# *Chapter 1*

# INTRODUCTION

# INTRODUCTION

## I-A- General Introduction:

In the past, many types of metal-chelating adsorbents have been synthesized(1). Syntheses have been accomplished with either polymerization or simple functionalization principles. The former involves the polymerization of monomers containing the desired ligands. The modification of a preshaped polymer by functionalization reactions is a favorite process of enhancing metal selectivity.

Functionalized polymers are used for a variety of applications, these include organic syntheses(2), metal ion separation(3),pollution control(4), polymer drug grafts(5), waste water treatment(6), and uptake of trace metal ions(7,8).

Three major techniques are currently used for the removal and / or separation of trace metal ions from aqueous solution : liquid-liquid extraction (LLX), ion exchange (IEX), usually involving chelating resins, and a combination of extraction / ion exchange, i.e. solvent impregnated resins (SIRs). Liquid – liquid extraction is widely used in the treatment of relatively concentrated aqueous solutions but it is less suitable for processing large volumes of solution containing trace amounts of metal due to solvent solubility losses and third phase formation (9-11).

The concept of SIRs has been known for at least twenty five years and is a compromise solution to this problem, relying on the synergistic benefit of liquid- liquid extraction and solid phase ion exchange(12, 13).

In view of the expectation for increasing of environmental pollution by toxic heavy metals like cadmium, zinc, nickel, lead, mercury and cupper , the need to look for selective resins to extract these metals should be increasing as some trials seen to be promising.

The term heavy metals that is in common use, refers to metals with a density greater than a certain value, usually 5 or 6 g / $cm^3$. Often it refers to metals discharged by industry of which the metalloid arsenic, cadmium, chromium, cupper, lead, mercury, nickel and zinc are listed by European Commission directive as representing the greatest hazard to plants or human(14).

The use of ion exchanger and metal complexing polymers for the recovery of heavy metals has not been thoroughly investigated like the solvent extraction reagents . Recently polymeric materials have an interest to use to the environmental remediation(15-21), owing to their high capacities(22,23).

Polymeric materials containing chelating groups which chelate heavy metal ions are applied in the solution of a variety of ecological and industrial waste problems(24-26). Therefore, such polymers continue to attract the attention of many researchers(26-30). In particular, inclusion of heterocyclic amine units into polymeric matrices as the chelating centers results in promising materials for the separation of heavy metal ions from aqueous solutions(31-41).

Chelating resins containing aminophosphonate(42), dithio-carbamate(43), hexylthioglycolate(44), iminodiacetate(45), isothiouronium(46), poly (ethylene mercaptoacetamide)(47), thioacetamide(48), thiol(48,50), thiosemicarbazide(51) are generally employed for heavy metal sorption.

## I-A-1- Health effect of heavy metals:

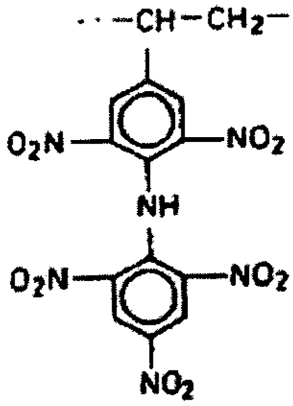
Removal of heavy metals from aqueous solution is necessary because of frequent appearance of these heavy metals in wastewaters from many industries, including electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries.

The toxic effects of heavy metals result in damaged or reduced function of the central nervous system, reduced availability of biological energy, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure to heavy metals may result in chronic physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. In addition, toxic metals can increase allergic reactions, cause genetic mutation, compete with good trace metals for biochemical binding sites, and act as broad range antibiotics against both harmful and beneficial bacteria (52). Heavy metal toxicity and the danger of their bioaccumulation in the food chain represent one of the major environmental and health problems of our modern society. Thus presenting a high health risk to consumers(53). Hence, removal of heavy metals from industrial wastewater is of practical interest. Many physicochemical methods have been developed for heavy metal removal from aqueous solution, including chemical coagulation, adsorption, extraction, ion exchange and membrane separation process(54-57). Among these methods, ion exchange is a highly popular one and has been widely practiced in industrial wastewater treatment process.

## I-A-2- Chelating Resins:

The chelating resin is an ion-exchange resin that has been developed as a functional polymer, which selectively catches ions from solution including various metal ions and separates them. It is made of a polymer base of three-dimensional mesh construction, with a functional group that chelate-combines metal ions.

The chemistry of these new types of complexing resin began when Skogseid(58) described the first such resin, a polystyrene derivative containing dipicrylamine groups (I) and specific for potassium ion. This was followed by incorporating a variety of chelating groups on different types of polymeric matrices(59).



I

## I-A-3- Properties of chelating resins:

Gregor, et al.(60)has suggested the following properties for a chelating polymer:

(1) The copolymer formed must have sufficient physical and chemical stability.

(2) The chelating monomer must not lose its complexing ability during polymerization.

(3) Chelate ring formation must not be obstructed by the polymer matrix. A compact chelating molecule may be more desirable .

(4) The ligand groups must be properly situated in the polymer matrix to achieve total complexation.

As a consequence of their electronnegativity; nitrogen, oxygen, sulfur, phosphorous and arsenic can function as electron donors in ligand molecules. Of course, ligand groups within chelating resins must contain these donor atoms, and they must be selected to give specific chemical and physical properties.

## I-A-4- Advantages of extraction by chelating resins:

Extraction of metal ions using chelating resins has several advantages over conventional methods as the following:

1- Selective determination of metal ions will be possible by using a chelating resins having a ligand possessing high selectivity to the targeted metal ion.

2- It is free from difficult phase separation, which is caused by the mutual solubility between water and organic solvent layers.

3- The chelating resin method is an economical method since it uses only a small amount of ligand.

4- Trace metal ions at as low as ppm can be determined because the targeted ion is enriched on the solid phase.

5- The concentration of metal ion can be visibly estimated from the color intensity of the solid phase if the metal complex formed possesses adsorption in the visible wave length region.

6- Use of carcinogenic organic solvents is avoided and thus the technique is eco friendly to nature.

### I-A-5- Synthesis of chelating resins:

D. Alelio et al.(61) proposed an orderly approach to the synthesis of a chelating polymer . They suggested that the synthetic steps should include the following:

1- Synthesize the model and monomer compounds and determine their chelating characteristics .

2- Synthesize and determine the chelating characteristics of the dimmer, trimer, and progressive low molecular weight oligomers of the model compound .

The various methods of preparing chelating resins are(62):

(a) Condensation resins incorporating a chelating ligand.

(b) Condensation resins chemically converted to chelating resins.

(c) Addition polymerization of vinyl monomers of chelate forming compounds.

(d) Crosslinked vinyl polymers chemically converted to chelating resins .

(e) Linear polymers chemically converted to chelating polymers followed by a cross linking reaction .

### I-A-6- Some general applications of chelating resins :

Chelating polymers containing silicon atoms or siloxane groups are useful for bonding glass, aluminum, iron, and other metals at high temperatures(63)and have possible application in the aerospace industry.

Luminescence studies,(64) magnetic susceptibility measurements, and studies regarding the semiconducting properties of complexed resins have been made (65).

Polymers of high light sensitivity were prepared by mixing polymers containing oxygen, sulfur, phosphorous, nitrogen, halogen, or a coordinating aromatic nucleus with transition metal salts to form coordination compounds that show reversible or irreversible color changes when exposed to visible, infrared, or ultraviolet light(66). These studies are directly related to electrophotography.

Poly(pyromellitimide) complexes with silver (I), chromium (III), and nickel (II), formed heat conductive dielectrics without appreciably increasing the electrical conductive coefficient of the metal chelate polymer(67). These resins may be useful in the construction of heat conductive coatings.

Chelate forming exchange resins have been studied for their application to analytical problems. As recent examples, two publications have cited chelating polymers in the microanalyses of copper and alkaline earth metals (68). Proven analytical applications and the emphasis placed on ecology has prompted the investigation of chelating polymers as water treatment agents(69).

Styrene-maleic anhydride resins have been incorporated into floor polishes to improve detergent resistance through ionic cross-linking of the functional groups in the resin with zinc and zirconium metals(70). Chelate polymers have also been studied as a new type of catalyst, Angelescu(71)has compiled a review on the preparation and catalytic properties of selected chelate polymers.

## I-A-7- Classification of chelating resins according to donor atom:

The analytical application of chelating polymers depends on many factors. Normally a metal ion exists in water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and/or donor atom capable of forming complexes with the metal ions in solution, and it is logical to classify chelating polymers on this basis. Also, for simplicity, it is desirable to classify chelating polymers according to Fig. 1. This method of classification is not meant to imply that these systems are mutually exclusive. Indeed, some polymers can belong to more than one class, depending on experimental conditions.

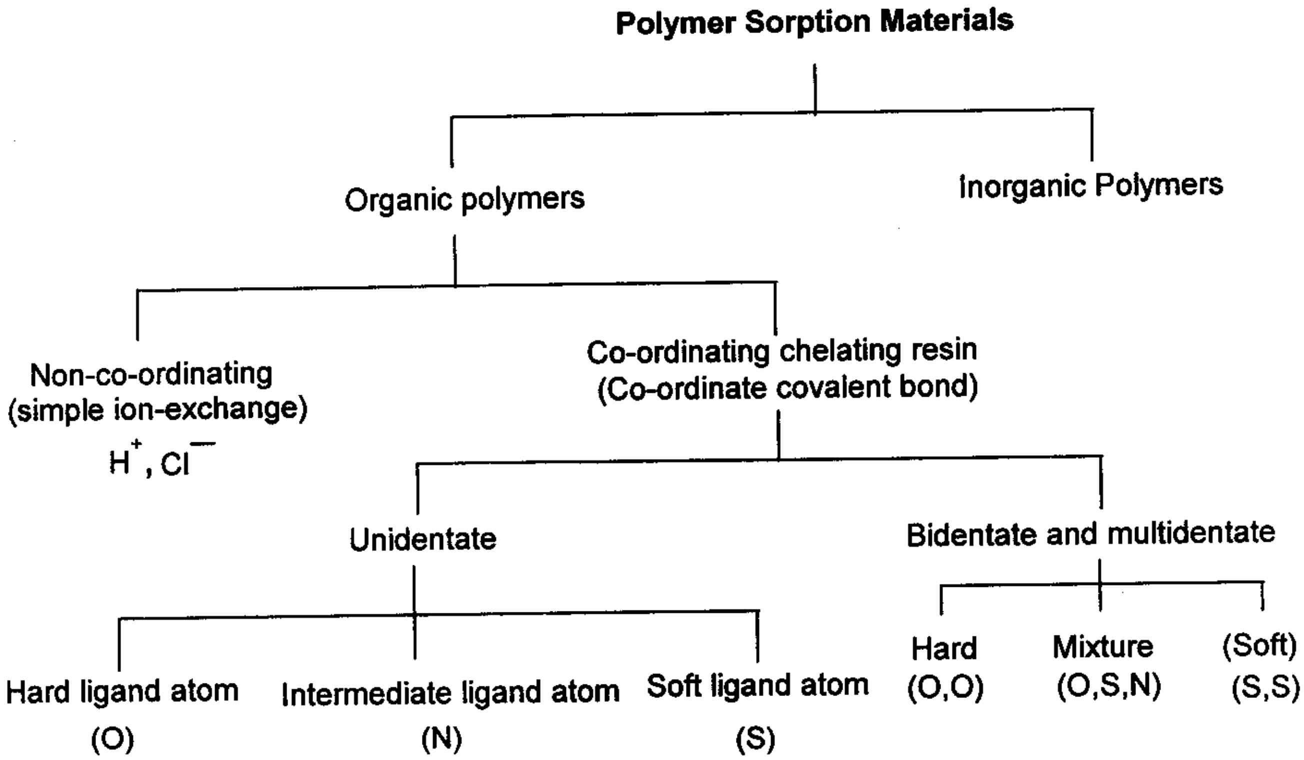


**Fig. (1):** Classification of chelating resin according to donor atom.

## I-A-8-Functional groups of chelating resins:

The functional group atoms capable of forming chelate rings usually include oxygen, nitrogen and sulfur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen is usually in the form of phenolic, Carbonyl, carboxylic, hydroxyl, ether, phosphoryl and some other groups. Sulfur is in the form of thiol, thioether, thiocarbamate, disulphide groups *etc.* These groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbents from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal ions or metal species under certain favorable conditions, to form chelate rings. The functional groups in the chelating polymer materials usually act as bases; oxygen-containing functional groups are hard while sulfur containing groups are soft. Functional groups with a basic nitrogen atom have an intermediate character.

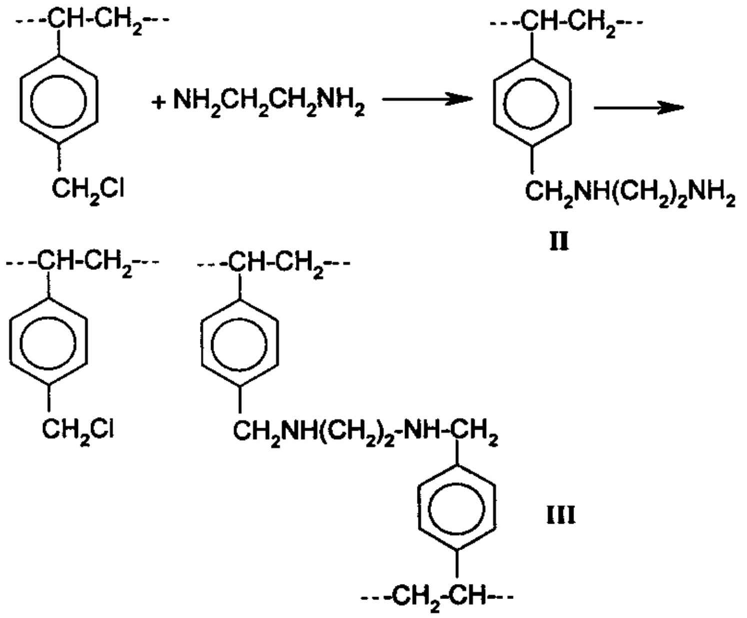
# I-B-Literature Survey

## I-B-1- Survey of available chelating ion-exchange resins:

In the following sections, a brief survey of available chelating ion-exchange resins will be presented, classified according to their donor atoms.

### I-B-1-a- Chelating ion-exchange resins containing nitrogen as the only donor atom:

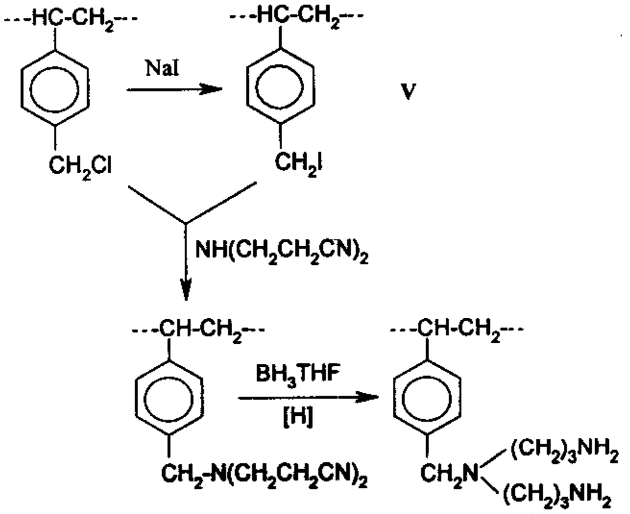
Chelating resins containing polyamine functional groups form an important class of such ligands. Several authors (72-76) have studied the modification of synthetic resins with polyamines, such as ethylenediamine, diethylenetriamine, and triethylenetetramine and conflicting claims regarding the constitution of these chelating resins have been made. The reactions of cross-linked chloromethylated styrene with several polyethylene polyamines indicates that these polyamines are linked to the matrix by one or more bridges by the amination reaction, depending upon their length(72,73). These reactions appear to proceed in a fashion depicted in (Scheme 1) for amination of chloromethylated polystyrene with ethylenediamine. Two products, monoaminated polystyrene (II) and diamineated polystyrene (III) are obtained(73).



**Scheme 1**

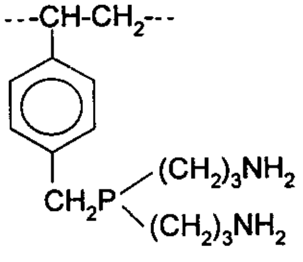
The reaction of several polyethylenepolyamines with chloromethylated "popcorn" polystyrene resins, using pyridine as reaction medium had been studied(74). It was observed that the rate of chloride displacement decreased with increasing molecular weight of the amine and higher degree of resin chloromethylation, while the extent of multiple attachments to the polymer matrix increased. The additional crosslinking, as a result of multiple attachments, caused the polyamine to swell to a lesser extent in pyridine and water. It has been found that the capacity of the resin containing ethylenediamine with respect to its adsorption of copper (II) ions from dilute solutions increases with increasing amount of ethylenediamine. With diethylenetriamine the capacity remains unchanged, while with triethylenetetramine, the capacity was found to decrease. The complexation and protonation of chelating ion-exchange resins containing ethylenediamine functional groups have also been studied and the apparent stability constants of copper (I), copper (II), nickel (II), zinc (II) and cadmium (II) complexes determined(77).

A versatile high-yield synthesis for covalently attaching multidentate chelating ligands to polystyrene matrices was described(78). Polymeric substrates containing polydentate amines as discrete units can be obtained by reacting chloro- or iodo- methylated polystyrene with bis(cyanoethylamine) (IV), followed by $BH_3$.THF reduction, to provide polymer-attached bis(3-aminopropyl)amine (V) as depicted in (Scheme 2).

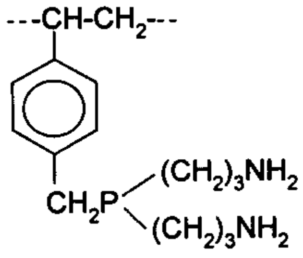


**Scheme 2**

Three polydentate amines, bis(3-minopropyl)amine, bis(3-aminopropyl) phosphine and diaminopropane have been anchored onto a polystyrene matrix to obtain three polymer-supported multidentate chelating ligands designated by structures such as, e.g., (VI) and (VII), respectively. These materials form the basis for the preparation of a wide variety of chelating ligands, e.g., through the Schiff base reaction with a variety of aldehydes and ketones.

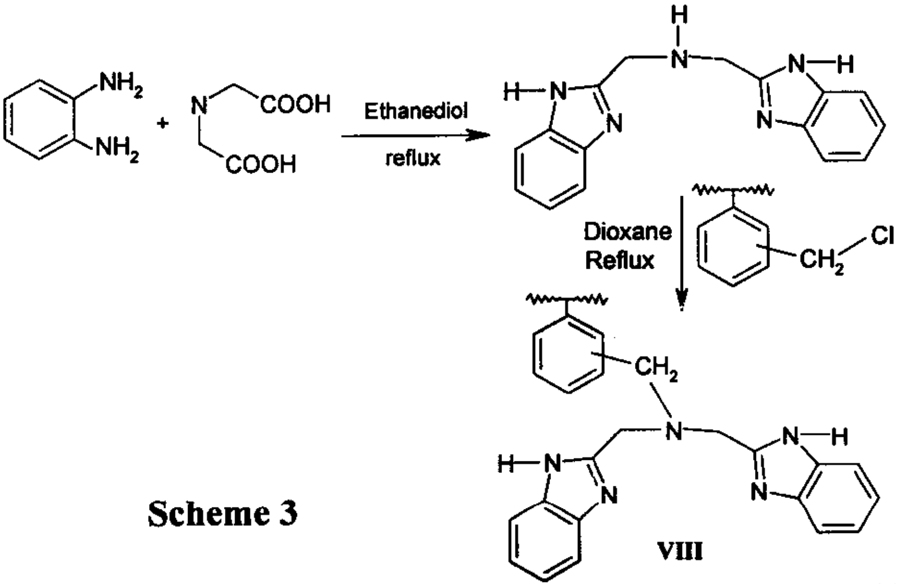


**VI**



**VII**

A new stable chelating resin [(VIII), Scheme 3] was synthesized by incorporating the bis(2-benzimidazolyl methyl)amine into Merrifield polymer through C-N covalent bond and characterized by elemental analysis, IR and thermal study<sup>(79)</sup>. The sorption capacity of the newly formed resin for Ag (I), Cu (II), Fe (III), Hg (II) and Pb (II) as a function of pH have been studied. The resin exhibits no affinity for alkali or alkaline earth metals. In column operation it has been observed that Ag (I) in trace quantities can be separated from different complex matrices and Hg (II) can be removed from the river water spiked with Hg (II) at usual pH of natural waters.



**Scheme 3**

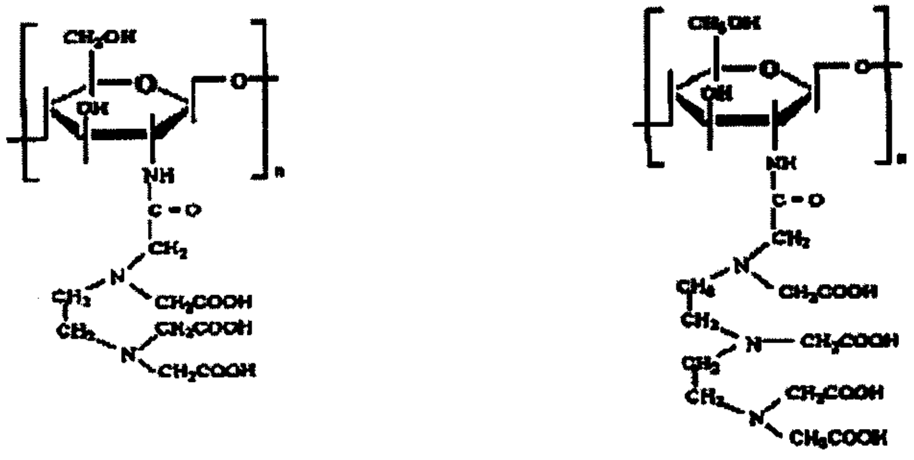
### I-B-1-b- Chelating ion-exchange resins containing nitrogen and oxygen as donor atoms:

This forms the largest group of chelating ion-exchange resins. The important ligands possessing nitrogen and oxygen as donor atoms include iminodiacetic acids, hydroxamic acids, oximes, amides, hydroxyquinoline derivatives and Schiff bases, which are discussed in this section.

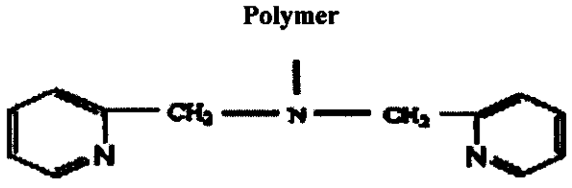
#### *(a) Chelating resins containing iminodiacetic acid and related ligands:*

Iminodiacetic acid and its derivatives have been incorporated into a variety of matrices, including both addition and condensation resins.

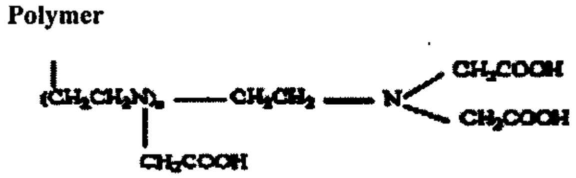
The selective recovery of Ni from slightly acidic sulfate solution was attempted by means of ion exchange with Dowex XFS 4195 resin and complexane types of chemically modified chitosan (Scheme 4)(80). The batchwise experimental results showed good selectivity for Ni over Al for both chelating adsorbents. Fixed bed experiments using a packed column were also carried out. The breakthrough experimental results showed that a large amount of Al is immediately brokenthrough just after the initiation of the feed, while in the case of XFS 4195 resin, the breakthrough of Ni begins at 40 bed volumes (BV), suggesting that it is possible to purify Al free from Ni contamination by stopping the feed before 40 BV and, in the case of complexane types of chemically modified chitosan (DTPA-chitosan), the breakthrough of Ni begins at 5 BV. The loaded adsorbent can be eluted effectively with 0.5 M sulfuric acid and only a trace amount of Al is eluted while Ni is eluted concentrated to more than 10 times its concentration in the feed solution in the case of XFS 4195 resin and more than 23 times its concentration in the case of complexane types of chemically modified chitosan. These results indicate the successful separation and purification of small amounts of Ni from a large excess of Al with XFS 4195 resin and complexane types of chemically modified chitosan.



**EDTA-Chitosan** **DTPA-Chitosan**



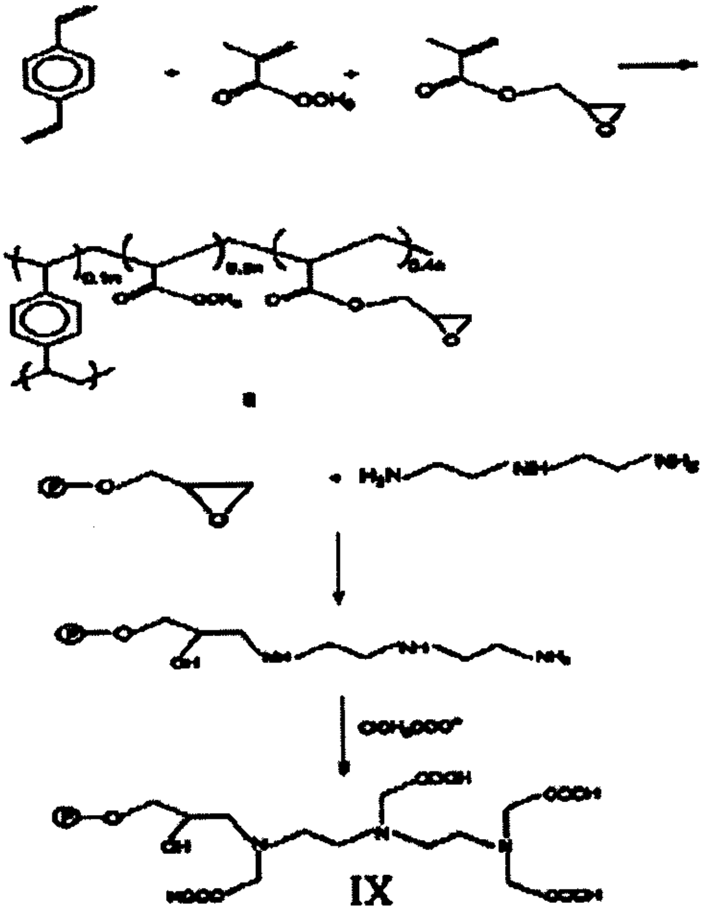
**Picolylamine resin**



**Polyamino carboxylic acid resin**

## Scheme 4

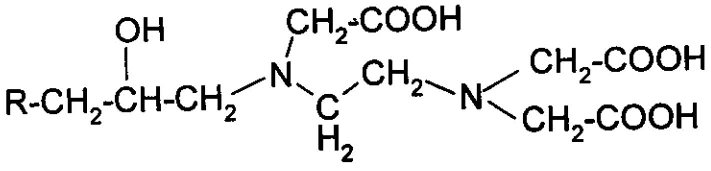
The Cross-linked terpolymer beads [(IX), Scheme 5] prepared by suspension polymerization of glycidyl methacrylate (GMA), methylmethacrylate (MMA) and divinyl benzene (DVB) mixtures have been modified through epoxy functions in two steps: (i) by treating with excess of diethylene triamine (DETA); and (ii) by subsequent reaction with potassium chloroacetate(81). The resulting polymer possessing diethylene triamine tetra acetic acid (DTTA) functions is an efficient sorbent for removal of Ca (II) and Mg (II) ions in ppm levels. Interestingly when the sodium form of the resin is used in relatively high concentrations (0.1 M) sorbed amounts will be 10-45% in excess of the theoretical capacity due to precipitation of the metal hydroxides on polymer particles beside chelation with the metal ions. Having EDTA-like chelating units, the polymer is able to absorb also heavy metal ions such as Fe (III), Zn (II), Cd (II), Pb (II), Ni (II), Cu (II), Co (II) ions. Not having hydrolysable linkages, metal-free resins can be obtained by acid treatment (4 M HCl) without loosing its activity. The resin with DTTA functions seems to be applicable in large scale water softening processes.



IX

**Scheme 5**

Glycidyl methacrylate-divinyl benzene (GMA/DVB) resin bearing minoacetate function (X) was prepared through subsequent treatment of (GMA/DVB) resin by ethylenediamine and potassium chloroacetate, respectively(82). The chelating resin obtained showed a powerful adsorption character toward non-transition metal ions ($Zn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$) as well as alkaline earth metal ions ($Ca^{2+}$ and $Mg^{2+}$). The sodium form of the resin gave a slightly higher uptake capacity towards metal ions compared to the hydrogen form. The resin sample loaded with metal ions was regenerated using HCl (0.5-2.0 M) without activity loss.



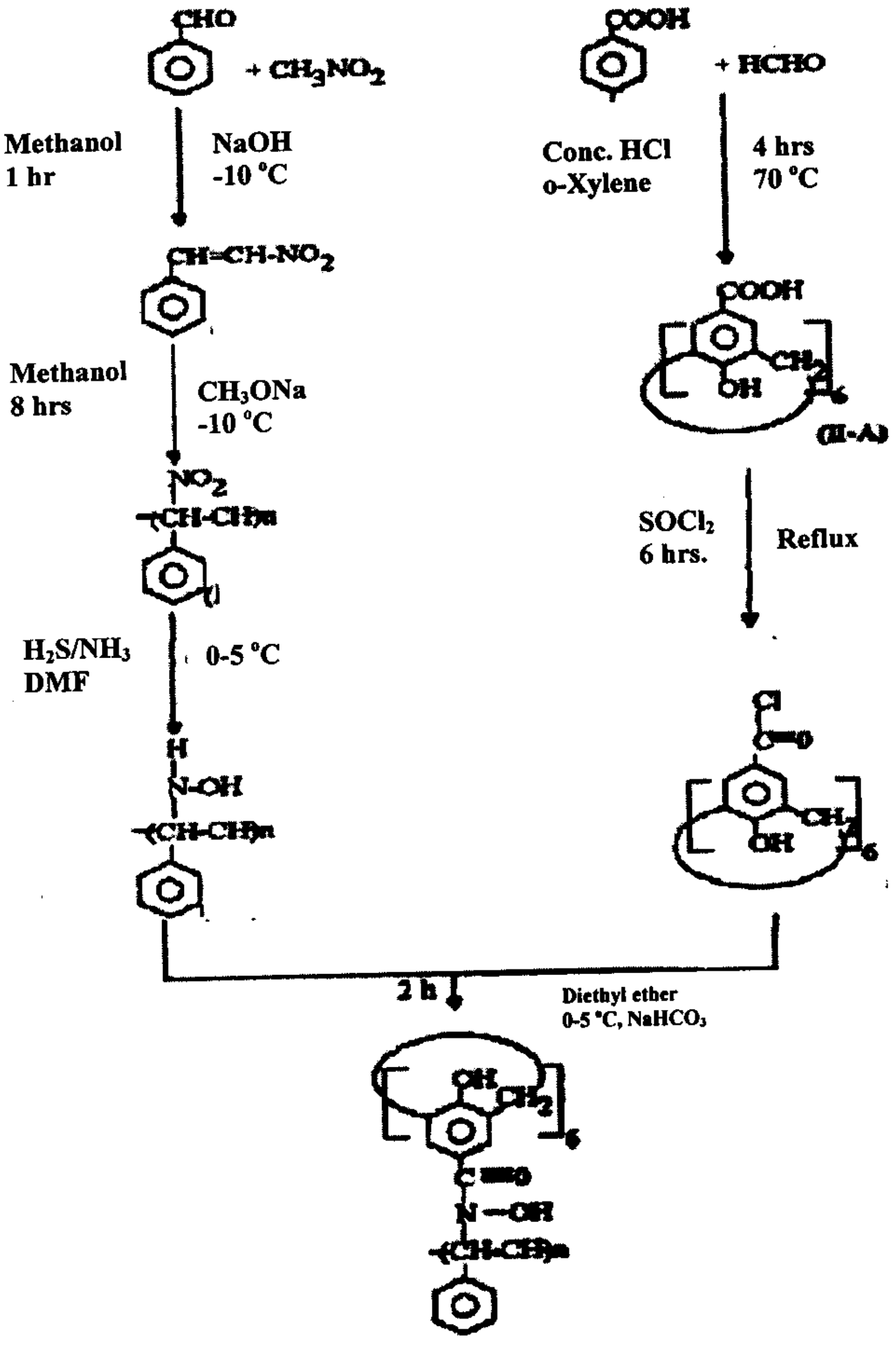
R = GMA/DVB Polymeric matrix

X

***(b) Hydroxamic acid, oxime, oxine, amides,*** **Schiff bases,** ***and azo-containing ion exchange resins:***

Development of polymeric ligands incorporating hydroxamic acids can be attributed to their ability to form stable complexes with heavy metals,

A new polymer-supported calix[6]arene hydroxamic acid [(XI) Scheme 6] has been synthesised by reacting the acid chloride 37,38,39,40,41,42 hexahydroxy 1,8,13,19,25,31 hexacarboxy calix[6]arene with poly(styrene b-hydroxylamine)(83). Physicochemical properties viz. swelling, wet-density, void-volume, exchange capacity etc. were determined. The resin has 4.46 mmol/g exchange capacity for rare elements. The resin was used for the chromatographic separation of U (VI), Th(IV) and Ce(IV) by the judicious adjustment of pH 4.0, 6.0 and 7.5, respectively. The thorium and cerium were eluted with 0.1 M HCl while uranium was eluted with 2M HCl. These rare elements were preconcentrated and determined in the presence of each other, monazite sand and environmental samples.



XI

Scheme 6

A related group of ligands, amidoximes, is the basis of the synthesis of some very useful chelating ion-exchange resins. Amidoxime resins are being increasingly studied because of their ability to selectively bind to several metal ions such as iron (III), copper (II) and uranyl (II) at very low pH range.

The preparation of a chelating ion-exchange resin containing amidoxime functional group was carried out by polyacrylonitrile (PAN) grafted sago starch(84). The PAN grafted copolymer was obtained by free-radical initiating process using ceric ammonium nitrate as an initiator. Conversion of nitrile groups of the grafted copolymer into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. The chelating poly (amidoxime) resin was characterized by FT-IR spectra, TG and DSC analyses. The chelating behavior of the prepared resin was carried out by using some metal ions. A significant binding property of metal ions by the chelating resin was observed and the maximum copper capacity was 3.0 mmol /g at pH 6. The sorption capacities of metal ions by the resin were pH dependent, and its selectivity towards these metal ions is in the following order: $Cu^{2+} > Fe^{3+} > As^{3+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Cr^{3+} > Pb^{2+}$. A possible chelation mechanism of amidoxime with bivalent metal ion for the complexation is shown below.

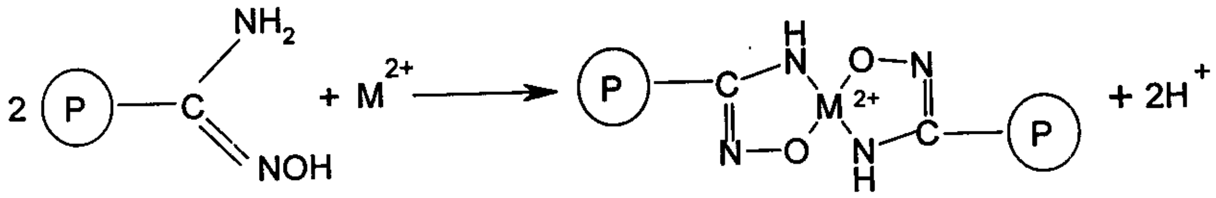
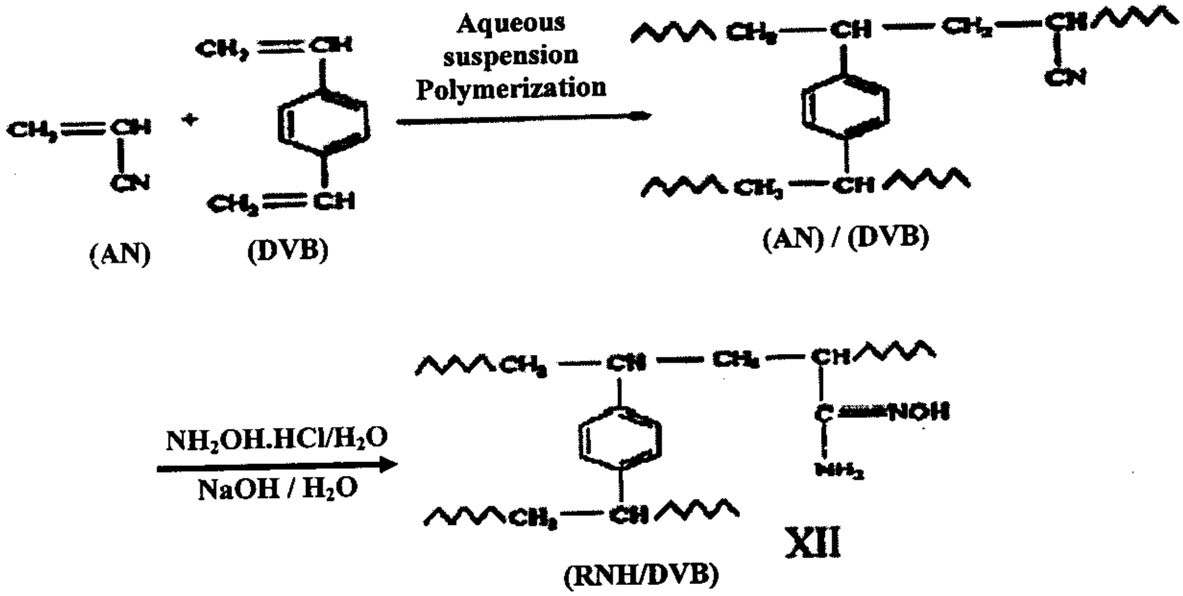


**Fig. (2):** Chelation mechanism of amidoxime with bivalent ion.

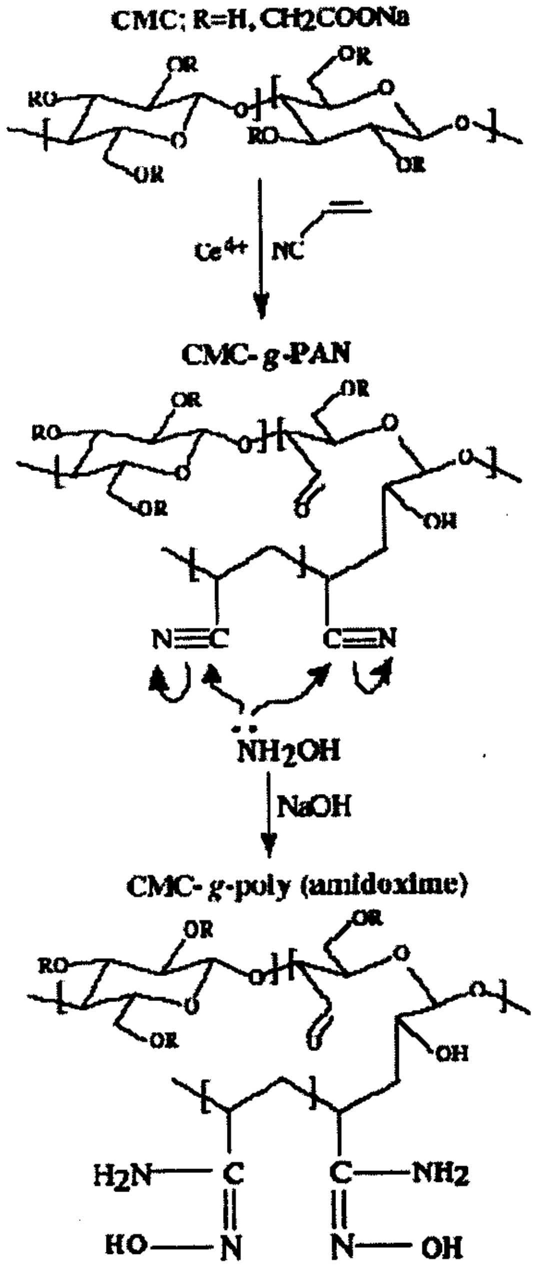
Macroreticular chelating resins containing amidoxime groups [(XII), Scheme 7] was prepared by aqueous suspension copolymerization of acrylonitrile (AN) and divinylbenzene (DVB) and subsequent chemical modification of cyano groups by reaction with hydroxylamine (85) . In the copolymerization, the effects of divinylbenzene proportion and dilution degree on the copolymer pore structure were investigated. The amidoxime resins were finally evaluated in relation to the complexation capacity of copper ion.



XII

Scheme 7

Carboxymethylcellulose sodium salt (CMC) which doubly modified to prepare a novel poly(acrylamidoxime) chelating resin [(XIII), Scheme8](86). Acrylonitrile was firstly graft polymerized onto CMC using cerium ammonium nitrate as an initiator. The polyacrylonitrile (PAN) grafted CMC was then amidoximized via treatment with hydroxylamine to prepare the ion exchange resin. The sorption capacity of the resin towards bivalent metal ions was evaluated while varying the pH, the loading of the PAN and the initial metal ion concentration. The adsorption kinetics were investigated for the cupric ion. The chelating resin exhibited very high metal sorption capacity in comparison with either synthetic or polysaccharide based resins and the sorption rate was also comparable. Therefore, the resin may be considered as a good candidate to develop as an efficient biopolymer-based chelating resin for water treatment.



XIII

Scheme 8

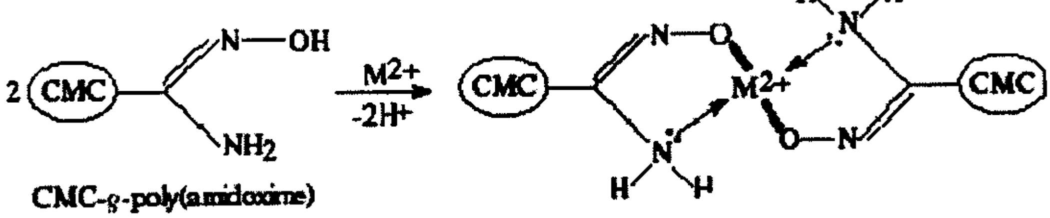
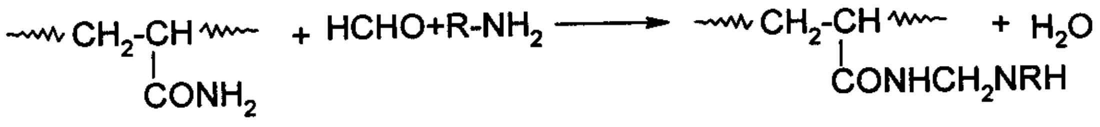


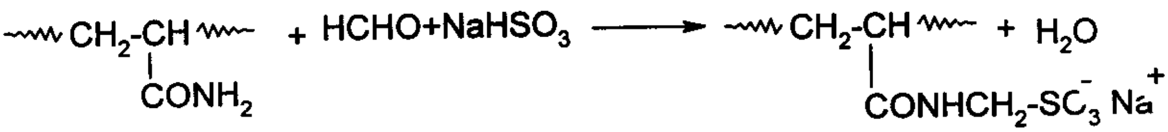
Fig. (3): Chelation mechanism of CMC-g-poly (amidoxime) with bivalent ion

Modified crosslinked polyacrylamides having different functional groups were made by Mannich reaction (Scheme 9) using different amine compounds such as ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) and sulfomethylation. Reaction products (Scheme 10) were characterized by determination of their basic group content (BGC), hydroxymethyl group content (HMG),equilibrium degree of swelling (EDS) and FT-IR spectra⁽⁸⁷⁾. For Mannich reactions, BGC and EDS changed with amount of employed amine compounds, reaction time and temperature. Sulfomethylation reactions gave products with high BGC and very high EDS. FT-IR spectroscopic analysis confirmed that a parallel hydrolysis reaction occurred along with the expected modification reactions. The products were used for removal of Cu (II), Cd (II) and Pb(II) ion under competitive and non-competitive conditions at different pH. The metal ion removal capacities changed depending upon their BGC and EDS. While the Mannich products were selective towards Cu (II) ion, the sulfomethylation products were highly selective to Pb (II) ions. The polymers were used several times by regeneration without loss of adsorption capacity and changing of selectivity properties.



$$\sim CH_2\text{-}\underset{\substack{|\\ CONH_2}}{CH}\sim \; + HCHO + R\text{-}NH_2 \longrightarrow \; \sim CH_2\text{-}\underset{\substack{|\\ CONHCH_2NRH}}{CH}\sim \; + H_2O$$

**Scheme 9**

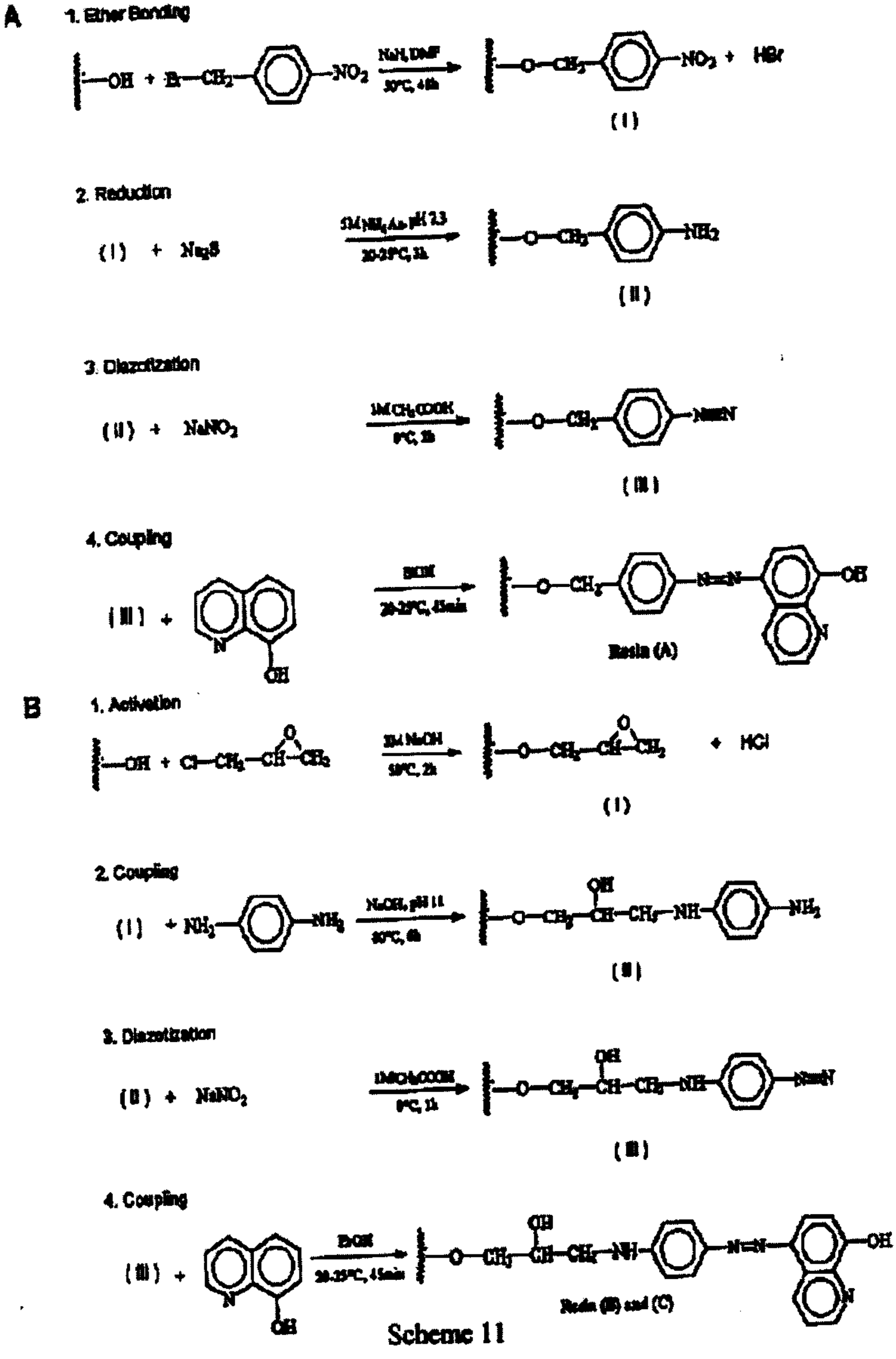


$$\sim CH_2\text{-}\underset{\substack{|\\ CONH_2}}{CH}\sim \; + HCHO + NaHSO_3 \longrightarrow \; \sim CH_2\text{-}\underset{\substack{|\\ CONHCH_2\text{-}SC_3^- Na^+}}{CH}\sim \; + H_2O$$

**Scheme 10**

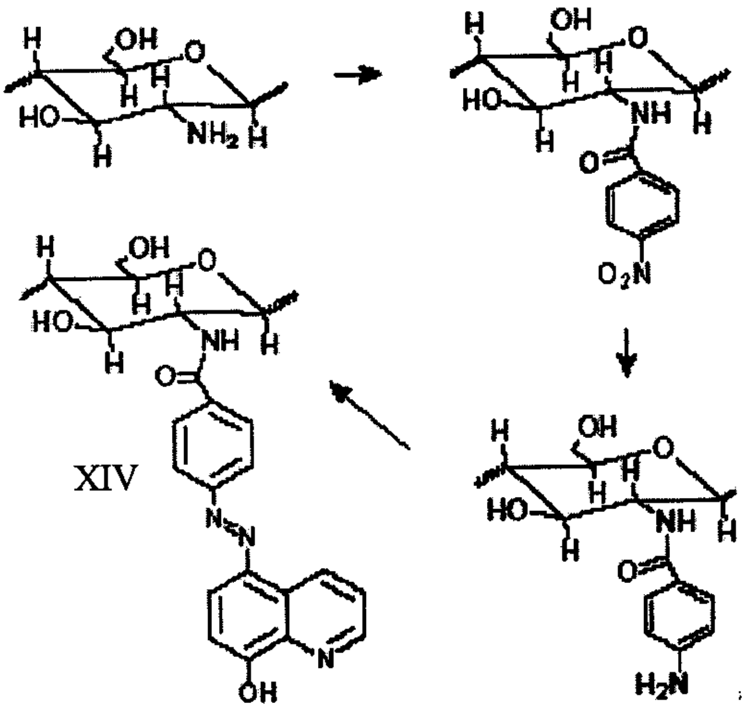
The chelating ion-exchange resins incorporating 8-hydroxy quinoline (oxine or 8-quinolinol) form an important and extensively studied class of selective ion exchangers. A simplified synthesis, and some performance characteristics, for

8-hydroxyquinoline 8-HOQ covalently bonded to a chemically resistant TosoHaas TSK vinyl polymer resin was done (Scheme 11)(88) . The resin was used to concentrate trace metals from stored, acidified seawater samples. The Mn, Fe, and Zn profiles determined from the 8-HOQresin extractions were similar to those determined using Chelex-100 resin. The Zn and Cd profiles did not exhibit removal by sulfide (Stripping) in contrast to other anoxic marine basins. The profiles of Co and Ni also exhibited elevated concentrations in the anoxic hypolimnion. The solution speciation and saturation states for the metals were calculated using revised metal-bisulfide stability constants. The calculations suggest that the MS $(HS)^-$ species dominates the solution speciation for Mn, Co, Ni, Zn, Cd, and Pb. Cu (I) is modeled as the $CuS^-$ or $Cu(HS)2^-$ species, while Fe( II )behaves as the free $Fe^{2+}$ cation. The Mn, Co, Ni, Cu and Cd concentrationsappeared to be at least. 10-fold undersaturated, while the Fe (II), Zn, and Pb concentrations were close to saturation with respect to their metal Sulfides·


A
1. Ether Bonding
NaH, DMF
30°C, 4h
(I)
2. Reduction
(I) + Na₂S
20-25°C, 2h
(II)
3. Diazotization
(II) + NaNO₂
1M CH₃COOH
0°C, 2h
(III)
4. Coupling
(III) +
Resin (A)
B
1. Activation
1M NaOH
50°C, 2h
(I)
2. Coupling
(I)
NaOH, pH 11
80°C, 6h
(II)
3. Diazotization
(II) + NaNO₂
1M CH₃COOH
0°C, 1h
(III)
4. Coupling
(III) +
EtOH
20-25°C, 45min
Resin (B) and (C)

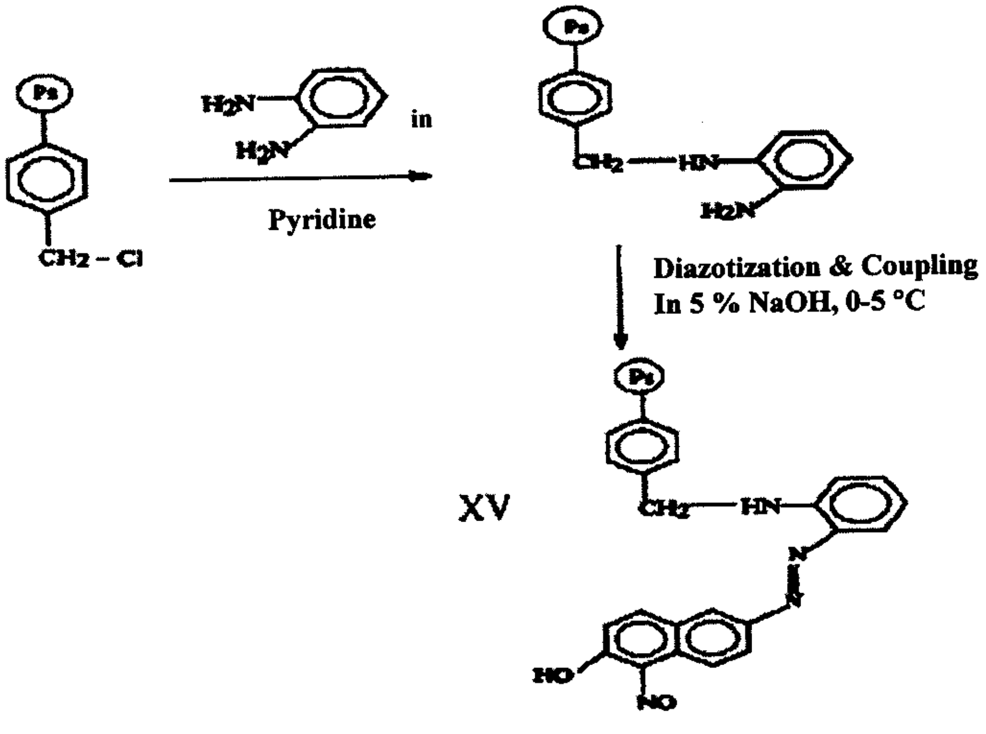
Scheme 11

This study describes the functionalization of biopolymer chitosan, using the complexing agent 8-hydroxyquinoline (oxine) [(XIV), Scheme 12] by reaction of diazotization (89). The efficiency of the chelating resin and accuracy of the proposed method was evaluated by the metal ion recovery technique in the analysis of potable water, lake water, seawater and a certified sample of oyster tissue. The metal ions Cd (II) and Cu (II) in the samples were previously enriched in a mini column and flow injection flame atomic absorption spectrometry (FI-FAAS) determined the concentrations of the analytes. The chelating resin exhibited high selectivity for Cd (II) at pH 7 and for Cu (II) at pH 10. The eluent concentration was tested by the use of $HNO_3$ in concentrations of 0.1-3 mol /L maximum response was obtained at 0.5 mol /L for Cd (II) and Cu (II), with R.S.D. values of 0.4%. The analytical properties of merit were obtained using the parameters previously optimized with preconcentration time of 90 s. The chelating resin showed chemical stability within a wide range of pH and the efficiency was not altered for the preconcentration of the metal ions during all the experiments



Scheme 12

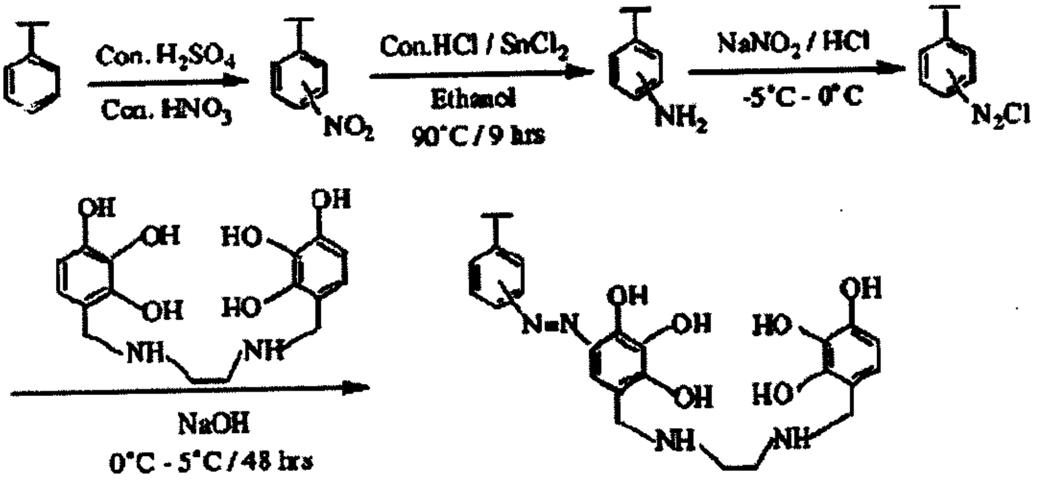
Chelating ion-exchange resin with a spacer $CH_2$-NH-$C_6H_4$- based on chloromethylated styrene-divinylbenzene copolymer containing α- nitroso-β-naphthol as a functional group has been synthesized [(XV), Scheme 13]$^{(90)}$. The sorption characteristics for manganese(II), iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) have been investigated over the pH range 1.0-7.0. The resin is highly stable in acidic and alkaline medium. Iron(III) and cobalt(II); copper(II) and iron(III) are separated very effectively in a column operation by stepwise elution·



XV

Scheme 13

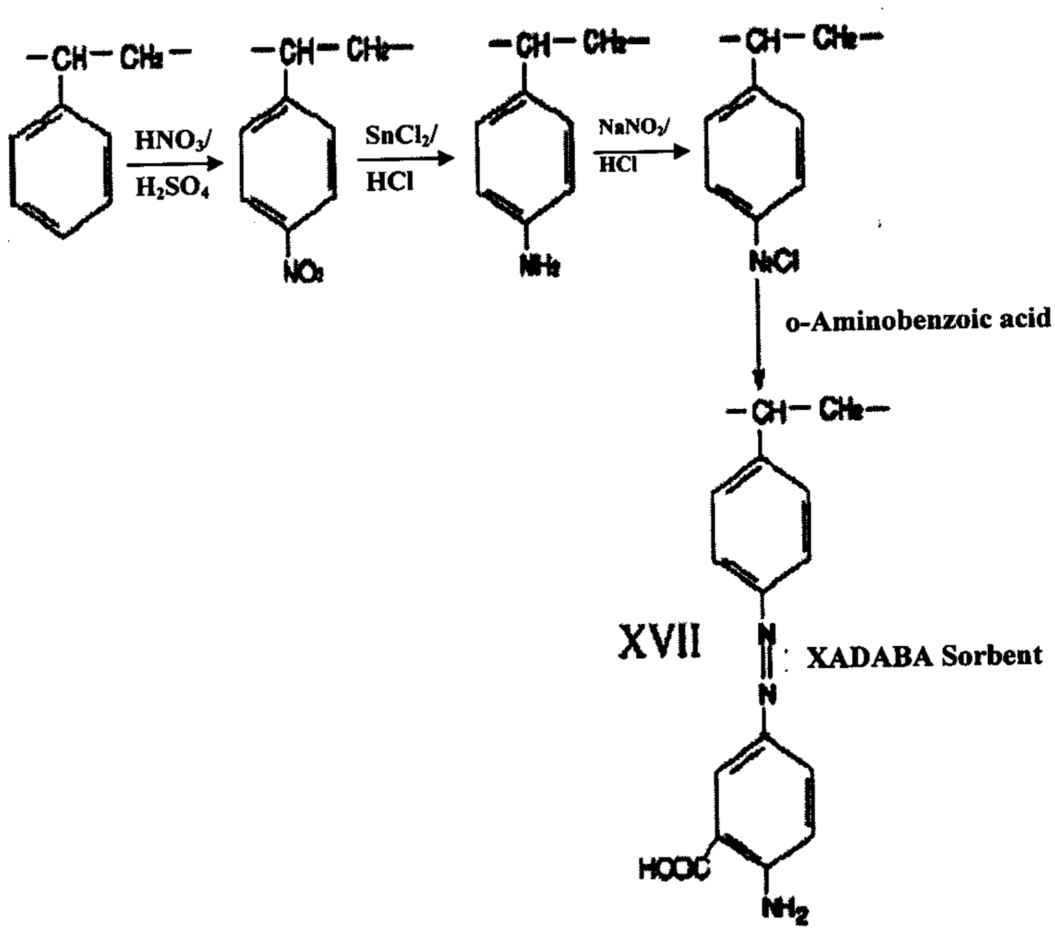
A new class of ion-selective chelating polymer has been developed, using Amberlite XAD-16 (AXAD-16) polymer support functionalized with (bis-2, 3,4-trihydroxy benzyl) ethylene diamine (BTBED) as metal chelatogen, through an azo spacer mechanism [(XVI), Scheme 14]$^{(91)}$. Various physico-chemical parameters like solution pH, metal exchange kinetics, metal loading capacity, diverse ion tolerance, sample breakthrough volume, etc., that influence the quantitative metal ion sorption to the resin phase were studied and optimized by both static and dynamic method. The resin showed exclusive ion-selectivity behavior towards actinide and post-transition ions under varying experimental conditions. Quantitative preconcentration and separation of analytes were possible by varying the solution pH and eluant concentration. The extraction efficiency of the chelating resin was investigated and it was found to have a high metal loading capacity value of 1.43, 1.19, 1.01, and 0.78 mmol /g for U (VI), Th (IV), Pb (II) and Cd (II), respectively



XVI

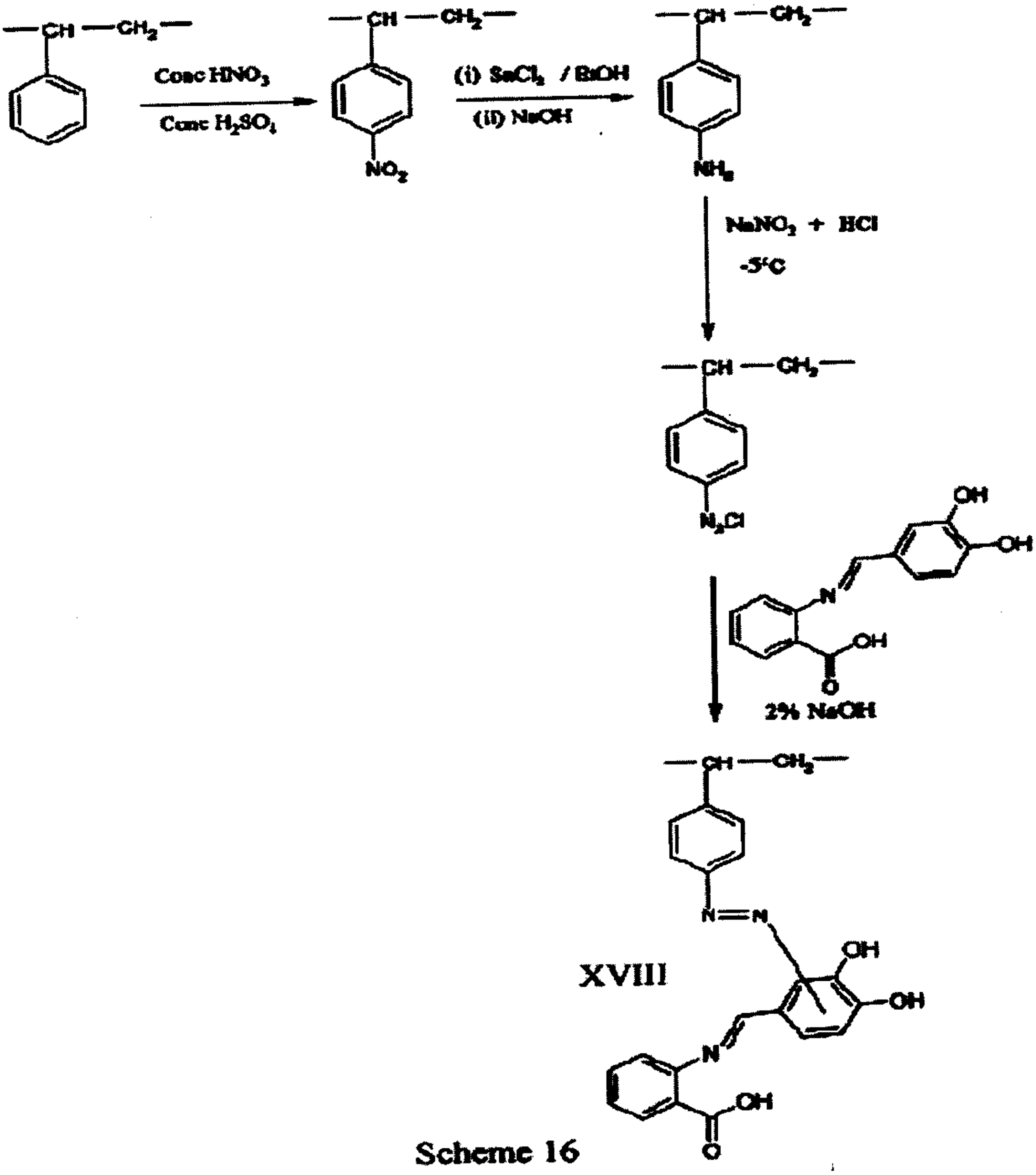
Scheme 14

o-Aminobenzoic acid (ABA)-immobilized XAD-4 copolymer resin was prepared [(XVII), Scheme 15] that is expected to preconcentrate a number of transition and heavy metals, the azo-linkage method was chosen(92). For this purpose the copolymer was nitrated, reduced to the corresponding amine, converted to the diazonium salt with nitrite, and reacted with o-aminobenzoic acid to produce the XAD-ABA sorbent. This sorbent was capable of preconcentrating Pb (II), Cd (II), Ni (II), Co (II) and Zn (II) from weakly acidic or neutral aqueous solution. The retained metals were eluted with 1 .0M $HNO_3$ from the resin column. The developed resin preconcentration and determination method was successfully applied to the analysis of a synthetic metal mixture solution, a certified reference material (CRM) of coal sample, and brackish lake water.



Scheme 15

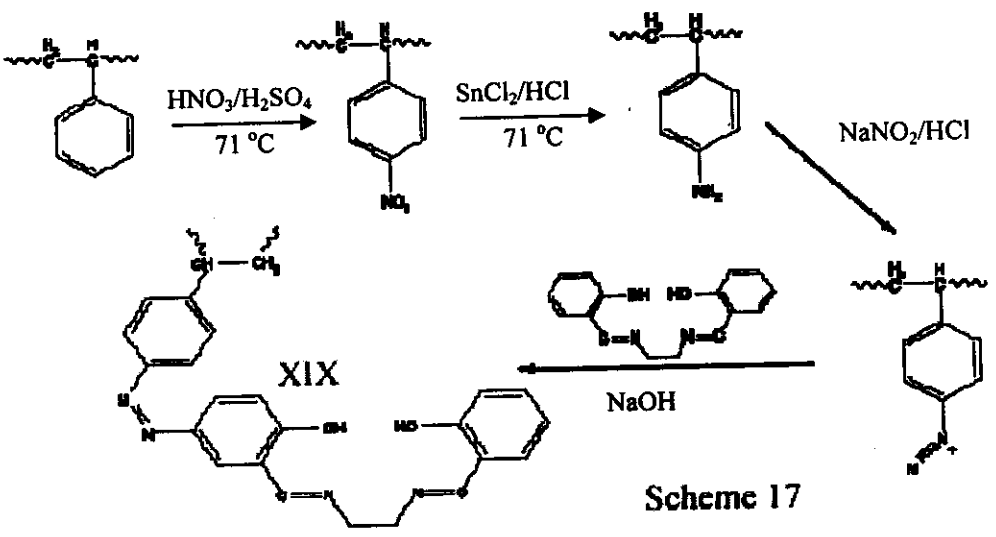
2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid (DMABA) was loaded on Amberlite XAD-16 (AXAD-16) via azo linker and the resulting resin AXAD-16-DMABA [(XVIII), Scheme 16] explored for enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II)(93) . The optimum pH values for extraction are 6.5-7.0, 5.0-6.0, 5.5-7.5, 5.0-6.5, 6.5-8.0, 5.5-7.0, 4.0-5.0 and 6.0-7.0, respectively. The sorption capacity was found between 97 and 515 μmol $g^{-1}$ and the preconcentration factors from 100 to 450. The chelating resin can be reused for 50 cycles of sorption-desorption without any significant change (<1.5%) in the sorption capacity. The enrichment on AXAD-16-DMABA coupled with monitoring by flame atomic absorption spectrometry (FAAS) is used to determine all the metal ion ions in river and synthetic water samples, Co in vitamin tablets and Zn in milk samples



XVIII

Scheme 16

The use of chemically modified XAD-4-salen chelating resin had been studied for the separative concentration of metal ions from an aqueous solution (94). XAD-4-salen was synthesized [(XIX), Scheme 17] by diazonium coupling reaction of salen[N,N-bis(salicylidene)ethylenediamine] and Amberlite XAD-4 resin. The distribution coefficient at various pH values and adsorption capacities were obtained with respect to Cu(II), Pb(II) and Bi(III). Trace elements were pre-concentrated on the synthesized XAD-4-salen by batch method for atomic absorption spectrometric determination. Some conditions, such as the pH of aqueous solution, amount of XAD-4-salen, kinds and concentration of acids were optimized for the analytical application of XAD-4-salen. For the pre-concentration of metal ions, the pH of the aqueous solution was adjusted to approximately 5.5, and then it was stirred 30 min after the addition of 50 mg of pulverized XAD-4-salen. The adsorbed metal ions were desorbed by 10 ml of 1.0 M $HNO_3$. The desorption efficiency of Bi(III) was enhanced by the addition of 30 mg/l of Pd(II). The addition of Pd(II) as a matrix modifier could improve the reproducibility and sensitivity in the Atomic Absorption Spectroscopy (AAS) determination of volatile lead and bismuth., this procedure has been applied for the determination of Cu(II), Pb(II) and Bi(III) in real samples of five kinds of river water, using a standard calibration curve method. Recoveries of 85-120% were obtained in the spiked samples in which given amount of analytes were added.

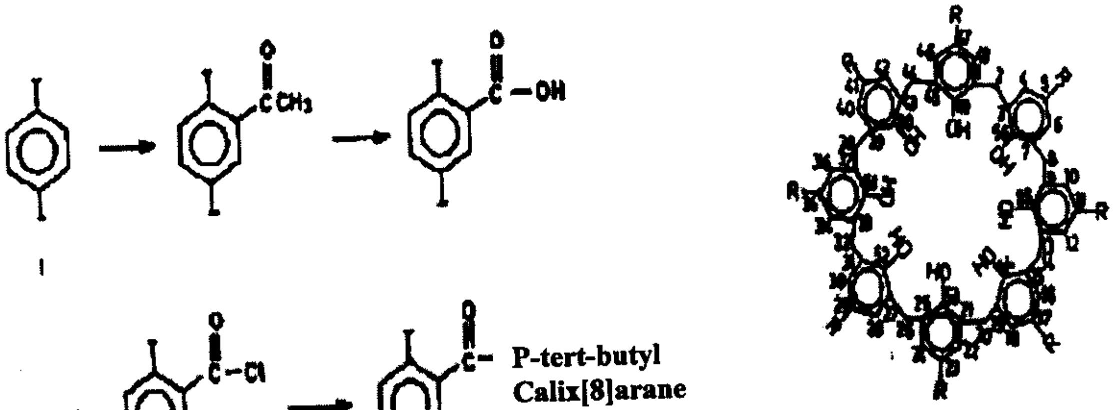


Scheme 17

### I-B-1-c- Chelating ion exchange resins containing oxygen as the only donor atom:

Several types of ligands containing oxygen as the only donor atom have been incorporated into different types of polymeric matrices. Some of the ligands used for such studies include polyphenols, polycarboxylic acids, 1,3-diketones, phosphonic acids, arsenic acids, polyphenolic carboxylic acids, fluorones, flavones and related compounds.

The synthesis of chelating resin, in which p-tert-butylcalix[8]arene is incorporated into a polymeric matrix (XAD-4) is reported [ (XX), Scheme 18] (95). The resin was used for the sorption of some transition metal ions, uranium and thorium from aqueous solution. The optimum conditions (pH effect, breakthrough curves, capacity, equilibrium time) were determined for Cu (II), Fe (II), Zn (II), Ni(II), Co (II), Cd (II), Pb (II), Th (IV) and U (V1). The resin shows high selectivity for Th (IV) and U (VI), and their separation from other metal ions has been carried out effectively.

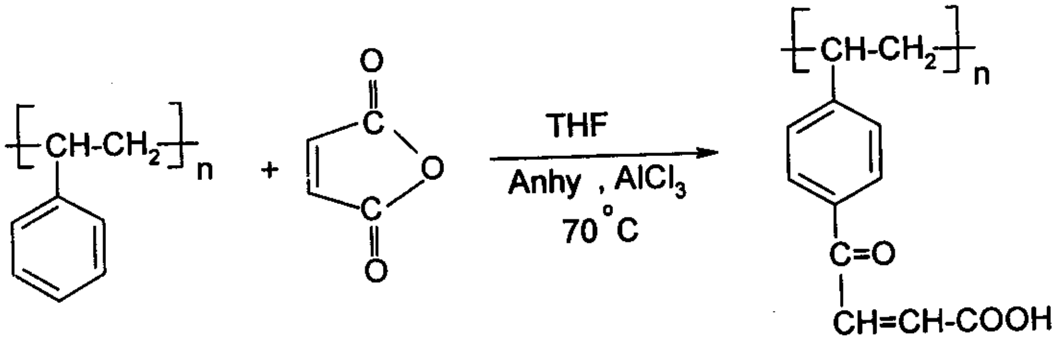


XX

R-C(CH$_3$)$_3$
p-Tert-butylcalix[8]arene

Scheme 18

Chromium may exist in environmental waters as Cr (III) and Cr (IV), the latter being the toxic and carcinogenic form. a polymer resin bearing O,O-donor chelating groups such as the maleic acid-functionalzed XAD-(CO)CH=CH-COOH resin was synthesized [ (XXI),Scheme 19] to selectively retain Cr(III) at pH 4.0-5.5 (96) . The dynamic breakthrough capacity of the resin for Cr (III) at pH 5.0 was 7.52 mg /g. and the preconcentration factor extended to 250-300. Chromium (III) in the presence of 250-fold Cr (VI) which was not retained could be effectively preconcentrated on the $NH_4^+$ form of the resin and determined by (AAS) or diphenylcarbazide (DPC) spectrophotometry. When Cr (VI) was reduced to Cr (III) with $Na_2SO_3$ solution brought to pH 1 by the addition of 1M $H_2SO_4$, and preconcentrated on the resin, total Cr could be determined. Since the adsorption behavior as a function of pH of possible interferent metal ions, e.g. Ni(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Fe(III), was similar to that of Cr(III), selective elution of Cr(III) from the resin was realized using a mixture of 1 wt.% $H_2O_2$ + 1M $NH_3$... Various synthetic waste solutions typical of electroplating bath effluents containing Cr, Cu, Ni, Zn, Na, Ca, cyanide (and chemical oxidation demand (COD), achieved by glucose addition) were subjected to pretreatment procedures such as hypochlorite oxidation (of cyanide) and catalytic oxidation (of COD) with peroxodisulfate. Chromium determination gave satisfactory results. The combined column preconcentration, selective elution, diphenylcarbazide spectrophotometric determination was also successfully applied to the determination of Cr in artificial and real seawater.

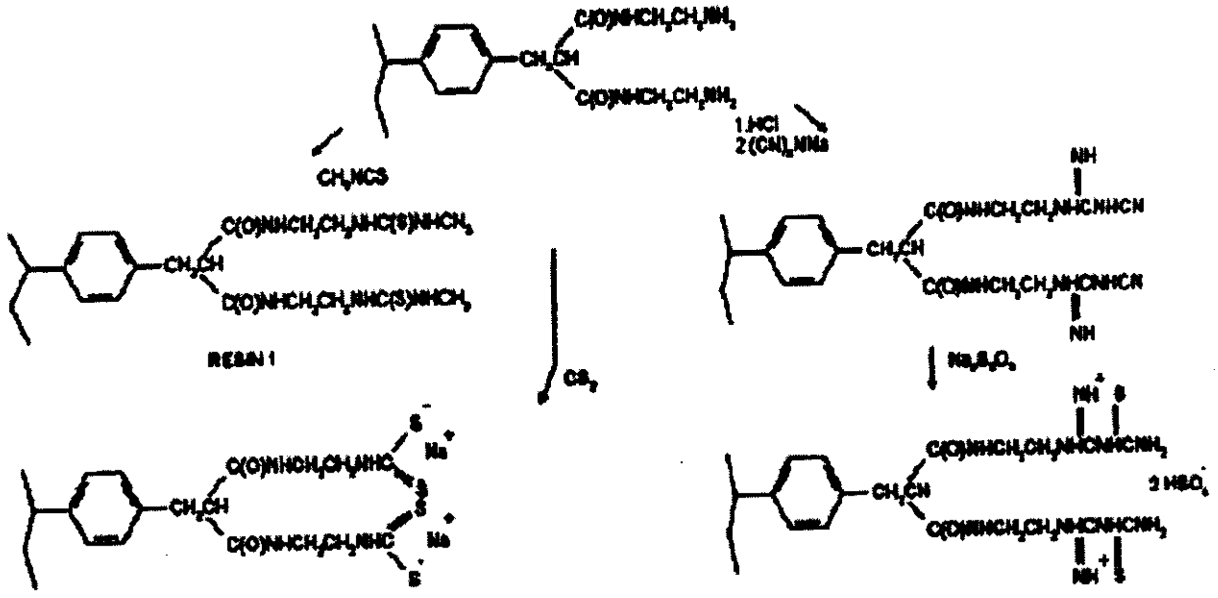


**XXI**

**Scheme 19**

### I-B-1-d- Chelating ion-exchange resins containing sulfur or nitrogen and sulfur or oxygen and sulfur as donor atoms:

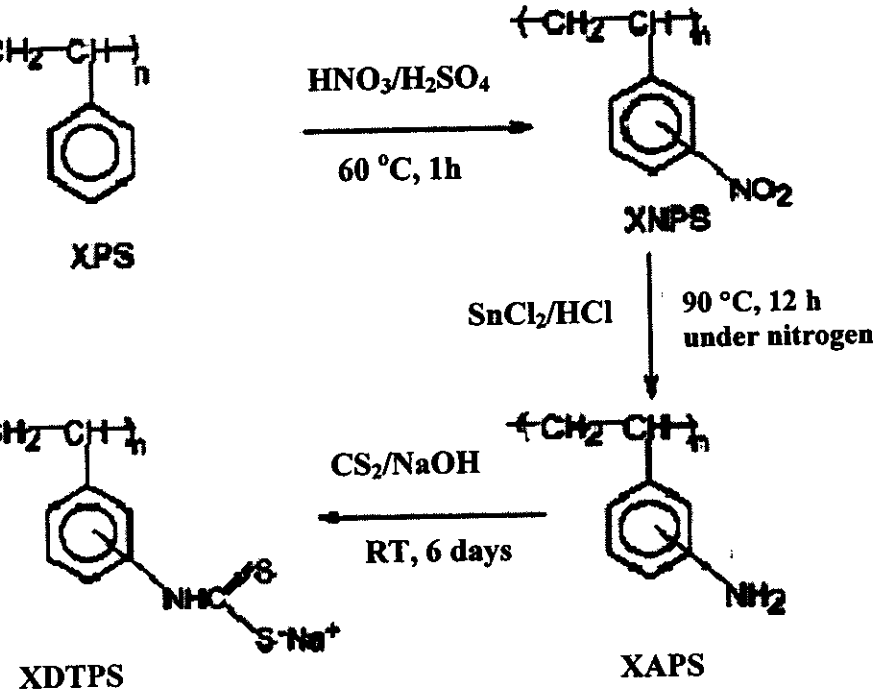
Three types of reactive groups: methylthiourea, dithiocarbamate and guanylthiourea are introduced into the structure of ion-exchange/coordinating resins having vinylbenzyl chloride/divinylbenzene matrix (Scheme 20)(97). All of them contain sulfur atom(s), and the presence of this element changes the affinity of the resins towards the investigated cations (Cu(II), Cd(II), Zn(II), Ni(II), Pb(II), Ag(I)). It has been found that the introduction of purely coordinating groups leads to the decrease in the distribution coefficient for all the investigated metal cations compared to the starting resin with amino groups. Introduction of dithiocarbamate groups results in a very high uptake of the metal ions at both the pH studied. The highest affinity displayed by this resin is towards silver for which $\log K_d$ was 4.42 at pH 5.6.



Scheme 20

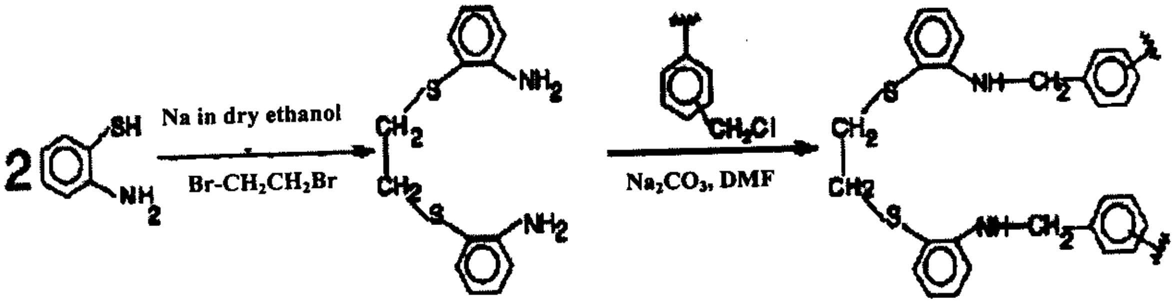
A new chelating resin was synthesised by the modification of styrene_ divinylbenzene (2%) copolymer and incorporation of dithiocarbamate groups [(XXII), Scheme 21](98). The analytical characteristics of the sorbent were established and optimum sorption conditions for Cu, Ni, Pb, Fe, As and Mn determined. The total sorption capacity of the resin was 37 mg g/L for Ni(II), 35 mg /g for Cu(II), 29 mg / g for Fe(III) and 23 mg / g for Pb(II). The optimum pH for the removal of metal ions was 3-5 for Ni (II), 5 for Cu (II), 4 for Fe (III) and 45 for Pb (II). High sorption capacity was observed when compared with other conventional chelating polymers

XXII



Scheme 21

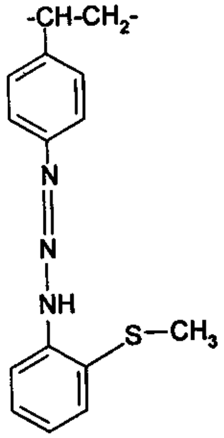
A method for the simultaneous preconcentration and determination of Hg (II) and MeHg(I) at the mg ml$^{-1}$. Level has been developed(99). This method is based on solid phase extraction using a newly synthesized chelating resin containing nitrogen and sulfur donor sites of the 1,2-bis(o-aminophenylthio)ethane moiety [(XXIII), Scheme 22]. The resin is highly selective for Hg (II) and MeHg (I) with an exchange capacity of 0.38 and 0.30 mmolg$^{-1}$, respectively. Various parameters like pH, column flow rate, desorbing agents are optimized. The recovery of Hg(II), and MeHg(I) was found to be $98.9 \pm 2.0$ and $98.0 \pm 1.1\%$, respectively.



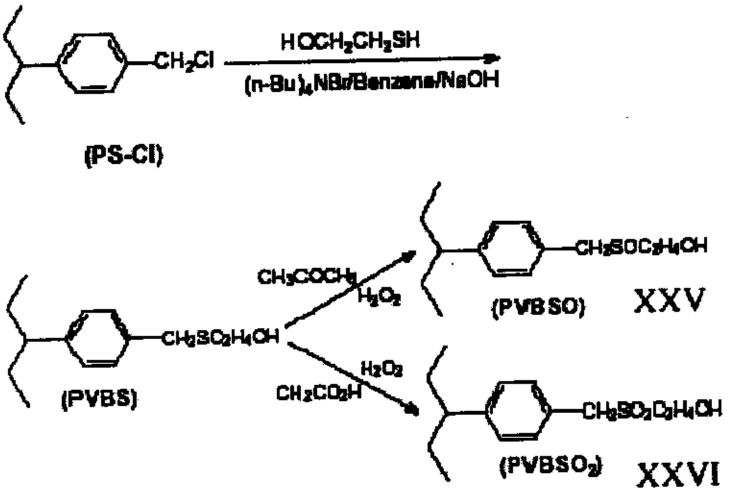
XXIII

Scheme 22

2-(Methylthio) aniline-modified Amberlite XAD-2 has been synthesized by coupling it through a -N=N-NH- group (XXIV)(100) . The resulting chelating resin, was used to preconcentrate Cd, Hg, Ni, Co, Cu and Zn ions. Several parameters, such as the distribution coefficient and sorption capacity of the chelating resin, pH and flow rates of uptake and stripping, and volume of sample and eluent, were evaluated. The effect of electrolytes and cations on the preconcentration was also investigated. The recoveries were >96%. The procedure was validated by standard addition and analysis of a standard river sediment material (GBW 08301, China). The developed method was utilized for preconcentration and determination of Cd, Hg, Ni, Co, Cu and Zn in tap water and river water samples by flame atomic absorption spectrometry with satisfactory results.



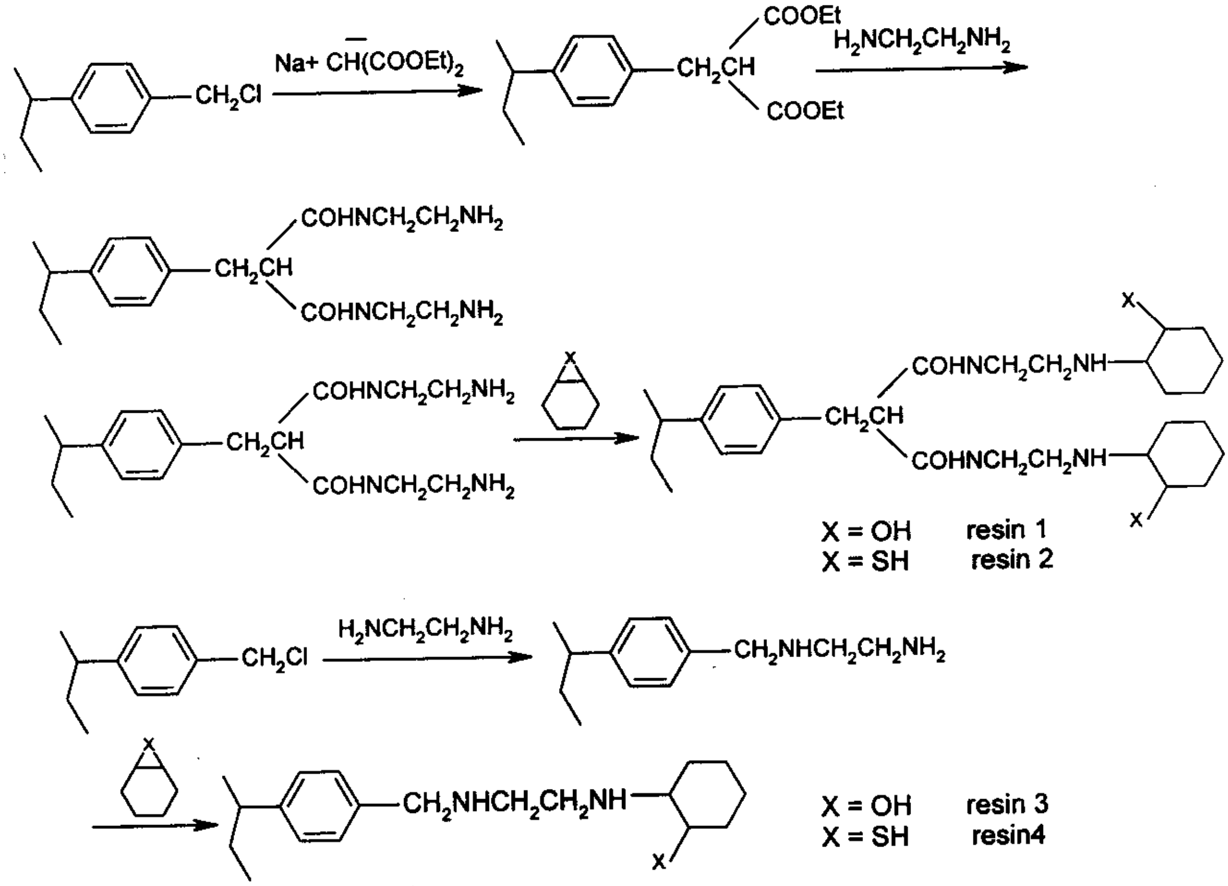
In order to explore the reuse properties of oxidized chelating resin containing sulfur after adsorption two kinds of chelating resins poly-[4-vinylbenzyl-(2-hydroxyethyl)] sulfoxide (PVBSO), (XXV) and poly-[4-vinylbenzyl-(2-hydroxyethyl)] sulfone ($PVBSO_2$), were synthesized [(XXVI),Scheme 23)] using poly[4-vinylbenzyl-(2-hydroxyethyl)] sulfide (PVBS)(101) . The adsorption properties and mechanism for metal ions such as $Au^{3+}$, $Pt^{4+}$, $Pd^{2+}$, $Hg^{2+}$, $Cu^{2+}$ , $Ni^{2+}$ , $Fe^{3+}$ , $Pb^{2+}$ , $Cd^{2+}$ , and $Zn^{2+}$ were investigated. Experimental results showed that PVBSO had good adsorption and selective properties for $Au^{3+}$, $Pd^{2+}$ and $Cu^{2+}$ when the coexisting ion was $Pt^{4+}$ , $Ni^{2+}$ , $Pb^{2+}$ or $Cd^{2+}$. In the aqueous system containing $Cu^{2+}$ and $Pb^{2+}$ or $Cu^{2+}$ and $Cd^{2+}$, $PVBSO_2$ only adsorbed $Cu^{2+}$.



Scheme 23

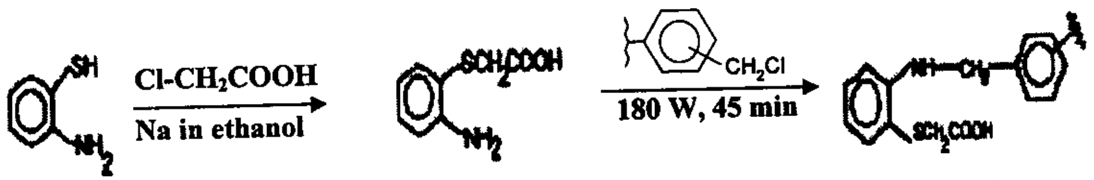
### I-B-1-e- Chelating ion exchange resins containing oxygen ,nitrogen, and sulphur as the donor atoms:

A ring opening reaction with either cyclohexene oxide or cyclohexene sulfide that has been used in the modification of two types of polymeric resins(102). Both resins contained amino groups, one being obtained by reacting the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer with ethylenediamine, the second by reacting the VBC/DVB copolymer with diethyl malonate followed by aminolysis with ethylenediamine (scheme 24). Modification resulted in a set of novel chelating resins, which has been characterized and used in metal ion uptake experiments. These resins are highly selective towards copper (II) in acetate buffered solutions. The selectivity of the modified resins decreases in the order, Cu (II) > Cd (II) > Zn (II) > Ni (II), which is different from the Irving-Williams series. The highest affinity towards Cu (II) ions has been found for the resin modified with cyclohexene oxide, for which log$K_d$ was 4.91 at pH 5.6.



Scheme 24

Chloromethyl polystyrene has been functionalised with 2-aminothiophenyl S-acetic acid using microwave assisted reflux(103). The resulting chelating resin (XXVII) Scheme 25 has been used for the preconcentration and separation of lead prior to its determination by flame atomic absorption spectrometry. The optimum conditions for both syntheses of the resin as well as the digestion of the road dust samples by microwave-assisted treatment have been evaluated. Parameters such as the amount of the resin, effect of pH, equilibration rate, sorption and desorption of metal ions, and effect of diverse ions have been studied. The maximum sorption capacity for lead was found to be 0.03-mmol / g at the pH range 5.5-6.0. Recovery of Pb (II) was 98.9 at the 99% confidence level with a detection limit of 40.6 mg/ml. The proposed method has also been applied for the determination of lead in road dust

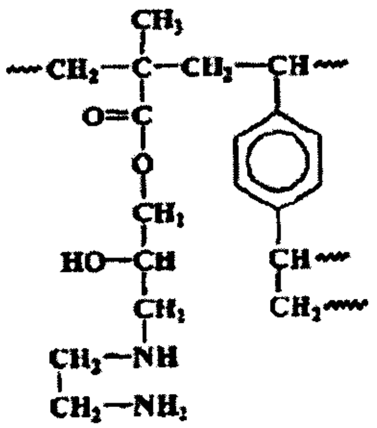


XXVII

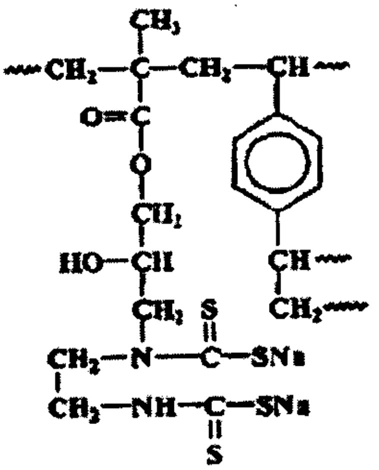
Scheme 25

Chelate forming resins containing amino (XXVIII) and thio (XXIX) groups have been prepared (104). The interaction of the obtained resins with Zn (II), Cd (II) and Hg (II) from their aqueous solutions was studied. The metal ion uptake behaviour and selectivity of the resins towards the metal ions were investigated by both batch and column methods. Hg (II) showed higher affinity towards the amino and the thio resins compared to Zn (II) or Cd (II). The mechanism of interaction between the resin and the studied metal ions could be explained on the basis of the formation of resin-metal complex in neutral conditions. In mediums acidified by HCl, the interaction of Hg (II) was interpreted to proceed via ion-exchange mechanism. Hg (II) could be separated from Cd (II) in acidic medium. The studied resins were regenerated using $HNO_3$ or acidified thiourea.

It was not recommended to use HCl for elution of Hg(II) from the loaded resins due to its affinity for interaction with resins via ion-exchange.



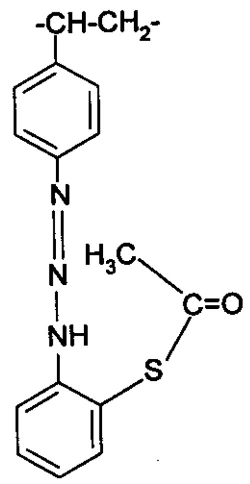
XXVIII



XXIX

2-Aminoacetylthiophenol (AATP)-modified AmberliteXAD-2 has been synthesized by coupling it through-N=N-NH-group. The resulting chelating resin was used to preconcentrate Cd, Hg, Ag, Ni, Co, Cu and Zn ions(105). Several parameters, such as distribution coefficient and sorption capacity of the chelating resin, pH and flow rates of uptake and striping, volume of sample and eluent, were evaluated. The effects of electrolytes and cations on the preconcentration were also investigated. The recoveries were >96%. The procedure was validated by standard addition and analysis of a standard reference sediment material (GBW 07309 China). The developed method was utilized for preconcentration and determination of Cd, Hg, Ag, Ni, Co, Cu and Zn in tap water, river water and sediment samples by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with satisfactory results.

**XXX**



## I-B-1-f-Chelating ion-exchange resins containing π electrons as donor:

Many polymers containing ferrocene have been proposed and discussed(106). Poly(ferrocenylethylene) has been made from vinylferrocene monomer, and the redox and potentiometric behavior, electrical and magnetic properties, and rates of the free-radical polymerization of the polmer reported (107).

Vinylferrocene has successfully been copolymerized with butadiene,(108) styrene,(109) methylacrylate,(109) and maleic anhydride(110). Pittman, et al.,(111) have recently reported new polymers containing organometallic monomers, including ferrocenylmethyl acrylate, ferrocenylmethyl methacrylate, vinylcyclo-pentadienyl manganese tricarbonyl(vinylcymantrene), π-chromium tricarbonyl benzyl acrylate, and π-iron tricarbonyl-2,4-hexadienyl acrylate.

Heat-stable ruthenocene and osmocene-containing polymers, useful for preparing transparent films, UV absorbers, coatings, and sealants, have been reported(112). These polymers are prepared by condensing ruthenocene and osmocene with various aldehydes in the presence of anhydrous zinc chloride.

### I-B-2- Survey of glycidylmethacrylate resins:

Resin containing phosphonium groups were prepared by reaction of chlorohydroxylated glycidyl methacrylate divinylbenzene macroreticulare resins with three trialkylphosphines. Adsorption and elution behavior of sodium benzene sulfonate (SBS) and sodium dodecyl benzene sulfonate (SDBS) on the resins were studied . Adsorption of (SBS and SDBS) increased with increasing the alkyl chain length of phosphoniun groups in the resins . The adsorption of (SBS) decreased with increasing the ionic strength of the solution, while the adsorption of (SDBS) increased with increasing the ionic strength of the solution.(113).

Six chelating hollow fiber membranes were prepared by radiation induced grafting of glycidyl methacrylate on a polyethylene hollow fiber membrane and subsequent amination . The adsorption characteristic of $Pb^{2+}$ and $Pd^{2+}$ for chelating hollow fiber membranes were presented when the solution of $Pb^{2+}$ and $Pd^{2+}$ permeates across the chelating membrane respectively . The degree of grafting for glycidyl methacrylate increases with the increase of monomer concentrations . The chelating hollow fiber membrane modified with iminodiacetic acid adsorbes $Pb^{2+}$ ions much more than $Pd^{2+}$(114).

A series of macroporous beads were synthesized by suspension copolymerization of glycidyl methacrylate (GMA) with divinyl-benzene (DVB) in presence of various diluents to act as precipitants, the effect of diluents on the surface appearance and the pore structure of copolymer beads was studied . The macroporous copolymer beads which have large specific surface area and pore volume could be prepared(115) .

Reactive glycidyl methacrylate (GMA) divinyl-benzene (DVB) copolymers of widely varying crosslink densities were synthesized in bead form. Porosity surface area and pore size were found to increase with concomitant increase in cross-linking monomer and volume of porogen. It was possible to control the pore volume in the range 0.0 to 2.06 ml / g.(116)

Two chelating resins beaded on poly (glycidyl methacrylate co-ethyleneglycoldimethacrylate) and two based on poly(styrene co-divinyl benzene) have been used in small scale column extraction of $Cu^{2+}$ from sulphate solutions containing 1.0 mg/l of metal ions at PH=5(118).

The selective properties of the two efficient resins in extraction of $Cu^{2+}$ ions from solution containing a large excess of $Zn^{2+}$ ions were also investigated . The effect of a 250 fold excess of $Zn^{2+}$ proved negligible in both cases and $Cu^{2+}$ was rapidly and selectivity extracted.(117)

Reaction of the glycidyl methacrylate-ethylene dimethacrylate with ethylamine, diethylamine, and 2-hydroxyethylamine were employed to prepare new types of macroporous resins . Reactions of macroporous copolymer(119) with $Cu^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions was studied . The amount of the metal ion sorbed as well as the selectivity coefficient for the reactions with $Cu^{2+}$ and $Co^{2+}$ ions were established . Different complexes were formed utilizing further OH groups or $H_2O$ molecules contained in the resin. The existence of the complexes were also demonstrated (118).

The complexing properties of the copolymer of glycidyl methacrylate- ethylenedimethacrylate (GMA-EDMA) with attached ethylenediamine (en) as a ligand were previously studied(119).

Three types of complexing polymers were allowed to react with bivalent ions of $Cu^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$. Their sorption ability and selectivity towards individual ions were investigated .(120)

Two chelating resins based on poly (glycidyl methacrylate-co-ethyleneglycol dimethacrylate) and two based on poly (styrene-co-divinyl benzene) have been used in small scale column extractions of $Cu^{2+}$ from sulphate solutions. Two of the resins bearing 2-aminomethyl-pyridine residues with saturation capacities up to 15g $Cu^{2+}$ /L resin .(121)

Phosphoric acid resins with large cation exchange capacities were prepared. The effects of porosity and crosslinking of the precursor poly (glycidyl methacrylate-co-divinyl benzene) beads on their function were also studied . Two series of precursor copolymers were prepared . It was clarified that the porosity plays an important role in the function of highly porous precursors. The selectivity study has revealed that the precursors exhibit characteristic selectivity among common divalent metal ions. In addition, the resin exhibits highest selectivity towards lead ion.(122)

The formation of transition metal complexes on the reactive hydrophilic copolymer glycidyl methacrylate-ethylenedimethacrylate, through the reaction with chemically bonded ethylenediamine molecules had been described . Particular attention has been paid to complexes of $Cu^{+}$, $Cu^{2+}$, $Co^{2+}$, $Co^{3+}$, $Fe^{2+}$ and $Fe^{3+}$. The different degrees of oxidation of the central metallic ions lead to the formation of active and inactive compounds against the magnetic measurements . Electronic paramagnetic resonance (EPR) was chosen as a method for providing a direct proof for chemical bond between the metal and the polymeric chelating sorbent.(123)

Recently cotton fabric was converted into an ion exchange by grafting it with (1) glycidyl methacrylate (GMA), followed by aminization with ethylene diamine, (2)dimethylaminoethyl methacrylate (DMAEMA), followed by quaternization and (3) acrylic acid (AA) . The so-obtained cotton graft copolymers were monitored for their ability to remove different dyes as well as heavy metals from aqueous solutions.(124)

Modification of cellulose for heavy metal adsorption was conducted by the graft polymerization of glycidyl methacrylate utilizing ceric ammonium nitrate initiator, followed by the reaction with polyethyleneimine to introduce nitrogenous ligands .(125)

The novel benzimidazole ligand 4-(2 prime-benzemidazole)-3-azabutanoic acid has been synthesized and anchored to poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate). The metal uptake capacity of the resin for some heavy metals have been described .(126)

A chelating vinyl monomer, glycidyl methacrylate(GMA)-iminodiacetic acid(IDA), was formed by the reaction between GMA and IDA.

Three polymeric chelating agents, PGMA-IDA, PGMA-ID-co-methyl acrylate (MA), and PGMA-IDA-co-acrylamide (AAm), were also synthesized . Acid dissociation constants and stability constants of these chelating agents with $Ni^{2+}$, $Zn^{2+}$ and $Co^{2+}$ were determined by means of potentiometric titration and ultraviolet-visible spectrophotometry, respectively.(127)

## I-C-Aim of work

In the last decades, synthesis of polymer carrying ligands as pendant groups on a polymer chain attracted the attention of several investigators. Chelating polymer consists of a polymer backbone and a grafted chelating group. This chelating group may be incorporated in the monomer structure or added to polymer backbone by polymer-analogous reaction.

The main application potential of chelating polymers is based on the possibility of achieving high selectivity of the materials for particular metal ions. Insoluble resins of polymeric ligands have been used for the adsorption of toxic metal ions or trace metals from sea and waste-water to clean-up the environment and to save energy . The selective adsorption of metal ions depends on the kind of polymers, ratio of cross-linking agent and the stability constant of the polymeric metal complexes formed.

The present work aim to find suitable method for synthesis of three a highly efficiency and new aminated chelating resins of glycidyl-methacrylatedivinylbenzene copolymer with 1,2-diamino benzene(DAB), 2-amino phenol(2Aph ) and 4-Amino-antipyrine (4aapy) .

The compounds obtained will be characterized by means of different analytical and spectral methods.

The uptake behavior of the chelating resins obtained towards metal ions such as $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Co^{2+}$, and $Ni^{2+}$ by batch and column methods , and the factors affecting the uptake values in aqueous solution like pH, concentration, shaking time, rate constant and ionic radius will also be studied.

# *Chapter 2*

# EXPERIMENTAL