II) and Co(II). Stability constants in the order of Cu(II)>Ni(II)> Pb(II)>Cd(II)>Zn(II)>Co(II).	36
17	Chelating resin containing aminomethyl phosphonic acid	Removal of Ca(II) and Mg(II) ions in a salt solution.	37
18	Poly (aniline)	Separation of Pd(II),Ir(IV), Pt(IV) and Au(III).Kd values of Pd(II),Ir (IV), Pt(IV) and Au(III) in 0.1-10 M HCl medium.	38

19.	Methylamino glucitol with Wofatit MK 51	Separation of oxoanions of Ge(IV), Sn(IV), As(III), Sb(III) Tl(IV), Mo(VI), W(VI).	39
20	N-hydroxyethylene thylene diamine with styrene-DVB	Sorption of Cu(II), Ni(II), Zn(II), Co(II), Fe(II), Cd(II), Pb(II), Mn(II) and Cr(III).	40

Resins containing azo groups

21	Chelating resin containing 4-(2-pyridylazo) resorcinol	Study of ion exchange properties for transition metals and separation of Cu(II)-Ni(II) and UO_2(II)-Zn(II).	41
22	Polystyrene based resins containing p-hydroxy-benzoic acid and azo salicylic acid	Ion exchange properties	42
23	Poly (acrylic acid) triazo/ethyl and acrylthio semi carbazide resins	Chelating affinity order : Cu(II)>Ag(I)>Cd(II)>Hg(II)	43
24	1-(2-pyridylazo) 2-naphthol on Amberlite XAD-4	Separation of Cu(II), Zn(II), Fe(II), Cd(II), Ni(II), Pb(II)	44

25	1,4,8,11-tetra azo cyclotetradacane on styrene-DVB copolymer.	Chelating affinity order Cu(II)>>Zn(II)>Cd(II)> Ni(II)>Co(II)>>Ca(II)=Mg(II).	45
26	C_{18} based polymeric derivatives containing 4-(2-pyridylazo) resorcinol, 1-(2-pyridylazo) 2-naphthol	Preconcentration of Cu(II), Pb(II).Elution with strong mineral acids of concentration 1-4 M.	46

Resins containing imino groups

27	Chelating resin with 2-hydroxy-iminoacetamide functional group.	Exchange behaviour of Cu(II), Pb(II), Ni(II), Zn(II), Co(II), Ca(II), Mg(II), Mn(II), Ag(I), Fe(II), Al(III), UO_2(II) under static and dynamic conditions upto 2 M HCl or HNO_3 and at pH < 6.	47
28	Poly (styrene-g-N-carboxy alkylated ethylene imine)	Forms chelates at pH 6 with exchange order Hg(II)>Cu(II) >Cd(II)>Ni(II)>Ca(II).	48
29	Glycidyl methacrylate-ethylene dimethacrylates polymers containing imino diacetic acid group	Chelating affinity order : Ni(II)>Mn(II)>Zn(II)>Pb(II) >UO_2(II)	49

30	Iminodiacetic acid on imidazolyl derivative.	Studies for Cu(II),Ni(II), Cd(II),Zn(II),Mg(II).	50
31	N-(2- and N-(4-hydroxybenzyle) iminodiacetic acid on phenol-formaldehyde resin.	Affinity order for Cu(II)> Ni(II)>Zn(II)>Co(II)>Fe(II)	51
32	Polyethylene iminemethyolated thiourea resin.	Removal of Hg(II) from waste water.	52
33	Iminodiacetic acid on cellulose derivative.	Cu(II) exchange study.	53
34	Phenolic resin with imino diacetic acid	Recovery and determination of Mn(II),Co(II),Ni(II),Zn(II), Cd(II),Pb(II) and Cu(II) from industrial effluent and food material.	54,56
35	Polyethylene imine type resin.	Retention and separation of Cu(II) and Fe(II) at pH 2 to 3.7.	55
36	Amberlite IRC 718 with imino-diacetic acid.	Recovery of Hg(II) from solutions containing Fe(II), Cd(II), Pb(II) in sulfuric acid at pH 1.5.	57

37	Polyethylene imine based chelating resin	Studies of cross linked density and surface properties relation with metal ion uptake.	58
38	Polyethylene imine on a cross-linked and activated agarose gel.	Adsorption of Cu(II),Ni(II), Cd(II), Zn(II).Binding capacity for Cu(II) was found to be 500 μ mol/ml packed adsorbent.	59
Resins containing oxime group			
39	Hydroxamic acid and N-methyl hydroxamic acid with XAD-4.	Separation of Ti(IV),Fe(II), and U(VI) from sea water.	60,64
40	Poly (amidoxime)/Poly (hydroxamic acid) resins on acrylonitrile-DVB, (acrylonitrile) fibers and polystyrene.	Removal of UO_2(II) from waste water and study of alkali,alkaline earth and transition metals.	61,65,66
41	Poly (hydroxamic acid) resins.	Study of UO_2(II),Ti(IV) and Zr(IV).	62,63
42	Poly (hydroxamic acid) resins derived from acrylonitrile-DVB copolymers.	Separation of Cu(II),Zn(II), Cd(II),Pb(II),Cr(III),Cr(VI), UO_2(II) and preconcentration of V(V).	67,68,69, 70,73

43	Tris (hydroxamic acid) cryptand.	Stability of Fe(III) and Ga(III) complexes.	71
44	Diaza-dihydroxamic acid resin.	Chelating properties of the resin.	72

Resins containing oxine groups

45	Oxine-formaldehyde resorcinol resin.	Increasing exchange capacity for Cu(II),Ni(II),Co(II), Mn(II),Ca(II) and Fe(II).	74,76
46	Oxine on XAD-2 resin.	Selective recovery of Hg(II) from industrial effluent.	75
47	Oxine and diethyl amino group with polystyrene	Exchange behaviour for Cu(II).	77
48	8-Oxime-5-sulfonic acid containing resin	Separation of Zn(II),Cu(II), Cd(II),Mg(II),Fe(II).	78
49	Quinoline-8-ol on porous glycidyl methacrylate	Sorption behaviour of Cu(II)	79
50	8-Oxine immobilised on the surface of styrene-DVB gel.	Exchange rate of metal ions.	80

51	8-Hydroxy quinoline attached to the surface of activated carbon.	Adsorption of heavy metals.	81
52	8-Oxine and 8-Oxine-5-sulfonic acid on Amberlite XAD-2	Enrichment of Ca(II),Cd(II), Cu(II), Mg(II),Mn(II),Ni(II),Pb(II) and Zn(II).	82
53	8-Hydroxy quinoline/resorcinol or hydroquinone and formaldehyde or furfuraldehyde or benzaldehyde terpolymeric resins.	Separation of Cu(II),Zn(II), Pb(II),Cd(II) and Ni(II).	83,84, 85,87
54	Chelating resin containing 7-alkyl-8-hydroxy quinoline	Recovery of Ru(III),Os(IV),Co(II), Rh(III),Ir(IV),Ni(II), Pd(II), Pt(IV), Ag(I) and Au(III) in presence of Pb(II),Al(III),Ba(II),Ce(IV),Zr(IV), Zn(II),Cu(II) and Fe(II).	86
55	Quinoline-8-ol on polymeric support based on C_{18} derivatives.	Sorption of Cu(II) and Pb(II).	46

Resins with thio groups

56	Poly (sucrose methacrylate) with thioglycolic acid and hexylthio glycolate on XAD-4.	Separation of Ag(I), Hg(II), Bi(II), Au(III).	88

57	2-mercaptobenzothiazole on silica gel.	Preconcentration of Cd(II), Cu(II), Pb(II) and Zn(II) from natural water.	89
58	Thiozole and Thiozoline on polystyrene-DVB copolymer.	Recovery of Hg(II) from sea water.	90
59	Chelating resin with thioglycoloyloxy methyl group	Separation of Ag(I),Bi(III), Sn(IV), Sb(III),Hg(II),Au(III), Cd(II), Pb(II) and UO_2(II) with acetate and HCl.	91
60	Poly (dithio carbamate).	Preconcentration of Cd(II), Co(II),Cu(II),Fe(II),Mo(VI), Cr(III),Ti(IV),W(VI),Th(IV), Pb(II),Se(IV),Ag(I),V(V) and Zn(II).	92,93,95
61	Thiosemicarbazide with polystyrene-DVB and with acrylamide.	Sorption studies for Pd(II), Pt(IV),Rh(III),Ir(III), Cu(II), Ni(II) and Pb(II).	94,96
62	Thiohydroxamate on Amberlite IRC-50	Good affinity for Co(II), Cu(II), Hg(II),Ni(II),Pb(II),Zn(II),Fe(III), Mo(VI),U(VI).	97
63	Styrene-DVB containing 5-chloromethyl-8-mercapto quinoline chloro hydrate.	Preconcentration study of Cu(II),Zn(II),Pb(II).	98

64	Semithiocarbazide on polystyrene.	Anchoring of Cu(II),Ni(II), Co(II),Fe(III),Zn(II),Cd(II), Mo(VI),UO_2(II).	99
65	Dithiocarbamate, methy, thiourea, thiol on styrene-DVB copolymer.	Removal of Hg(II),Pb(II) from waste water.	100
66	2-mercaptobenzothiazole on natural clay	Preconcentration of Hg(II), Zn(II), Pb(II),Cd(II),Cu(II),Mn(II).	101
67	Dithizone on polyurethane foam.	Collection and detection of Ag(I).	107
68	Dithizone on polyurethane foam and polystyrene beads	Preconcentration of Hg(II) from sea water.	108,109, 111
69	Dithizone on Amberlite-IRA 400	—	110
70	Dithizone and dehydrodithizone with polystyrene.	Sorption and desorption studies of Au(III),Pt(IV), Os(IV),Ni(II),Ir(IV),Cu(II), Pd(II),Ag(I),Rh(III),Ru(III), Cd(II),Pb(II),Co(II),Zn(II).	113,114, 115
71	Thionalide,dithizone, bismuthol-II on polymeric matrix.	Removal of As(III),Sb(III) and Cu(II) from industrial waste water.	116

72	Diethyl dithiocarbamate,pyrrolidine-1-yldithioformate and dithizone on silica C_{18}	Preconcentration of inorganic mercury and methyl mercury from sea water.	117

Resins with miscelleneous groups

73	Polystyrene containing β-naphthol.	Preconcentration of Fe(III)	118,119
74	Polystyrene based anthranilic acid hydrazide group containing resins	Selective sorption of Pd(II), Pt(IV),Rh(III),Ru(III), Os(IV), Au(III) and Ag(I).	128
75	Polystyrene based 3-hydroxy-2-naphthoic acid with tetra-phenylene pentamine,catachol, nitroresorcinol,cystein, phenanthreno quinone.	Preconcentration and separation of transition elements, coinage metals and lanthanides.	120,121, 122,42, 130
76	1-nitroso-2-naphthol on polystyrene.	Preconcentration of Cu(II), Fe(III),Co(II),Ni(II),Pd(II) and UO_2(II).	123
77	2-nitroso-1-naphthol on poly-styrene-DVB copolymer	Preconcentration of V(V), Cr(III),Mn(II),Fe(II),Co(II), Ni(II),Cu(II),Zn(II),Hg(II), Pb(II),U(VI).	124

78	Pyridine grafted on polystyrene and poly 4 or 2 (vinyl pyridine).	Selective for transition metals.	125
79	Polystyrene based resorcinol formaldehyde and β-resorcylic acid formaldehyde.	Preconcentration of Pb(II), Cu(II),Zn(II),Ni(II),Ca(II), Mg(II),K(I),Na(I).	126
80	1,3-diketones on polystyrene.	Adsorption of Fe(II).	127
81	Polystyrene containing piperidine or piperazine.	Preconcentration and separation of Cu(II),Fe(III),Zn(II),Co(II), Ni(II) and Cd(II).	129
82	2,6-diformyl pyridine bis (2'-pyridyl hydrazone) with polystyrene.	Higher chelating capacity for Cu(II),Co(II),Ni(II),Zn(II).	131
83	Tris (2,6-dimethoxyphenyl) phosphin on polystyrene.	Adsorption behaviour for Au(III),Pt(IV).	132
84	Hydrazone and phenyl hydrozone on macroporous acrolein-sytrene copolymer.	Chelating properties for Au(III) and Pt group metals.	133
85	Tetradecyl dimethyl benzyl ammonium iodide on naphthanlene as an adsorbent.	Preconcentration of Fe(III), Co(II),Cu(II).	134

86	Acetonaphthene quinone monoxide supported over naphthalene.	Preconcentration and separation of Co(II) in vitamins, alloys and ores.	135
Commercial resins			
87	Dowex 50 X4	Separation of La(III)-Th(IV), Sm(III)-Fe(III),Y(III)-Sc(III) and Mg(II)-Al(III) and La(III), Nd(III),Pr(III) from Ce(IV) and Sm(III).	136
88	Chelex-100	Removal of Ba(II),Ca(II), Cd(II), Ce(IV),Co(II),Cr(III), Cu(II),Fe(II), La(III),Mg(II),Sb(III),Sc(III),U(VI), V(V) and Zn(II) from river and sea water.Removal of Cu(II),Pb(II), Cd(II) and Zn(II) from coastal and sea water.	137,138, 140, 145
89	Dowex A-1	For actinides and lanthanides. Separation of Pu(IV)-UO_2(II), Ni(II)-Co(II), UO_2(II)-Th(IV).	139,142, 144
90	UR-10	Removal of Zn(II) from industrial effluent.	141

91	Zeokarb 226	Separation of UO_2(II)-Th(IV) and transition metals.	143
92	Duolite ES-63	Separation of Zr(IV) and Hf(IV).	146

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