CHAPTER - I

A BRIEF REVIEW
ON
SOLID PHASE EXTRACTION USING FUNCTIONALISED CHELATING RESIN COMPOUNDS

1.1 Introduction

In the environment waste water, geological samples, industrial effluent, medical and radio active wastes are found in complex mixtures [1-4].These mixtures often contain trace amounts of toxic heavy metals. In addition small concentrations of precious metals are also found in natural conditions. To isolate these metal ions from these sources raises a stiff challenge. The available instrumental procedures need in general a certain minimum concentration of these ions before detection and quantitative estimation. More over the complex nature of the metal ions present in the matrix poses difficulties to retrieve them for direct detection and estimation. Hence separation and pre-concentration of the metal ions from these sources are the two necessary conditions for their estimations. Separation by solvent extraction should be avoided in many cases because of the requirement of large volumes of undesirable solvents. Similar is the case for ion exchange processes.

Therefore, search for other techniques in recent years for separation and pre-concentration of low concentrations of undesirable metal ions are on:

1.1.1 Pre- concentration

The presence of heavy metals in the environment is a great concern because of their acute and long term effects. Low concentration and potential interfering matrix constituents in environmental samples require the pre-concentration of metal ions present as an essential task before the quantitative analysis as mentioned.

Pre-concentration is a process in which concentration or amount of desired trace elements is increased - it improves the analytical detection limit and increases the sensitivity by several order of magnitudes. It is an enrichment process consisting of either stripping the major components from the minor ones or extraction of analyte into a second phase of less volume than the original sample [5].

Enrichment is achieved by the use of various pre-concentration techniques, such as,

a. Precipitation
b. Evaporation
c. Electro-deposition
d. Floatation
e. Ion-exchange
f. Liquid-Liquid extraction
g. Solid phase extraction

Of all the above mentioned pre-concentration techniques, solid phase extraction (SPE) is among the best methods owing to its low cost compared to the high cost of the sophisticated instrumental techniques and its ease of use [6]. It also reduces the consumption and exposure to hazardous solvents.

1.2 Solid Phase Extraction

Solid phase extraction is an extraction method which uses a solid phase and a liquid phase. In this method the dissolved ions or suspended materials are separated from other components in the mixture by taking advantage of their physical and chemical properties [7]. It is a powerful technique and has been used recently to pre-concentrate and separate trace and ultra-trace amounts inorganic and organic species from complex matrices. It involves partitioning between a liquid (sample matrix or solvent with analytes) and a solid (sorbent) phase instead of partitioning between two immiscible liquid phases which is done in case of liquid-liquid extraction. The SPE is always achieved by the interaction of three components - the sorbents, analyte and the solvent. The analyte must be attracted more strongly to the sorbent than the solvent. The most common retention mechanism in solid phase extraction is based on weak non covalent interactions:

a. van der Waals forces (non polar interaction)
b. Hydrogen bonding
c. Dipole-dipole forces (polar interaction)
d. Cation-anion interaction (ionic interaction)

There are many commercially available solid sorbents. The most frequently used sorbents [6, 8] are:

a. chemically modified silica gel.
b. graphitised or porous carbon, functionalized carbon nano tubes [9]
c. polymer sorbents.

The good qualities for a solid sorbent should have the following characteristics:

a. It should be able to extract a large number of trace elements over a wide range of pH.

b. The sorption and elution should be fast and quantitative.

c. The capacity for absorption should be high.

d. The sorbent should be easily regenerated for reuse.

For the actual separation, different types of sorbent formats such as micro column, syringe barrels, cartridges and discs are in use [6].

The basic approaches involved in the SPE methods to pre-concentrate the sample are:

i) passing the liquid sample through a column or a cartridge or a disk containing an adsorbant.

ii) washing the sorbent surface.

iii) retained analytes are recovered by elution with an appropriate solvent.

There are many polymer based sorbents which are being used in SPE technique. The following sorbents are used frequently:

a. Polystyrene divinyl benzene (PS-DVB)

b. Divinyl benzene-vinyl pyrrolidone co-polymers

c. Polyacrylate polymer

d. Polyurethane polymers

e. Polyethylene polymers

f. Poly-tetrafluoroethylene polymer

g. Polystyrene polymer

h. Polyamide polymer

Recently used porous polymer sorbents are generally co-polymers of styrene and divinyl benzene. The porous polymers have moderate surface areas ($< 600m^2/g$) and are highly cross-linked. The most widely used polymeric sorbents are the styrene-divinyl benzene co-polymers. Amberlite XAD series, XAD-1,XAD-2,XAD-4,XAD-16 and Merrifield polymers are good examples and widely used polymers in this field [8]. All these compounds are macro porous hydrophobic resins which overcome many of the limitations of bonded silicas. These sorbents have greater efficiency for analyte retention e.g., for polar compounds.

1.3 Functionalised chelating resins

The mostly used polymer sorbents (PS-DVB) have large surface area constituted with rigid materials. However, due to hydrophobic characters of these resin compounds, retention of trace elements is hindered and poor retention efficiency is found. For this reason, efficient retention of trace elements require the addition of ligand/s to the sorbents. Two broad classes of methods are generally applied for the preparation of chelating exhanger resins:

i) sorption of the chelating ligand on the polymer backbone

ii) covalent linkage of the ligand to the polymer matrix via the functional group-N=N- (diazotization product of polymer is formed) or via $-CH_2$ formed by methylene chloride reaction.

Although the resin compounds produced by impregnation (method i) have good absorption capacity, they suffer from lower stability and are difficult to reuse due to partial leaching of the ligand. The second method (method ii),based on covalent binding of the chelating ligand has gained special attention due to high degree of selectivity, versatility, durability and a good metal loading capacity. In addition to the suitable functional group the efficiency of functionalized chelating resin depends on various physiochemical parameters such as surface area, particle size, pore diameter, pore volume and degree of cross linking.

The procedures for the functionalisation of the organic ligands on the polymer matrix may be carried out generally by one of the following routes:

1.3.1 Incorporation through CH_2 - carbon of the polymer resin

In this case chloromethylated polymer is reacted with the amine or thiol or carboxylic acid group of the chelating ligands producing immobilized solid support consisting of various donor atoms as present in the ligands.

Incorporation through N- atom of the ligand: the first example of such incorporation is between the reaction of iminodiacetic acid [9] and the resin.Ligands like calyx[4]arene-semicarbazone [10], thiourea [11], nitrosoresorcinol [9], thiazole and thiazoline [12], phenyl alanine [13], anthranilic acid azide [14], triazoethiol [15], piperazine [16] were also efficiently incorporated.In a microwave assisted reaction 2-aminothiophenyl S-acetic acid [17] and 2-aminothiazole [18] were immobilized on chloromethyl polystyrene whereas 1,2-bis(*o*-aminophenylthio)ethane [19] and dithiooxamide [20] were immobilized by refluxation in DMF.

As an example of the carboxylic acid containing ligand mention may be made to the work of C.Y.Liu [21] who introduced histidine with additional N,S atom donors. Recently Iravani et al [22] described the synthesis of a functionalized resin containing pyridine 2,6-dicarboxylic acid. Further P. Metilda and his co workers immobilized succinic acid [23] on the resin. In a very recent work [24] salicylic acid functionalized silica coated magnetite nanoparticles used to pre-concentrate Cu(II),Cd(II),Ni(II) and Cr(III) ions successfully.

Mention may be made for other ligands such as aminopyrazolone [25], lysine N , N - diacetic acid [26], 8-hydroxoquinoline [27] and methyl urea [28] which were introduced into the polymeric matrix. By an interesting ring opening reaction of cyclohexene oxide and sulfide by the amino group, immobilization was achieved on a VBC/ DVB co-polymer leading to the formation of a series of novel chelating resins [29].

Incorporation through S atom : A few examples of S containing ligands are available in the literature. The important description was the reaction of thiol group of methyl marcaptan [30], dithizone or dehydrodithizne [31] with the chloromethyl polystyrene divenyl benzene. The products were characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) by Saha et al [30].

1.3.2 Incorporation through -N=N- linkage

Following types of ligands were incorporated through the –N=N- linkages generated in situ in the polymer via NH_2 diazotization.

Incorporation of chelating ligand containing phenolic -OH groups :

The first report of the introduction of phenolic OH group was demonstrated by Davies et al [32] who utilised *o*-hydroxy arsonic acid and kojic acid in strong basic solutions for the purpose via the -N=N- linkage.

Following this method J.P. Ghosh and his co workers [33, 34] synthesized the resin containing 1-nitroso 2-napathol and 2-nitroso1-napathol. Styra-Braijter and Zlotorzynska [35] synthesized pyridyl azo resorcinol (PAR) containing chelating resin. Amberlite-XAD-2 was modified by Alizarin red- S [36], salicylic acid [37] and pyrocatechol violet [38] by Saxena et al. Lim et al [39] synthesised thiazolylazophenol containing resin. On the other hand, an N,O,S containing Schiff base ligand, namely,*o*-Vaniline thiosemicarbazone was successfully incorporated in the resin by Jain et al [40] to separate Cu(II),Zn(II) and Pb(II) ions. Other important literatures include the works of C.H.Lee and his coworkers [41] on 4-(2-thiazolylazo) resorcinol,Kenawy et al [42] and W.Lee and his coworkers [43] who used pyridylazo naphthol (PAN) and 1-(2-thiazolylazo)-2-naphthol (TAN) ,

Other important works were by Tewari and Singh [44-47] who immobilized the modified chromotropic acid, thiosalicylic acid, xylenol orange and pyrocatechol as chelating ligands, Kumar et al [48-51] described the functionalization of Amberlite XAD-2 with *o*-aminophenol, tiron, quinalizarin and pyrogallol. Mondal et al [10, 52] incorporated 6-mercaptopurine,2-naphthol-3.6-disulphonic acid on the resin to separate Hg(II) and Cr(III,VI) respectively, Cekic et al [53] immobilized o-amino benzoic acid through –N=N- linkages and utilized the functionalized resin to separate divalent ions of Pb, Cd, Ni, Co and Zn. An important inclusion was the work of Rao et al [54] in which they described the incorporation of 2-hydroxy-acetophenone-thiosemicarbazone and then to utilize the resin to separate divalent ions of Cd, Cu and Ni from vegetable and plant leaves.

Incorporation of chelating ligand containing a heterocyclic N-donor site: N atom containing hetero-cyclic compounds were identified as having special affinity for class-b metals.On the basis of this some workers studied the synthesis of the chelating resins having hetero-cyclic N atom. Chattopadhyay et al [55] and Das et al [56] prepared resins respectively with imidazole and benzimidazole on styrene-divinylbenzene. On the other hand, Banerjee et al [11] reported the synthesis of the chelating resin from imidazole 4,5-dicarboxylic acid.

1.3.3 Incorporation through amide linkage

Linkages through amide group(though acid sensitive) was first introduced by Phillips and Fritz [57] who incorporated N-phenyl hydroxamic acid into the styrene divinylbenzene copolymer. By following the same method successful introduction of various ligands like tertiary aliphatic amide [58], acyl oxime [59], cystein [60], 8-aminoquinoline [61], thiosalicylamide [62], benzoyl acetanilide [63], quinaldinic acidamide [64], piconilamide [65], thiopropionamide [66], thioacetamide [67], mercaptoacetamide [68] into the polymeic matrix were achieved.

1.3.4 Polycondensation method.

Polycondensation method was based on the capacity of some monomeric organic ligands to react with aldehydes forming polymeric sorbents. Polycondensation of the monomeric chelating ligands could be utilized to synthesise the functionalized resins.In this way resins containing ethylenediamine [69], dithiocarbamate [70], 8-

hydroxyquinoline 5-sulphonic acid [71], vinylphosphamidic acid [72], 1,1-vinylidenediphosphonic acid [73], azacrown [74] were synthesized. Alexandretos et al [73] characterized a phosphorous containing resin by solid state ^{31}P NMR spectra. The peak at 27.5 ppm confirmed the presence of -PO_3H moeity in the polymeric matrix. B.A. Shah and his coworkers [75] synthesized a polycondensed resin with three monomers - salicylic acid,formaldehyde and resorcinol by microwave assisted method.

1.3.5 Incorporation through esterification reaction

The first group to synthesise an esterification link in the resin by the reaction of polystyrene-DVB resin with propylene diaminotetraaceticacid (PDTA) was demonstrated by Moyer and Fritz [1]. The reaction followed a general synthetic route in which the acid chloride group of the resin was treated with the alcohols to generate the ester link in the functionalized resin. Dev and Rao incorporated bicine [76], bis-(N,N'-salicyldene)-1,3-propane diamine [2], N-hydroxylethyl ethylenediamine [77] moieties through esterification reaction. The separations of toxic heavy metals were achived by using these resins. Other workers introduced hexylthioglycolate [78], thioglycolate [79] and 1-hydra-zinophthalazine [1] in the solid matrix by following the general route. The macrocyclic ligand 7-aza-1,4,10,13-tetrathia cyclohexadecane was introduced to poly-(glycidylmethacrylate) [80] to produce an interesting matrix which depending on the cage size was very selective for noble metals .

1.4 Analytical applications

The selective sorption of certain metal ions individually or in mixtures, the different stabilities of the complexes formed by functional groups of the sorbent lead to the use of these materials for pre-concentration and separation of different metal ions present in environmental, biological or industrial matrices. It may be noted that the separation of metal ions could be carried out by (i) azo functionalized resins having phenolic -OH group or heterocyclic N- donor atoms, (ii) resins anchored by -CH_2 group, (iii) resins having amide linkage, (iv) esterified resins or (v) polycondensed resins, the general route for their syntheses have been discussed above. After separation, metals are usually analyzed by spectrophotometric methods or atomic absorption spectrometry techniques suitable for trace metal ion analyses. However, in some cases fluorimetry and radiochemical methods like NAA have been used. It is evident that a large volume of works have been carried out on separation of transition metals present in environmental samples. Some of the methodologies appeared in the literatures are discussed below:

1.4.1 Applications of azo functionalized resins having phenolic -OH group:

The resin containing 1-nitroso 2-naphthol as the ligand was used by Ghosh and Das [33] for the separation of Pd(II) and U(VI).The functionalized resin has exchange capacities of 0.67 and 0.43 mmol g^{-1} respectively. Separation of Pd(II) was based on the pH of the solution when at pH 1.0 appreciable amount of Pd(II) was sorbed on the resin column but other metals are not sorbed. On the other hand,at pH 5.9 most of the metal ions were sorbed along with U(VI) which may be eluted with 0.5 M Na_2CO_3. The resin was thus useful particularly for the separation of U(VI) in sea water. The same group of workers also described the use of the resin produced by 2-nitroso 1-naphthol [34] to determine the exchange capacities of the metal ions like Hg(II), Ni(II), Zn(II), Cd(II), Mn(II), V(V), Cr(III), Fe(III), Co(II), Cu(II) and Pd(II). It was found that the values are high for Pd(II), Cu(II), Hg(II) and U(VI) with exchange capacities of 0.93 mmol g^{-1} for Pd(II) at pH 1.0, 0.87, 0.98 and 1.2 mmol g^{-1} for Cu(II), Hg(II) and U(VI) respectively in the pH ranges of 5.5-6.0. Separation of Pd(II) was achieved by taking the advantage that at pH 4.5 when no Pt(IV) ions were sorbed and hence complete separation of these two metals were possible.

Saxena et al [36] used Alizarin Red -S immobilized on Amberlite XAD -2 for the determination of Zn(II), Cd(II), Ni(II) and Pb(II) with exchange capacities of 0.008, 0.001, 0.0024 and 0.0015 mmol g^{-1} respectively in pH ranges of 5 - 6. All four metals were simultaneously separated from well water samples with an average recovery of 97-98% (RSD 4.1 - 8.2 %). Salicyclic acid anchored on Amberlite XAD-2 was used by Saxena et al [37] for Zn(II) and Pb(II) recoveries. The resulting chelating resin was found to be very selective for Zn(II) and Cd(II) having the maximum capacities of 0.018 and 0.002 mmol g^{-1} respectively. Pyrocatechol violet immobolized Amberlite XAD-217 was also used by same group of workers for the separation and determination of Zn(II), Cd(II), Pb(II) and Ni(II). These four metals could also be simultaneously separated from well water samples with an average recovery of 98%. *o*-vanillinthiosemicarbazone immobilized on Amberlite XAD -2 [40] which has three different donor atoms (N,S and O) creating a possibility to form two chelate rings.

The exchange capacities were found to be 0.013, 0.023 and 0.01 mmol g^{-1} for Cu(II), Zn(II) and Pb(II) respectively in the pH ranges of 5 - 7. Both the uptake and stripping processes for these metal ions took place with ease presumably due to better accessibility of the chelating donor atoms. All the metals were eluted by 2 - 4 M HCl with an average recovery of 99% (RSD 2.7 - 3.2%). Lee et al used the resin containing 4 - (2-thiazolylazo) resorcinol (TAR) for the pre-concentration of trace amounts of Cu(II), Ni(II), Pb(II), Co(II), Cd(II) and Mn(II) ions with exchange capacities of 0.81, 0.36, 0.32, 0.27, 0.27 and 0.05 mmol g^{-1} at pH 5.4. Except Cu(II) and Co(II), most of the metal ions were recovered quantitatively (96%) by elution with 10 ml 1 - 2 M HNO_3 at a flow rate of 0.2 ml min^{-1}.Complete desorption of Cu(II) was achieved by using 2M HNO_3 with 98.8% recovery at a flow rate of 0.08 ml min^{-1}. But it was concluded that 100% recovery of Co(II) was not possible due to oxidation of Co(II) to Co(III) and subsequent formation of Co(III)-TAR complex. Interestingly, chloromethylated - PS functionalized with pyridylazonaphthol (PAN) was very effective for the selective separation of Au(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II) and Zn(II) with the distribution co-efficient (log K_d) values in the range 2.5 - 7.9. The method had been examined for application for the pre-concentration of the above metals from tap, river and natural water, human urine, milk and from ores with a considerable recovery of 95 - 99 %. Because of their chemical similarities, it was very difficult to separate group 4 metals like Zr(IV) and Hf(IV). However, Lee et al modified Amberlite XAD-16 by immobilizing 1-(2-thiazolylazo)-2-naphthol (TAN) on it for the separation of Zr(IV) and Hf(IV) from each other in a mixture with exchange capacity values of 0.92 and 0.87 mmol g^{-1} at pH 4.0. Pyrocatechol when immobilized on Amberlite XAD-2 was used by Tewari and Singh [47] and the exchange capacities were found to be 0.040, 0.023, 0.092, 0.073, 0.053, 0.028 mmol g^{-1} for Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II) respectively. The average recovery was found to be 97 to 100 % with a RSD of 1.4 to 2.1 %. The separation method had been found to be useful for the pre-concentration of these metals from river and tap water and from certain medicines. *o*-Aminophenol when it functionalized Amberlite XAD-2 was used by Kumar et al for the separation of Cu(II), Cd(II), Co(II), Ni(II), Zn(II) and Pb(II) with exchange capacity values of 0.053, 0.030, 0.056, 0.055, 0.045 and 0.016 mmol g^{-1} respectively. These metals are desorbed efficiently with 4 M HNO_3 with 91-98 % recovery. Kumar et al [49] also reported the use of Tiron anchored Amberlite XAD-2 for the pre-concentration of trace transition metals including uranium from river water and well water with exchange capacities of 0.22, 0.085, 0.11, 0.22, 0.054, 0.15, 0.18, 0.098 and 0.032 mmol g^{-1} for Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II), Mn(II), Fe(III) and U(VI) respectively in the pH range 4.0-6.0. The presence of a common electrolyte did not interfere in the sorption step. All the metals can be desorbed simultaneously by 4 M HNO_3 or HCl with 91 - 99 % recovery (RSD 8 %). The limits of detection were found to be 2.0, 1.3, 5.0, 4.0, 24.0, 0.5, 2.5 and 5.0 ng ml^{-1} for Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II), Mn(II) and Fe(III) respectively. Quinalizarin anchored Amberlite XAD-2 [50] was used for the recovery of Cu(II), Cd(II), Co(II), Pb(II), Zn(II) and Mn(II) in trace amounts with the exchange capacities of 0.05, 0.015, 0.027, 0.025, 0.02 and 0.017, mmol g^{-1} respectively in the pH range 5.7-7.0. The river water was passed through the column containing the modified resin after adjusting the desired pH and desorbing simultaneously all the metals by 2 - 4 M HNO_3 (RSD 6.5%). Pyrogallol immobilized Amberlite XAD-230 could also serve as a trace metal pre-concentrator. The loading capacities of 0.041, 0.020, 0.046, 0.051, 0.016, 0.032, 0.046, 0.036 and 0.012 mmol g^{-1} were obtained for Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II), Mn(II), Fe(III) and U(VI) respectively at the pH range 5.5 - 7.0. The retained metal ions can be simultaneously desorbed by 2 - 4 M HNO_3 or HCl with an average recovery of 90 - 99 % from river water (RSD 7 %) and well water (RSD 8 %). The azo groups having N chelator and phenolic -OH having O donor made the resin (N,O) donors and should be selective for transition metals ions. The above discussion reflected that most of the designed functionalized resins were selective for transition metal ion separation and thus it could be concluded that the active group containing phenolic -OH if anchored by azo function , should be selective for these metals.

1.4.2 Applications of azo functionalized resins containing heterocyclic N donor sites:

Chattopadhyay et al [55] utilised a resin containing imidazole moiety for the separation of Hg(II) and Ag(I) form waste water. They found that the exchange capacities to be 0.62 and 0.75 mmol g^{-1} respectively for the two metal ions at pH 6.0. Recovery of the sorbed metal ions was quantitative and satisfactory. Das et al reported the use of resin containing imidazole moiety and used it for the separation of Pd(II) and Ag(I) from geological and medicinal samples. The maximum exchange capacities for Pd(II) at pH 5.5 to 6.5 is 0.67 mmol g^{-1} and for Ag(I) 1.49 mmol g^{-1} at pH 4 - 5. The resin produced from the functionalization of polystyrene-DVB with benzimidazole was highly selective for heavy metals like Ag(I), Pd(II) and Hg(II) due to the presence of heterocyclic N atom and the exchange capacities are 1.00, 0.83 and 0.62 mmol g^{-1} for the respective metals in the pH range 4 - 6. The method was applied for the quantitative separation of Ag(I) and Pd(II) from geological samples and Hg(II) from waste water. Banerjee et al separated V(IV) and V(V) from natural water by using a immobilised resin containing imidazole 4,5-dicarboxylic acid. The exchange capacities of V(IV) and V(V) were found to be 0.45 and 1.57 mmol g^{-1} respectively at pH 3.0.

1.4.3 Applications of resins anchored by -CH2- group:

Nitrosoresorcinol functionalized on polystyrene resin was used for the separation of Fe(III) and Co(II) from each other by sorbing the above metals at pH 4 in a short column using a flow rate of 2.5 ml min^{-1}. The retained Fe(III) was eluted first by [35] ml 0.01 M oxalic acid followed by 3 M HCl for Co(II).

The resins containing thiazole and thiazoline [14] was found to be very effective for Hg(II) separation with an exchange capacity of 2.8 mmol g^{-1} in the pH range 1 - 5. Hg(II) ions could be removed from sea water by the use of the solid resin. The resin containing phenylalanine was used by Sugii et al [15]. The resin was highly selective for Cu(II) and Hg(II) at pH 2 -3. In the column method Cu(II) can be separated from Ni(II) and Co(II) and may be used for the pre-concentration of these metals from sea water. Separation of precious metals like Pd(II), Pt(IV), Ru(III) and Rh(III) by the use a chelating resin containing anthranilic acid azide moiety was described by Siddhanta and Das [16]. The metals were separated by sorbing all the ions in a short column at a flow rate of 1.5 ml min^{-1} followed by sequential elution. Sugii et al [14] applied a chelating resin containing triazoethiol and used it for the separation of Ag(I) and Hg(II) with exchange capacities of 7.56 and 3.23 mmol g^{-1} at pH 7. The sea water was pre-concentrated in a short column at a flow rate of 20 ml min^{-1}. The resin containing piperazine as active group was found to be selective for Cu(II). The maximum capacity, 2.4 mmol g^{-1} was achieved at pH 3.0 - 10.5. At this pH, alkali or alkaline earth metals are not chelated or retained. The resin containing histidine moiety [21] was found to be highly selective for Cu(II), Zn(II), Hg(II), Ni(II), Ag(I) and Co(II) with exchange capacities of 2.06, 1.55, 1.50, 1.33, 1.24 and 1.06 mmol g^{-1} respectively at pH 5.5. Chloromethyl polystyrene-DVB functionalized with a series of amino pyrazolone compounds were used by Todorova et al [43] for the recovery of precious metals. The resin exhibited selective separations towards Pd(II), Ag(I) and Au(III) at pH 1.0 with exchange capacities of 0.56, 0.30 and 0.30 mmol g^{-1}.

Phenol-formaldehyde resin anchored with 8-hydroxy quinoline was found to bind Cu(II) selectively at nanogram level with a capacity of 1.74 mmol g^{-1} at pH 3.0. In the column operation Cu(II) can be separated from various synthetic mixtures by sorbing the metal ions in that column after maintaining the pH of the solution at 3.0 under a flow rate of 1 ml min^{-1}. The resin containing thiol and alcoholic –OH groups [29] were reported to be highly selective for Cu(II) over Cd(II), Ni(II) and Zn(II) at pH 5.6. Saha et al used polystyrene functionalized with thiomethyl group for the separation of Cu(II), Cd(II), Ni(II) and Zn(II) with the exchange capacities of 0.13, 0.03, 0.008 and 0.03 mmol g^{-1} respectively at pH 4. Elution was carried out by using 4 M HCl. Poly(vinyl pyridine) functionalised dithizone was used by Shah and Devi for the separation of Pd(II) and Pt(IV) from various metal ions with exchange capacities of

1.0 and 1.29 mmol g^{-1} at pH 5. Thus binary and ternary mixtures containing Pd(II) and Ni(II), Pt(IV) and Au(III), Pt(IV) and Ni(II), Pd(II), Pt(IV) and Ni(II) could be separated from each other by column method. However, separation of Pd(II) from Pt(IV) was not possible because of their similar distribution coefficients. The resin containing dehydrodithizone [49] as a chelating agent was used for the separation of Au(III), Pd(II), Pt(IV), Os(IV), Ir(IV), Ru(III) and Rh(III) with exchange capacities of 0.74, 0.68, 0.31, 0.12, 0.14, 0.14 and 0.16 mmol g^{-1} in 1 M HCl. This resin has been used for the recovery of precious metals.

A chelating resin containing mercapto and amino groups for the collection of Au(III), Pd(II) and Hg(II) along with some transition metals was reported by Zhang et al. The method showed excellent exchange capacities of 4.55, 2.44 and 1.49 mmol g^{-1} for Au(III), Pd(II) and Hg(II) respectively in 2 M HCl solution. Ag(I) was also sorbed at pH 7 with a value of 3.69 mmol g^{-1} .The desorption of palladium [11] was done by 2M HCl containing 1% thiourea with a recovery of 96.5%. Singh and Gupta used diethylenetriaminepentaacetic acid anchored resin for Th(IV) recovery from sea water. The resin was very selective for Th(IV) and In(III) with an exchange capacity of 1.86 and 1.75 mmol g^{-1} respectively at pH 6 for both. The two ions were separated from tap water and sea water by the column method under the flow rate of 4 - 5 ml min^{-1}. The metals were eluted by 1 M HNO_3 and subsequently estimated by EDTA titration.

1.4.4 Applcations of resins having amide linkage:

The resin containing N- phenyl hydroxamic acid [55] utilised its (O, O) donor atoms to bind strongly the metal ions like Cu(II), Fe(III), Ti(IV), U(VI) and Th(IV). pH of the medium played a vital role in the sorption process. Th(IV) and Ti(IV) were sorbed by the resin at pH 1 whereas Cu(II), Fe(III), Al(III) and U(VI) were retained at pH 4. Strongly adsorbed Cu(II), Th(IV) and U(VI) could be eluted with acidic eluents. Orf and Fritz [58] reported the separation of U(VI), Th(IV) and Zr(IV) by the use of a tertiary amide resin from ores like uranite and carnotite at pH 3. At this pH most of the foreign metals did not sorb.The sorbed metal ions then could be desorbed preferentially by using suitable eluting agents. This resin was also used to sorb Au(III) from aqueous HCl solution with an exchange capacity of 1.7 mmol g^{-1}. The sorbed Au(III) was eluted by 0.1 M NaCN and the resin can be used for many sorption and elution cycles. Sugii et al [59] used acyl oxime functionalized resin which washighly selective for Cu(II). The loading capacity for Cu(II) was found to be 2.0 mmol g^{-1} at pH 6 in batch experiment. Sorbed Cu(II) was quantitatively recovered by the use of 1M HNO_3 or HCl.

Cystein anchored polyacrylonitrile was used for Ag(I), Au(III) and Pt(III) recovery by forming chloro complex of the metals. The resin showed high sorption capacities for Au(III), Ag(I), Hg(II) and Pt(IV) with maximum values of 1.22, 0.97, 0.65 and 0.39 mmol g^{-1} respectively. Thiosalicylamide anchored polystyrene-DVB was used by Dasgupta et al [62] for the selective separation of Pt(II) and Pt(IV) with exchange capacities of 0.71 and 0.68 mmol g^{-1} respectively at pH 4.38. Pt(II) was separated quantitatively by 0.5 % KCN. The resin containing benzoyl acetanilide [63] was very selective for Ti(IV) with an exchange capacity of 0.14 mmol g^{-1} at pH 2.1. Das and Das [64] used the chelating resin containing quinaldenic acid amide which they found to be very selective for Hg(II) due to the presence of heterocyclic N donor atom. The exchange capacity of the resin was found to be 1.98 mmol g^{-1} at pH 5.5 in which other elements like Zn(II), Cd(II), Cu(II), Ni(II), Fe(III) were negligibly sorbed. Thus Hg(II) could be separated from waste water by taking the resin in a column at pH 6 and desorbing the metals by 10% thiourea in 1.0 M $HClO_4$. The chelating resin containing quinaldenic acid amide group sorbed metal ions with a sorption capacities for Pt(IV) and Pd(II) to be 0.19 and 0.36 mmol g^{-1} respectively at pH 1. Both the species were sorbed in a short column at a flow rate of 0.5 ml min^{-1}. Pd(II) was eluted by 1% dimethyl glyoxime in chloroform. Then Pt(IV) was eluted by 4M HCl with a recovery of 99 %.

The same resin was used to sorb Ag(I) at a pH of 7.6 with an exchange capacity of 0.68 mmol g^{-1} but Au(III) was preferentially sorbed by the resin at pH 1 with a maximum value of 3.92 mmol g^{-1}. Thus a clear cut separation of Au(III) from Ag(I) was achieved by simply varying the pH of the solution.

The resin immobilized by thioacetamide was used by Konar and Basu [65] for the selective complexation of Cu(II) with a capacity of 0.85 mmol g^{-1} at pH 6. The metal can be separated from a number of foreign metal ions. A binary mixture of Cu(II) and Ni(II) was separated by sorbing both the metals in a column and desorbing Ni(II) by alcoholic DMG and Cu(II) by 4 M H_2SO_4. The recovery was quantitative (99.5%). In an important investigation Styles et al [68] used mercaptoacetamide functionalized resin for the determination and removal of arsenic. The sorption of arsenic was pH depended and it was found that As(V) was effectively sorbed at pH 2 whereas As(III) at pH 8. Both the species were stripped by 0.2 M NH_4OH with an average recovery of 99%. Poly (hydroxy methacrylate) microbeads carrying thiazolidine was used by Saglam et al [60] for the removal of Pb(II) and Cd(II) from an aqueous solution. The maximum exchange capacities of Pb(II) and Cd(II) were found to be 0.336 and 0.0397 mmol g^{-1} showing strong preference towards Pb(II) over Cd(II).

1.4.5 Applications of esterified resins:

Dev and Rao [77] modified Amberlite XAD-4 by functionalizing it with N,N-bis-(2-hydroxyethyl) glycine (bicine) for the studies on the sorption of Cu(II), Fe(II), Ni(II), Co(II), Zn(II), Hg(II) and Pb(II) which gave the exchange capacities of 0.38, 0.44, 0.39, 0.42, 0.38, 0.32 and 0.40 mmol g^{-1} respectively at pH range 5.5-8.0. This process could separate Pb(II) ions in the presence of various metal ions. The same group of workers also used modified Amberlite XAD-4 with bis-(N,N'-salicylidine)-1,3-propanediamine [76] for the separation of Cu(II), Fe(II), Ni(II), Co(II), Zn(II), Hg(II) and Pb(II) ions. The sorbed metal ions were eluted by 1M HCl with a recovery of 98 - 100 %.

Moyer and Fritz used the chelating resin containing hexylthioglycolate (HTG-4) groups for selective sorption of Ag(I), Hg(II), Au(III) and Bi(III). The

exchange capacities were found to be 1.93, 0.99 and 0.76 mmol g^{-1} for Ag(I), Hg(II) and Au(III) respectively at pH1. Amberlite XAD-4 functionalized with 1-hydrazinophthalazine [74] was selective for Fe(III) over Cu(II), Cd(II), Pb(II), Co(II), Ni(II), Zn(II) and Cr(III). Their exchange capacities were found to be 1.32, 1.24, 0.96, 0.86, 0.85, 0.82, 0.74 and 0.62 mmol g^{-1} in the pH range 4.5 - 8.8. The incorporation of 7-aza-1,4,10,13-tetrathia cyclohexadecane into poly-(glycidylmethacrylate) [75] leads to a solid phase resin which was very selective for Ag(I) over Cd(II), Cu(II) and Zn(II) with distribution co-efficient (log Kd) of 3.56 at pH 5.5 - 6.0.

1.4.6 Applications of polycondensed resins:

Polyacrylonitrile functionalized with 1,1-divinylidenediphosphonic acid was very efficient for the sorption of one of the lanthanides- Eu(III) [73]. The complexation was quantitative in 0.04 M HNO_3 solution. A resin obtained from the monomer of dipyridylamide on polymerization was able to separate Pd(II) and Hg(II) from aqueous solutions. The exchange capacities for Pd(II) and Hg(II) were found to be 0.14 and 0.005 mmol g^{-1} at pH 5.5.

The resin having pyridine moiety was selective for Hg(II), Cd(II) and Zn(II) at pH 1. The maximum sorption capacity for Hg(II) was found to be 6.0 mmol g^{-1} in the pH range 1-5. However, the resin also sorbed Cu(II) at pH 4 with a maximum value of 10.2 mmol g^{-1} which was encouraging to pre-concentrate this metal from sea water with a recovery of 98.7 %.

Thus the solid phase extractions using functionalized resins improve the quality,sensitivity and reliability of determination of elements in a wide variety of samples including waste water, industrial and biological materials and contaminated soils. It can be observed from the above discussions that most of the synthetic routes involved classical techniques. A few literatures on the use of microwave irradiation for the purpose were available for the functionalization of the resins. Chelating ligands immobilized on the resins were mainly used for the pre-concentration and separation of ions in low concentrations in the environmental, industrial and biological samples but the chemical speciation studies have been carried out only to a very limited extent. Thus the synthesis of the chelating functionalized resins in large numbers using conventional or microwave irradiation path ways and to examine their applications in the separations and pre-concentration of toxic metal ions from the environment offer excellent area for scientific investigations particularly because of increasing pollution hazards.

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