APPLICATION OF FUNCTIONALISED CHELATING RESINS FOR SELECTIVE SORPTION OF METAL IONS WITH SPECIAL REFERENCE TO HEAVY METALS

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DECLARATION

I hereby, declare that the work presented in this thesis entitled "APPLICATION OF FUNCTIONALISED CHELATING RESINS FOR SELECTIVE SORPTION OF METAL IONS WITH SPECIAL REFERENCE TO HEAVY METALS" is entirely original and was carried out by me under the supervision of Professor Abhijit Roy, Department of Chemistry, University of North Bengal, Darjeeling for the award of Doctor of Philosophy in Chemistry.

To the best of my knowledge, the thesis has not been submitted previously for the award of any degree to this University or any other University.

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RIVER WATER

Abstract

INDUSTRIAL WASTE WATER

AGRICULTURAL SOIL

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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 pyrogaliol. 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 thc 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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CHAPTER II

AIM AND OBJECTIVES OF THE PRESENT INVESTIGATION

Abstract

This chapter describes the aim and objectives of the present investigation. Solid phase extractions are employed to separate individual or mixtures of some heavy metal ions which are known to be toxic. For this purpose several new functionalized solid resins have been synthesized and charecterised using modern analytical techniques.The compounds are synthesized both by the conventional heating under reflux method or by using the microwave heating techniques.The yield of the products for both methods have been compared.

Further in this study several Schiff base compounds (containing N,O,S atoms) have been designed to act as suitable chelating ligands. None of these ligands are used so far for the purpose.

2.1 Introduction

Heavy metals are accumulating in nature by both natural and anthropogenic causes. The major causes are anthropogenic. Metals like Cu, Zu, Pb, Cd, Cr, Co, Ni, Fe are released into the environment from industries, including mining, refining and production of textiles, paints, dyes, alloys, batteries, pesticides, preservatives, metal plating, the manufacturer of electrical equipment, fly ash from incinerators, the processing of radioactive materials etc. to name a few [1, 2]. Heavy metals are mixed in the environment both in elemental and compound (organic and inorganic) forms. These solid pollutants greatly threaten the health of human populations and the natural eco-systems as they do not degrade biologically - rather it enters into the food chain through bio-accumulation from the contaminated water, soil and air. Although the ions of Mn, Fe, Cu, Zn are essential minor nutrient in soil for plant life as well, excess of these metal ions and other heavy metals like Cd, Pb, Cr are able to disrupt the activities of enzymes and micro- organism in the system [1, 3].

Again water soluble and exchangeable metal forms are more harmful than those which are existing as carbonates, oxides and other non soluble compounds. Water soluble metal ions can easily bind soil enzyme and hinder their normal activities.

The toxic effects of heavy metals are due to their interference in the normal metabolic processes. When the metal ions are ingested in acid medium of the stomach, they are converted to their stable oxidation states and combine with the bio-molecules such as proteins and enzymes to form strong and stable chemical bonds.

Though the metals copper and zinc play an important role in biological system, the overdose of these metal ions toxify the species by bio-accumulation. Excess copper metal ions in soil toxify the micro-organisms and disrupt the process of nutrient cycling or inhibit other process such as mineralisation of nitrogen, phosphorus etc. Short term exposure to copper may lead to gastrointestinal disorder, decrease haemoglobin and erythrocyte levels in the blood, impair immune system of human body. Short term exposure of zinc (Zn) metal lead to stomach cramps, nausea and vomiting. However, long term exposure of this metal may cause anemia, damage to the pancreas and decrease the levels of lipoprotein cholesterol.

Excess exposure of the metal lead (Pb) affects the brain and kidney, the central nervous system, blood pressure and vitamin D metabolism. Even small amount of lead ingestion by the children under the age of six could slow down the mental development of a child. Cadmium (Cd) and its compounds are extremely toxic even in low concentration. Cadmium can replace zinc in many biological systems, in particular, systems that contain softer ligands such as containing sulfur atom donors. Cadmium can bind up to ten times more strongly than zinc in certain biological systems.

Bio-accumulation of cadmium metal in animals is high compared to most of the other metals as it is assimilated rapidly and excreted slowly. Ingestion of high levels of cadmium may lead to stomach irritation, vomiting, diarrhea, it also causes kidney damage. Of all the metals chromium is the most harmful in crippling the soil enzymes. Cr(III) is relatively non toxic. On the other hand, Cr(VI) compounds are extremely irritating and toxic to human tissues - long term exposure can damage the liver, kidneys and also the circulatory and nervous systems.

The accurate determination of trace amounts of heavy metals and their removal from the environment has gained considerable importance because of their low concentration in environmental matrices. Thus, now - a - days removal of heavy metals is an area of increasing interest and there is a need for reliable analytical procedure to pre-concentrate the trace amount of metal ions. One of the important methods of current interest for such separation is solid phase extraction [4, 5]. The efficiency of the solid support may be enhanced by functionalising it with appropriate chelating ligands to bind the desired toxic metal ions. Further these functionalised materials have many fold advantages for their simplicity to handle, greater reproducibility and higher pre-concentration factor. Several types of chelating resins have been developed so far by functionalising polymer matrix by various chelating agents [6, 7].

Yet the search for even better and more useful ligands immobilized on solid matrix is ought to be a never ending research area. To indulge ourselves to join in such a search we aimed initially to design , synthesise and characterize ligands with appropriate donor atoms. We aimed then to immobilize the new ligands on the solid matrix to obtain the functionallised solids [8]. These then will be studied thoroughly to estimate their efficacy for pre-concentration and separation of toxic heavy metals initially under laboratory conditions. If found suitable we also like to extend our studies to examine the usefulness of these new solid supports for their applications in industrial waste waters, to examine water pollution by dyes, colours and paints after immersion of idols specifically in Mahananda river at Siliguri, Dt. Darjeeling, W.B. and heavy metal contaminations in soils of environmental concern [9].

2.2 Objectives of the present work:

The development of pre-concentration procedures is a challenging problem. So our main objective of this work is to synthesise new functionalised resin compounds and to develop simple and inexpensive methods for metal ions separation from environmental samples. In the process we have synthesised (nine) new functionalised resin compounds and have explored their activities thoroughly. Our primary goals are to :

(i) Synthesis of ligands containing N,O,S or N,S donor atoms.

(ii) Synthesis of new polymer based functionalised resin compounds both by Micro-wave assisted heating and heating under reflux conditions.

(iii) Characterisation of the new ligands and new synthesised functionalised resin compounds produced by using these ligands.

(iv) Development of suitable procedure for pre-concentration and separation of toxic heavy metal ions in the laboratory by studying various sorption parameters of the new resin compounds.

(iv) Application of these new solid based functionalized compounds for pre-concentration and separation of heavy metals from environmental samples, separation of metal ions from the binary and ternary mixture depending upon the pH of the medium and by changing the eluting agents.

2.3 Microwave assisted Synthesis

The literature was followed [10, 11]

In recent years the use of microwave irradiation in the synthesis of certain types of organic compounds has rapidly increased to reduce specially the time of the synthesis. Several workers have used this thermal energy source in synthesising the functionalised resin compounds also. We have used this technique to reduce the time for synthesis of the functionalised resin compounds compared to the conventional heating under reflux.

2.3.1 Microwave assisted digestion

This technique (details are described elsewhere) has been utilised to digest soil samples for this work.

2.4 Choice of the chelating ligand

The concept of hard and soft acid and base concept and the idea of co-ordination chemistry is the basis for selection of the ligand.

Different atoms are capable of binding trace elements by coordination. Generally nitrogen atoms (nitrogen present in amines, amides, nitriles etc.), oxygen atom (oxygen present in carboxylic, hydroxylic, phenolic, carbonyl etc.) and sulphur (sulphur present in thiols, thio-carbamates, thioethers etc.) are used for the preparation of chelating complex compound.

According to Pearson hard soft (Lewis) acid base (HSAB) principle -

hard (Lewis) acid prefer to bind hard (Lewis) base and soft (Lewis) acids prefer to bind to soft(Lewis) bases. Hence hard and soft acids and bases are:

Group I hard cations

This group includes alkali and alkaline earth metal also.

H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+},

Al^{3+}, Ga^{3+}, La^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}

Group II Borderline cations

These have an intermediate character

Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}

Group III Soft cations

These cations are

Cu^{+}, Ag^{+}, Au^{+}, Hg^{+}, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}

For soft metals the following order of donor atoms affinity is observed

S>N>O.

A reversed order is found for hard metals. For a bidentate ligand affinity for a soft metal increases with overall softness of the donor atoms (O,O)<(O,N)<(N,N), (N,S).

The order is reversed for hard metals. Binding of metal ion to the ligand is dependent on several factors, such as,

(i) Nature, charge, and size of the metal ion

(ii) Nature of the donor atoms of the ligand

(iii) pH of the medium or buffering condition of the medium.

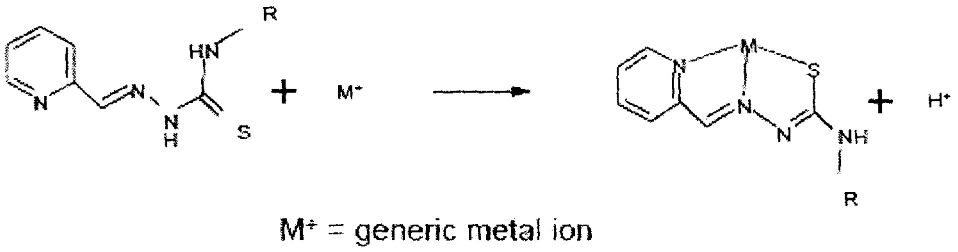
(iv) Nature of the solid support

Following the above principle, nine new ligands have been chosen for the present investigation.

The three ligands salicylaldehyde thiosemicarbazone,5- chloro salicylaldehyde thiosemicarbazone and 2- hydroxy napthaldehyde thiosemicarbazone, have three binding sites as nitrogen, oxygen, and sulphur (N,O,S) atoms and are expected to form two chelate rings which make them good reagents for metal ion binding and enrichment.

The chelating ligands pyridine carboxaldehyde thiosemicarbazone, 2- mercapto isothiocyanate, 2- amino- 1,3,4- thiadiazole, 5- amino- 1,3,4- thiadiazole- 2- thiol have two binding sites nitrogen and sulphar (N,S atoms), they are able to bind soft metals.

Figure 2.1 : metal complex of thiosemi carbazide derivative.



The ligand 2,4,6 - trihydroxy benzoic acid has two binding sites (O,O) which may bind with the hard metal ions.

The ligand pyridine - 2,5 – dicarboxylic acid has two binding sites (N,O), which can bind the soft metal ions.

The probable structures of the nine ligands synthesized are shown in the following figures:

Figure 2.2. Salicylaldehyde thiosemicarbazone (1)

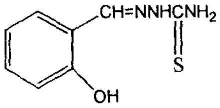


Figure2.3. 5- chloro salicylaldehyde thiosemicarbazone(2)

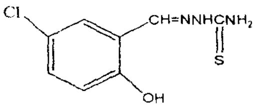


Figure2.4. pyridine - 2,5 – dicarboxylic acid(3)

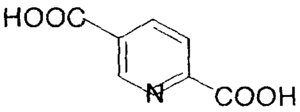


Figure2.5. 2- mercapto isothiocyanate(4)

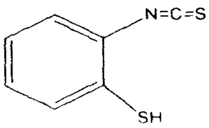


Figure 2.6. 2,4,6 - trihydroxy benzoic acid(5)

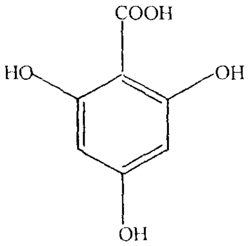


Figure 2.7. 2- hydroxy napthaldehyde thiosemicarbazone(6)

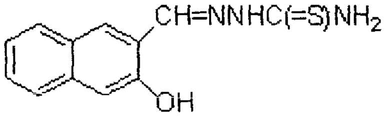


Figure 2.8. pyridine 1-carboxaldehyde thiosemicarbazone(7)

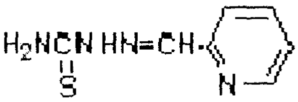


Figure2.9. 5- amino- 1,3,4- thiadiazole- 2- thiol(8)

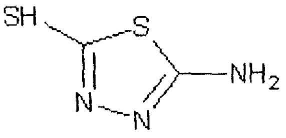
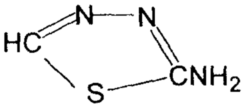


Figure2.10. 2- amino- 1,3,4- thiadiazole(9)



2.5 Designing of the chelating ligand

The choice for an effective chelating resin and its application in the field of analytical chemistry is determined by its properties, like polarisibility, selectivity, exchange capacity, kinetics, stability characteristics of the compound.

Our aim, in this investigation, is to introduce the above nine ligands in polymer matrix. The nucleophilic displacement of chlorine atom by H atom of the amino group (-NH_2 gr) of six ligands (Figures 2.2, 2.3, 2.7 - 2.10) offer a good method for incorporating functional group into chloromethylated polystyrene followed by SCHOTTEN-BAUMANN reaction. For other three ligands (Figures 2.4-2.6) which contain –COOH, -SH or -OH groups – functionalisation is carried out involving one of these groups.

2.6 Approach to the synthesis of the resin

Chelating resin compounds are three dimensional polymer of crystalline structure attached with a particular functional group to bind metal ions selectively. Organic ligand or functional group is covalently linked to the polymer matrix and it is fixed by functionalisation reaction.

The six ligands containing one primary amino group each reacts with chlorine atom of chloro methylated polystyrene divinyl benzene to produce six functionalized chelating resin compounds.

The rest of the ligands containing either carboxylic acid or thiol group produce similarly the functionalised resin of chloromethylated PSDVB.

Details of the syntheses and characterization of all the functionalised chelating resin compounds are presented in the chapter III. Further the details of the sorption behaviours of these compounds towards various toxic heavy metals either individually or in mixtures are investigated in the laboratory conditions, the results of which is described in the Chapter IV.

The field applications of these compounds for various environmental samples are also carried to find out their efficacy. The results in details are presented in chapter IV.

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CHAPTER III

SYNTHESIS AND CHARACTERISATION OF FUNCTIONALISED CHELATING RESIN COMPOUNDS

Abstract :

Syntheses of nine new functionalised chelating resin compounds and five organic chelating ligands have been described in this chapter. The description of the characterization of the synthesized compounds are established on the basis of their elemental analyses,IR spectra,TGA, DSC and SEM analyses. The general stability of the compounds are also determined.

3.1 Introduction

The analysis of trace elements in natural samples is a challenging problem due to low concentration and complex nature of the environment [1]. Although many instrumental techniques have been developed recently yet a direct determination of the trace amount of the heavy metals is difficulty. Various pre-concentration techniques such as solvent extraction, co-precipitation, electro-deposition, ion-exchange and solid phase extraction [2] have been used for trace metals separation and estimation. Among these, the solid phase extraction method has been used widely due to its certain advantageous characteristics [3]. The solid phase extractor in these studies - the functionalised chelating resin compounds have been synthesized in the laboratory and used to find out its sorption capacity and selectivity. New ligands are mainly N, O, S atoms containing Schiff base ligands [4] and other is only N,S atoms containing ligand which are being synthesised to study their sorption behaviour.

Nine functionalised chelating resin compounds have been synthesised and characerised and individual and mutual separation of the heavy metals from their binary and ternary mixtures are investigated by their solid compounds – the results of which are presented in chapter IV.

3.2 Instrumentation

pH of the solutions were measured by using Systronics MK-IV 5631 pH meter while the metal analyses were performed by atomic absorption spectrometer VARIAN model No. 55 with air-acetylene flame and spectra AA-50B. C, H, N analytical data were obtained either from (i) IACS, Kolkata, India or (ii) SAIF, NEHU, Shilong India. The SEM,

FESEM (JEOL JSM-6700 F), micrographs were obtained from IACS, Kolkata, India, DSC used was of PYRIS 6DSC-Perkin Elmer model where as the TGA were done on SHIMADZU TG50/DT50. The IR spectral analyses were recorded as nujol mull on KBr windows using FTIR-8300-SHIMADZU spectrometer. A domestic Samsung MW73V micro wave oven with a 2450 MHz frequency magnetron and 800 Watt maximum power and PTFE reactors (with 100ml internal volume, 1cm cell wall thickness and hermetic screw caps) were employed to synthesise the funtionalised resins.

3.3 Materials

The reagents were procured from

1) Sd fine - chem limited, India - $Pb(NO_3)_2$, $3CdSO_4.8H_2O$, $CdCl_2.2.5H_2O$, $CuSO_4$, $5H_2O$, $ZnSO_4$, $7H_2O$, $MnSO_4$, H_2O, $HgCl_2$, $Co(NO_3)$, $6H_2O$ and Thiosemicarbazide (all AR grade).

2) Merck-Inida - Sodium acetate (AR) and Isobutyl methyl ketone

3) HiMedia Lab. Pvt. Limited, India - $Cr_2(SO_4)_3$(AR)

4) Aldrich, USA - 5 - amino - 1, 2, 4 - thiadiazol-2-thiol (98%) and 2-hydroxy - 1-naphthaldehyde (technical grade) and 5-chloro salicydaldehyde

5) Across Organics, USA - Merrifield chloromethylated (3mmol/g chlorine) polymer 1% cross-linked with DVB, 100-200 mesh, 2-Pyridine-carboxaldehyde (GR) and used as received.

6) Fluka, Switzerland - 2, 4, 6 Trihydroxy Benzoic acid

7) Lan Caster,USA - Pyridine 2, 5 dicarboxylic acid

8) Merck, Germany - $Ni(NO_3)_2$, $6H_2O$

9) Loba Chemie Pvt. Ltd,India. - Ammonium Pyrolidine Dithiocarbamate

All other chemicals used during the study were of reagent grade procured from commercial sources.

3.4 Preparation of the Ligand

The literature [5] was followed for Ligand 1 5]

1g of thiosemicarbazide was dissolved in 50ml warm dehydrated alcohol and 1.2 ml of salicylaldehyde was dissolved in 3ml dehydrated ethyl alcohol. Both the solutions were then mixed in a 100 ml round bottomed flask and boiled upon water bath for 10 minutes. A white precipitate appeared which on crystallision yielded silver white coloured crystals collected by filtration and dried at room temperature, mp 230^{0}C.

Preparation of the Ligand 2

The literature [5] was followed

1g of thiosemicarbazide was dissolved in 50ml warm dehydrated alcohol and 1.70gm of 5, Chloro Salcylaldehyde was dissolved in 30ml warm alcohol, then two soloution were mixed in a 100 ml round bottomed flask and heated under reflux for 1 hour. A white coloured solid appeared which on recrystallisation yielded a square shaped crystalline product - collected by filtration and dried at room temperature, mp 235^0C.

Preparation of the Ligand 4

The literature [6] was followed

2- aminothiophenol (10.6ml) was dissolved in ammonia solution (20ml, d 0.888) in a 100 ml round bottomed flask and CS_2 (8ml) was added to it gradually with stirring and cooling below 30^0C. 25ml ethanol was then added with continued stirring till CS_2 had completely dissolved. The reaction mixture was allowed to stand for 2h and a solution of sodium chloroacetate (11.69g) was added to it followed by hydrazine hydrate (10ml, 50%). The mixture was then warmed and cooled to room temperature and filtered. The filtrate was concentrated to half its volume and left to stand overnight. The yellow coloured crystals separated were filtered and recrystallised from ethanol, mp 178^0C.

Preparation of the Ligand 6

The literature [5] was followed

The ligand was synthesized by following the literature method.

1.889g of 2-hydroxy napthaldehyde and 1g of thiosemicarbazide were dissolved in 15ml and 50ml warm dehydrated ethyl alcohol respectively. The clear solutions were then mixed in a 150ml round bottomed flask and heated under reflux for 1.5h. A yellow precipitate appeared which on recrystallixation yielded a brownish yellow crystal, collected by filtration and dried at room temperature, mp > 245^{0}C.

Preparation of the Ligand 7

The literature [7] was followed

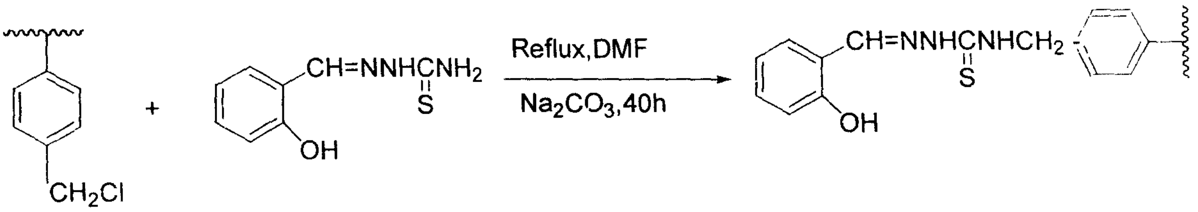
The ligand was synthesized by following the literature method.

A mixture of 1.0435 ml of 2-pyridine carboxaldehyde and 1g of thiosemicarbazide dissolved in 50ml ethyl alohol were placed in a 100ml round bottomed flask and was heated under reflux for 1h. A yellow precipitate was formed. The solid after filtration and further recrystallisation from the same solvent produced a yellow crystaline material, mp 210^{0}C.

3.5 Synthesis of the functionalized chelating resin compounds :

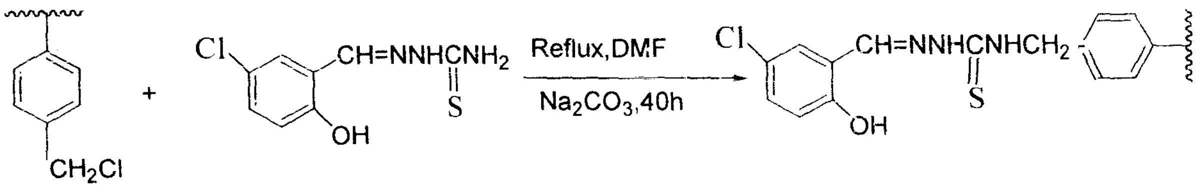
The overall reaction scheme for the syntheses of the compounds is presented in Figure 3.1.1.

1.



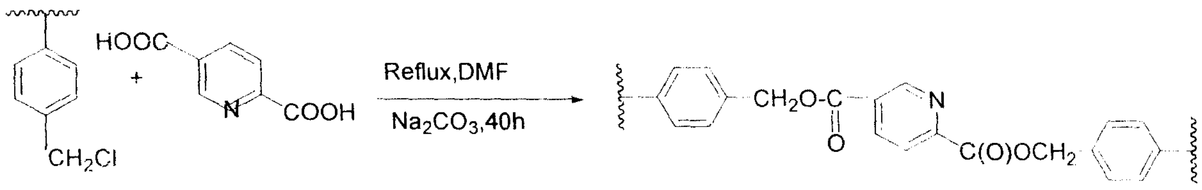
Ligand 1 Compound **1**

2.



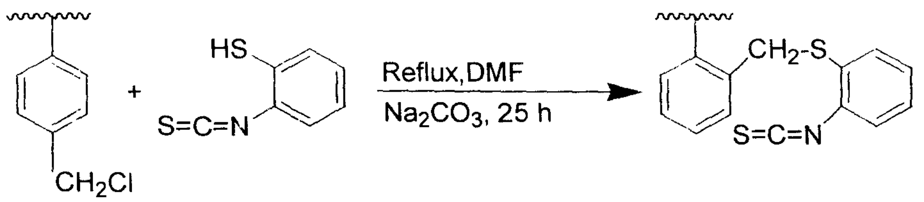
Ligand 2 Compound **2**

3.



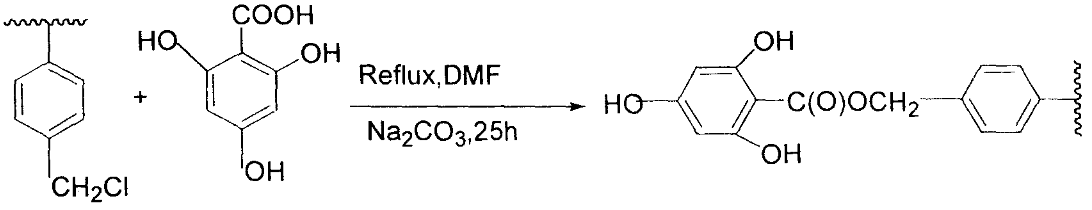
Ligand 3 Compound **3**

4.



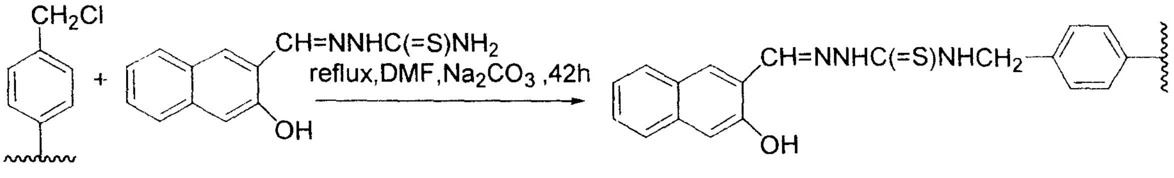
Ligand 4 Compound **4**

5.



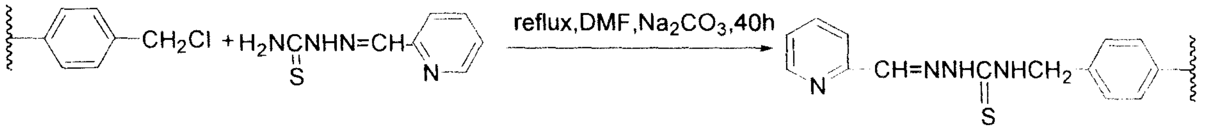
Ligand 5 Compound **5**

6.



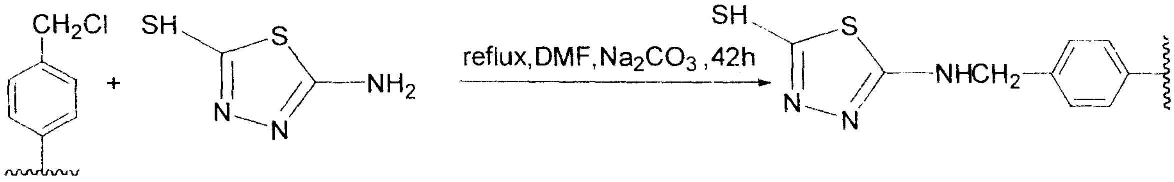
Ligand 6 Compound **6**

7.



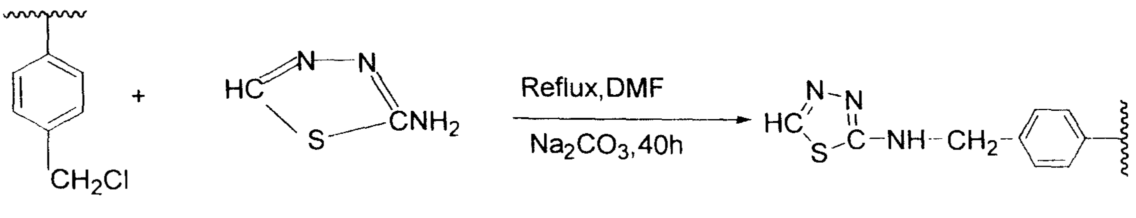
Ligand 7 Compound **7**

8.



Ligand 8 Compound **8**

9.



Ligand 9 Compound **9**

However, the details of the method for the syntheses of the compounds are given below:

3.5.1 Compound **1**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene divinyl benzene (1% cross linked) was used as starting material. The co-polymer bead (1 g, 100-200 mesh) was heated under reflux with 800mg salicylaldehyde thiosemicarbazone in presence of sodium carbonate (400g) in N, N- dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a new yellow polymer compound **1**. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

3.5.2 Compound **2**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene divinyl benzene (1% cross linked) was used as starting material. The co-polymer bead (1g. - 200 mesh) was heated under reflux with 700mg 5, chloro salicylaldehyde thio semicarbazone in presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a pale yellow polymer compound 2. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and kept at room temperature.

3.5.3 Compound **3**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene co polymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 505mg 2,5, dicarboxylic acid pyridine in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a pale yellow polymer compound **3**. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

3.5.4 Compound **4**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene co polymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 600mg 2, mercapto isothio cyanate in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 25 h to obtain a pale yellow polymer compound **4**. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

3.5.5 Compound **5**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene co polymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 700mg 2,4,6- trihydroxy benzoic acid in the presence of sodium carbonate (400g) in N, N dimethyl benzoic formamide (DMF, 100ml) in a 150 ml round bottomed flask for 25 h to obtain a deep yellow polymer compound **5**. The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed with distilled water, air dried and stored at room temperature.

3.5.6 Compound **6**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene copolymer containing 1% divinyl benzene was used as the starting material. The co-polymer bead (1g. 100 - 200 mesh) was heated under reflux with 750mg of 2 - hydroxy napthaldehyde thiosemicarbazone in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 42 h to obtain a new pale yellow polymer compound **6**. The product was washed throughly with DMF to remove excess ligand

and then by 1M HCl to remove excess base. Finally it was washed with distilled water (50ml in several portions), air dried and stored at room temperature.

3.5.7 Compound **7**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene copolymer containing 1% divinyl benzene (1g, 100-200mesh) was heated under reflux with 540mg of 2 - Pyridine carboxaldehyde thiosemicarbazone in the presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h. A brown yellow polymer resulted. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess base and finally by distilled water and dried at room temperature. The solid was collected and stored at room temperature.

3.5.8 Compound **8**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene crosslinked with 1% divinyl benzene (1g, 100 - 200 mesh) was heated under reflux with 400mg of 5 - amino 1, 3, 4 thiadiazole 2-thiol in the presence of sodium carbonate in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 42 h when an orange yellow polymer compound **8** was obtained. The product was washed thoroughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed by 50ml distilled water, air dried and stored at room temperature.

3.5.9 Compound **9**

The literature [8, 9] were followed

Air dried chloromethylated polystyrene divinyl benzene (1% cross linked) was used as starting material. The co-polymer bead (1g. - 200 mesh) was heated under reflux with 700mg 2, amino 1, 2, 3 thiadiazole in presence of sodium carbonate (400g) in N, N dimethyl formamide (DMF, 100ml) in a 150 ml round bottomed flask for 40 h to obtain a yellow functionalised resin compound **9**.The product was washed throughly with DMF to remove excess ligand and then by 1M HCl to remove excess base. Finally it was washed by 50ml distilled water, air dried and stored at room temperature.

The numbers for the ligands and the compounds as assigned in this chapter have been followed throughout this dissertation in the following chapters.

3.6 Microwave assisted synthesis:

The literature [8 - 10] were followed

A selection of the ligands was used to carry out the microwave assisted functionalisation .

Air dried chloromethylated polystyrene crosslinked with 1% DVB (50mg, 100 - 200 mesh) was reacted with required amount (1 : 1 ratio based on the percentage of chlorine present) of the respective organic chelating ligand in presence of sodium carbonate in N, N dimethyl formamide (20ml). The mixture was placed in 100ml polytetrafluoro ethylene (PTFE) reactor inside the microwave oven. The time and power level to attain the optimum condition for synthesis of the resin compounds were adjusted as shown in the Table 3.1.

Table 3.1.1. Optimisation of power and time for microwave assisted synthesis of the functionalised resin compounds.

Compound **2**

Power (Watt)	Time (Minute)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
100	60	75.48	6.16	3.35
180	40	77.28	6.07	4.32
300	30	75.77	5.87	6.42
450	10	79.00	6.08	5.12

Compound **6**

Power (Watt)	Time (Minute)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
100	60	80.97	6.62	7.04
180	40	81.19	6.51	3.84
300	30	80.38	6.34	4.70
450	10	80.89	6.33	5.90

Compound **7**

Power (Watt)	**Time (Minute)**	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**
100	60	80.16	6.69	3.55
180	40	80.30	6.62	2.26
300	30	80.07	6.53	6.44
450	10	81.53	6.63	6.47

Compound **8**

Power (Watt)	**Time (Minute)**	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**
100	60	70.27	5.53	9.07
180	40	73.93	5.80	8.43
300	30	74.85	5.74	11.15
450	10	74.79	5.79	9.89

The physical characteristic parameters of the compounds **1-9** are presented in Table 3.1.2

Table 3.1.2.Physical Characteristics of the new functionalised resin compounds

Compounds	**colour**	**beadsize**	**elemental analysis found (%)**	**% of liganad introduction in the polymer complex**
1	Yellow	100 - 200 mesh	C - 79.16 H - 6.68 N- 4.20	30.55
2	Pale yellow	100 - 200 mesh	C - 75.77 H - 5.87 N - 6.42	35.3
3	Yellow	100 - 200 mesh	C - 81.40 H - 7.15 N - 2.46	45.3
4	Light yellow	100 - 200 mesh	C - 75.98 H - 5.92 N - 5.53	40.55
5	Deep brown	100 - 200 mesh	C - 77.45 H - 6.84	52.79
6	Pale yellow	100 - 200 mesh	C - 75.96 H - 6.89 N - 5.22	89.36
7	Brown yellow	100 - 200 mesh	C - 78.28 H - 6.44 N - 6.20	42.0
8	Orange yellow	100 - 200 mesh	C - 69.80 H - 5.92 N - 5.96	31.80
9	Yellow	100 - 200 mesh	C - 74.02 H - 6.91 N - 7.77	45.6

The IR data (Figure 3.1.2 – 3.1.16) and their tentative assignments for the ligands and the new compounds **1-9** are presented in Table 3.1.3 and 3.1.4 respectively.

The literature [11, 12] were followed

Table 3.1.3 The IR Data(cm^{-1}) for the ligands.

Compound Ligand	ν_{OH}	ν_{NH2}	$\nu\ (C=N)$	$\nu_{(N=C=S)}$	ν_{SH}	$\nu_{(C=S)}$
1	Merged with γ_{NH2}	3442 (m,b)	1612(s)			777(m)
2	”	3406(m,b)	1610(s)			777(m)
4				2090(w)	2340(w)	
6	”	3448(m,b)	1610(m)			775(m)
7	”	3425(m,b)	1620(s)			776(m)

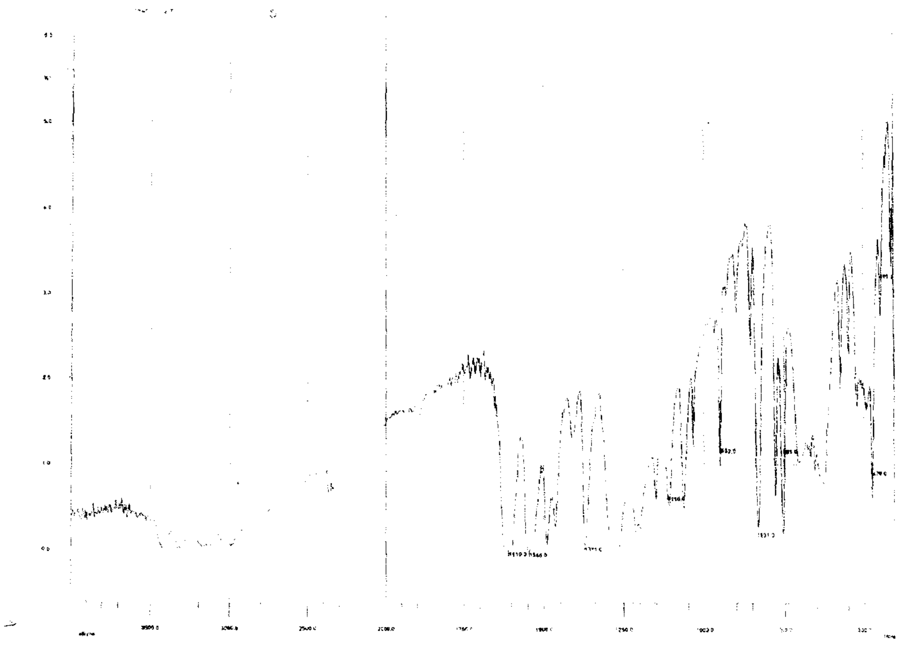
s = strong, m = medium, w = weak b = broad

Table 3.1.4.The IR data (cm^{-1})* for functionalised chelating resin compounds (**1-9**)

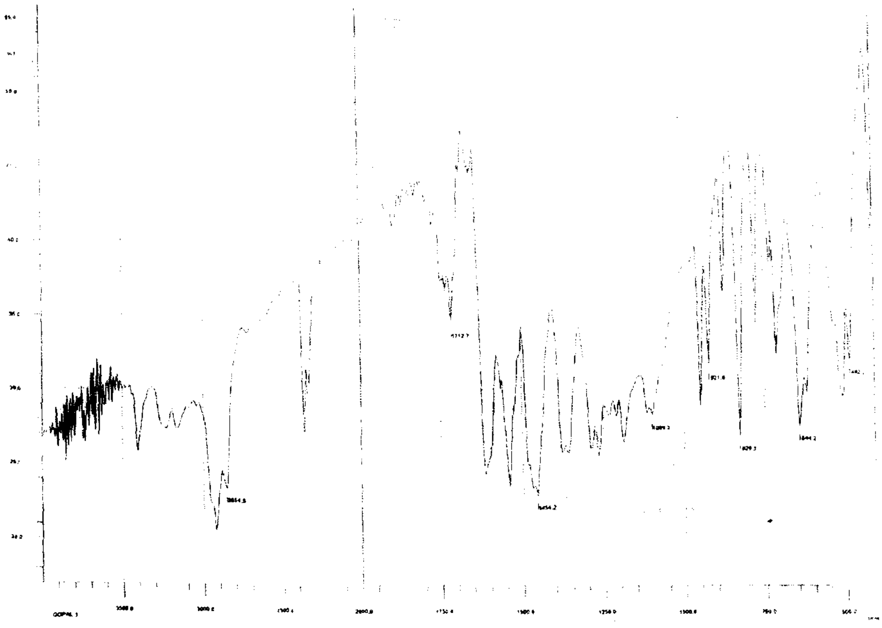
Compound	ν_{OH}	ν_{NH}	$\nu_{C=N)}$	$\nu_{(COO)}$	$\nu_{(C=S)}$	$\nu_{(CSC)}$	$\nu(_{C-Cl)}$
Merrifield Resin	—	—	—	—	—	—	699(s)
1	3300(b,m)	3450(b,m)	1650(m)	—	777(m)		
2	3325(b,m)	3450(b,m)	1650(m)		776(m)		
3	—	—	—	1595(m)			
4	—	—	1596	—	—	659(w) 2376(m)	
5	3400(b,m)	Merged with ν_{OH}	—	1600(s)			
6	3400(b,m)	3391(b,m)	1654(m)	—	775(m)	—	
7	3425(b,m)	3150(b,m)	1600(m)	—			
8	—	3400(b,m)	1653(m)	—		670(w) 2319(w)	
9	—	3400(b,m)	1652(m)	—	675(w)		

* s = strong, m = medium, w=weak, b = broad

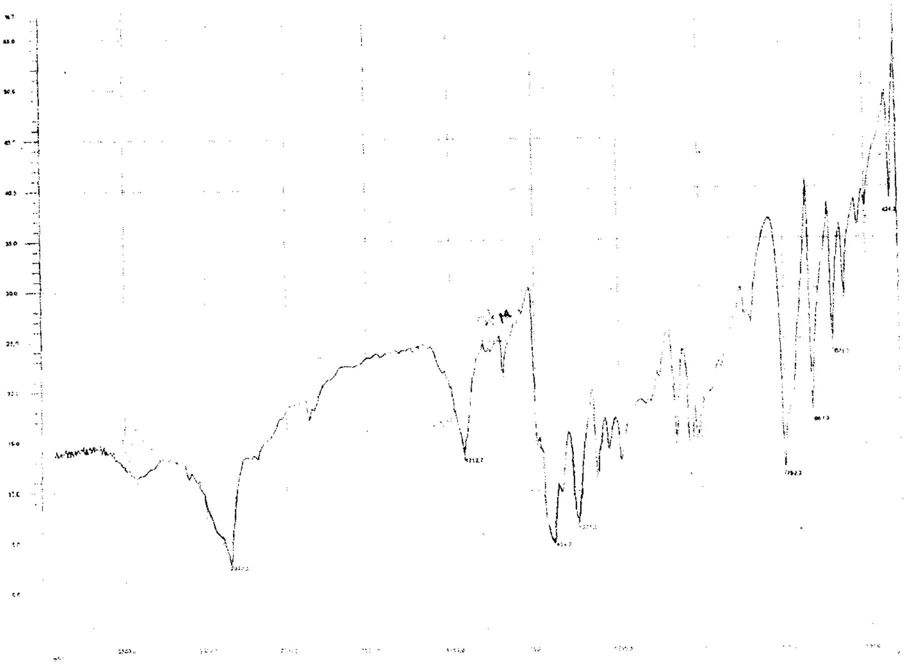
FIGURE : 3.1.2 – 3.1.16 The following are the IR Spectra of Ligand 1, 2, 4, 6, 7 and the Compound (**1** to **9**)



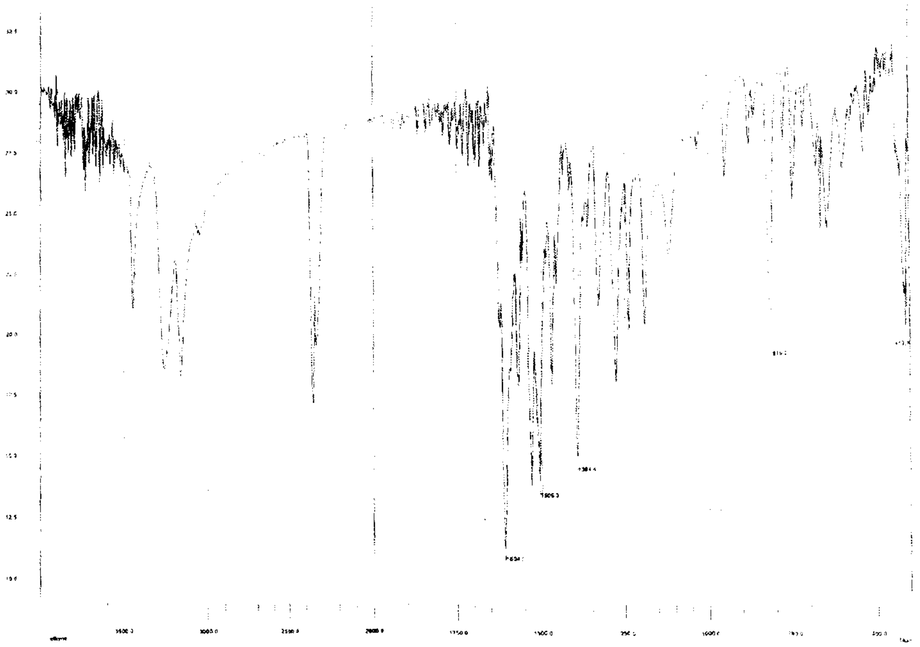
Ligand 1



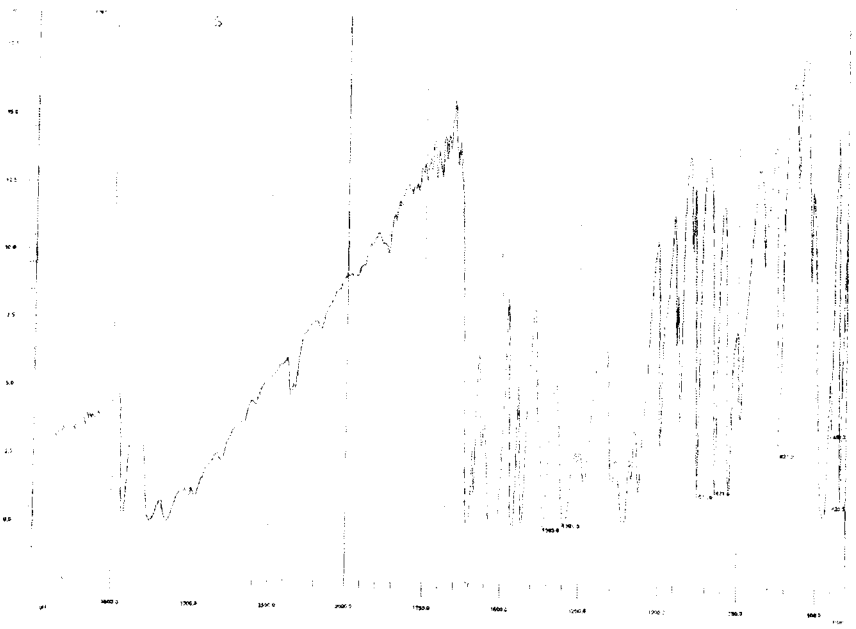
Ligand 2



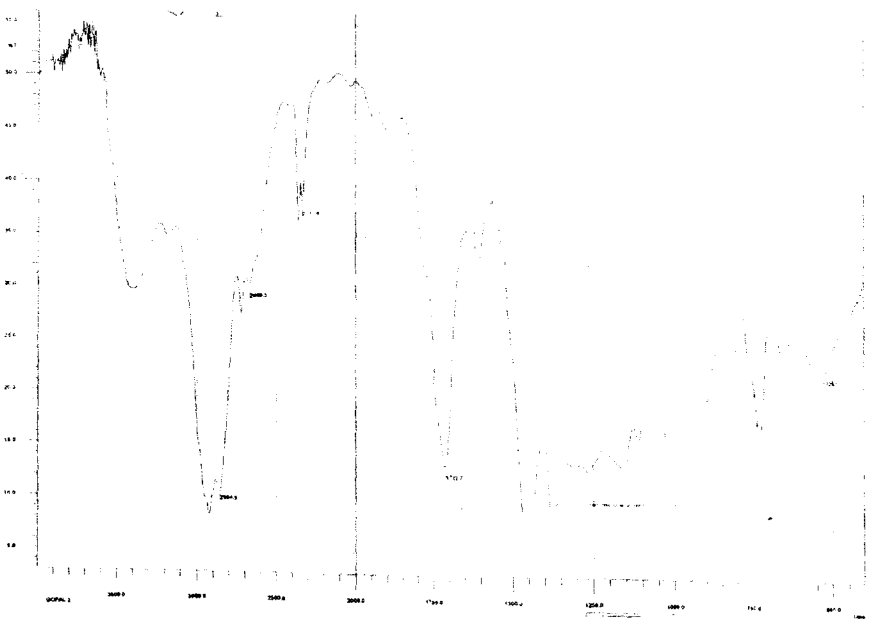
Ligand 4



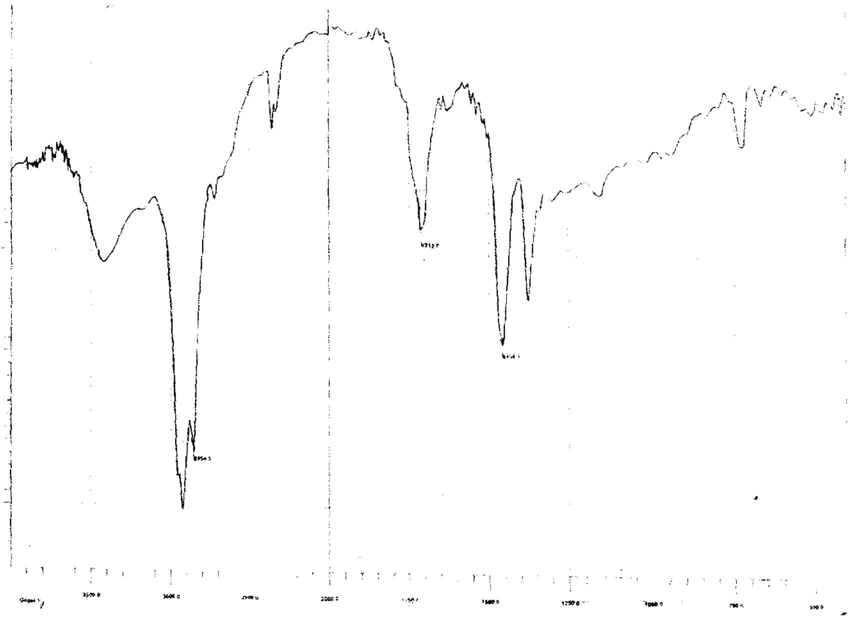
Ligand 6



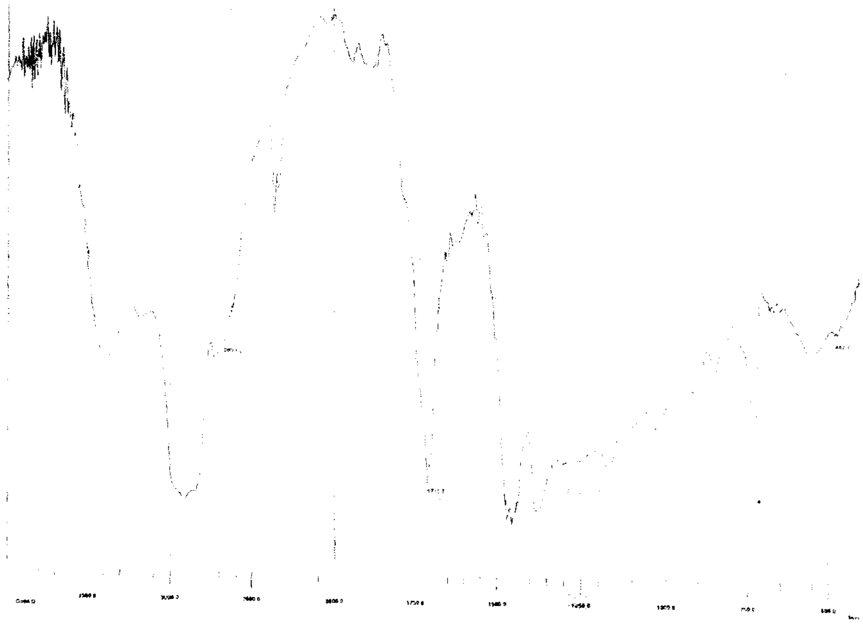
Ligand 7



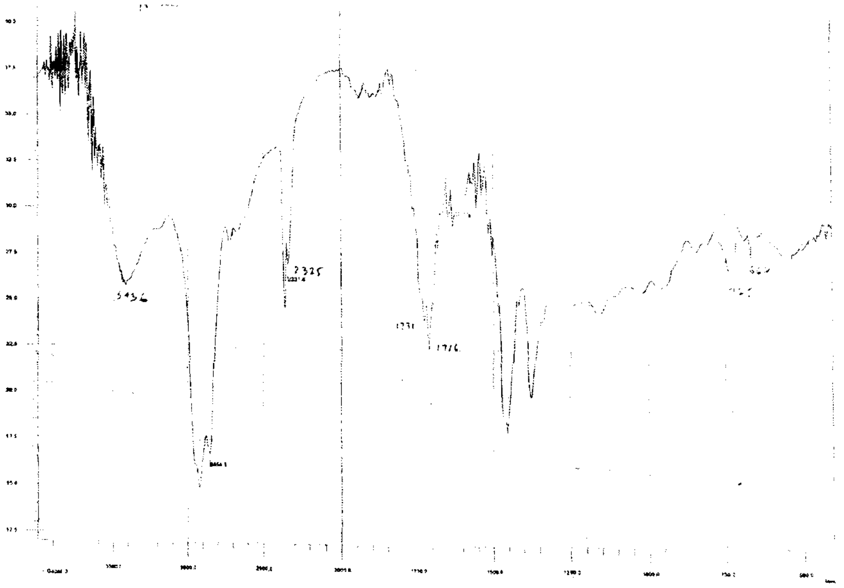
Merrifield Polymer



Compound **1**

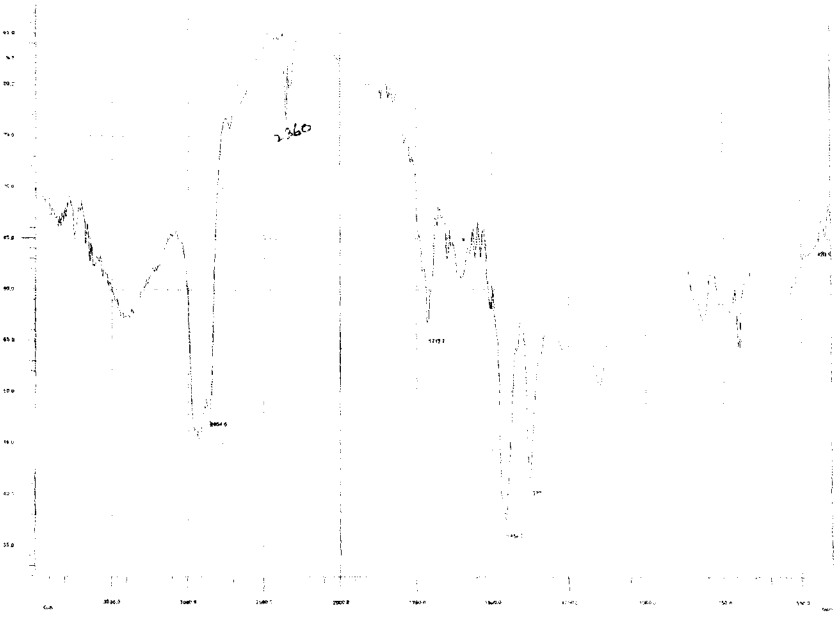


Compound **2**

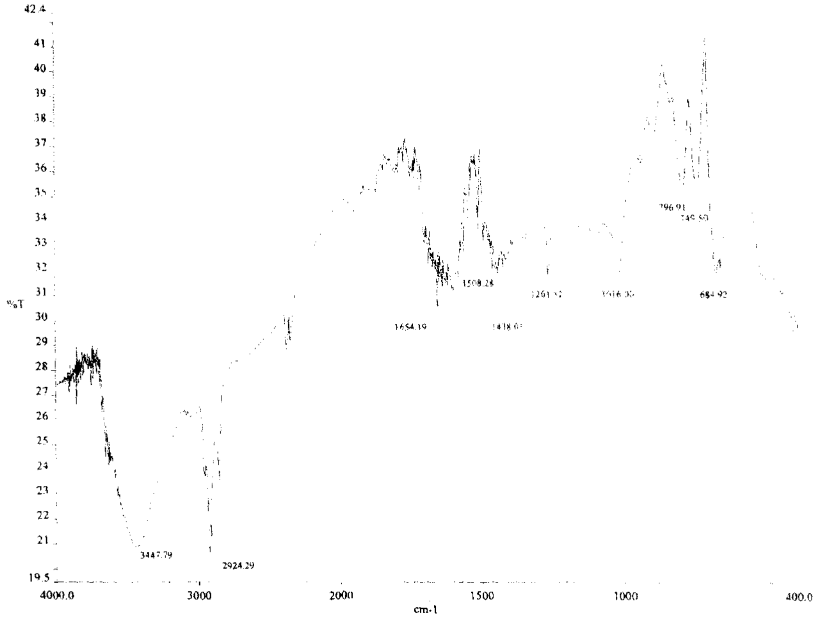


Compound **3**

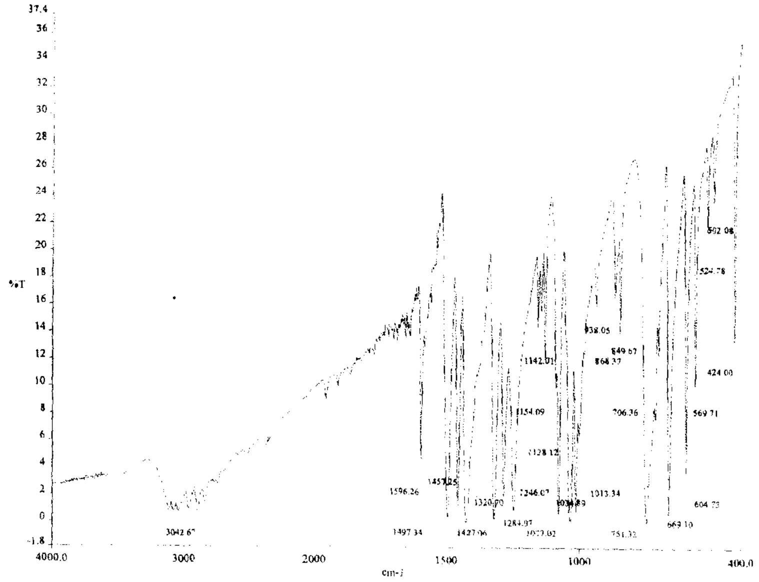
Compound **4**



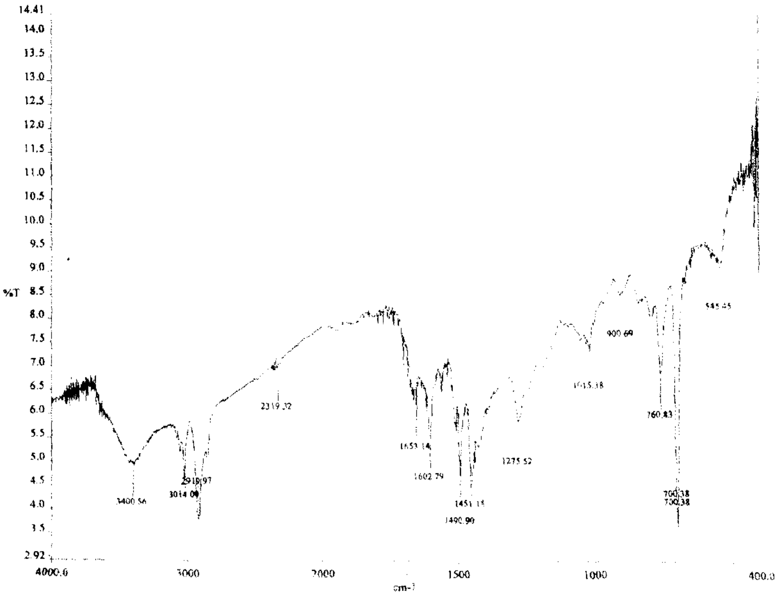
Compound **5**



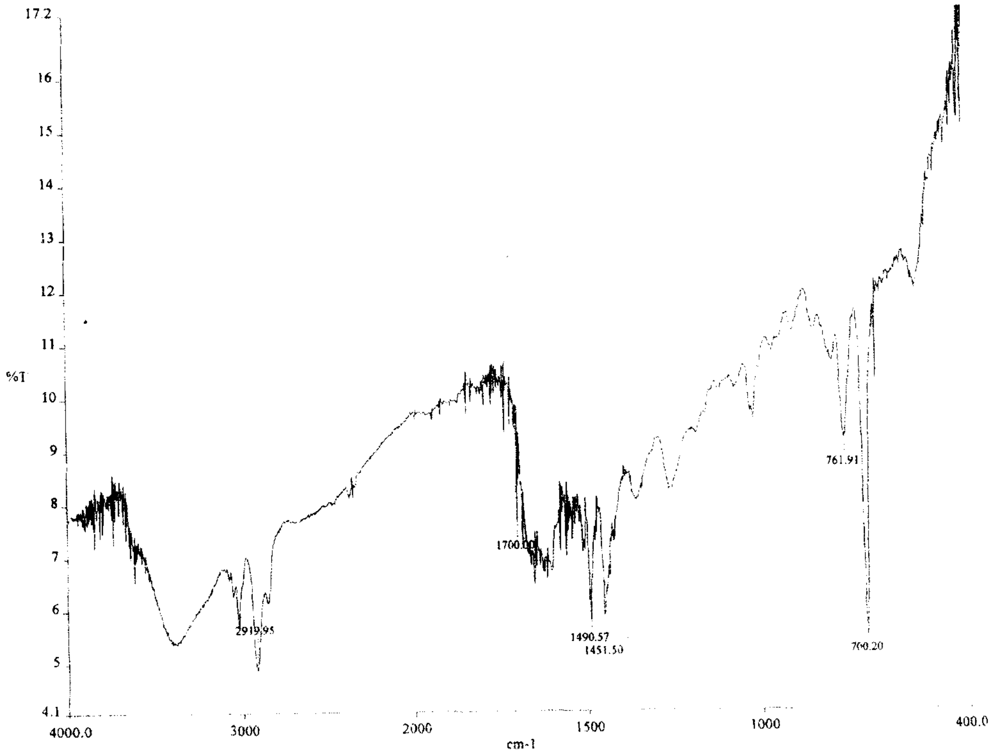
Compound **6**



Compound **7**



Compound **8**



Compound **9**

3.7 Scanning electron microscopy

The literature was followed [13 - 14]

The surface morphology of an adsorbent could be extensively characterized using scanning electron microscopy. The SEM images of (i) chloro-polystyrene divinyl benzene, (ii) functionalized Cl-PSDVB (compound **6**), (iii) copper metal sorbed on the surface of the functionalized resin **6**, (iv) functionalized Cl-PSDVB (compound **8**) and (v) cadmium metal sorbed on the surface of the functionalized resin **8** was presented in the different figures (3.1.17 – 3.1.22).

Evidently the micrograms on comparison clearly indicated the incorporation of the ligands and sorbed metal ions on the resin bed.

FIGURE : 3.1.17 SEM image of chloro-polystyrene divinyl benzene

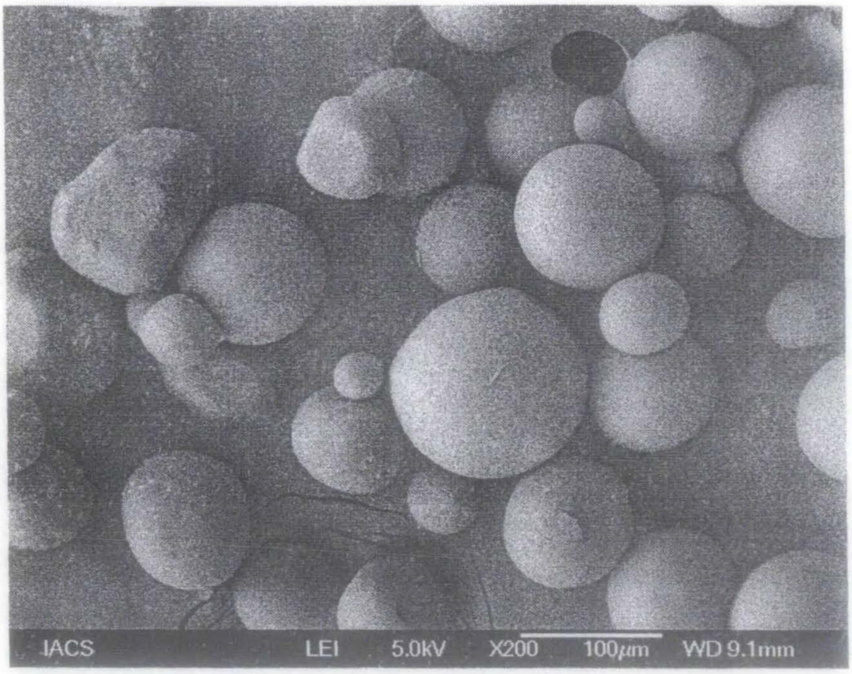


FIGURE : 3.1.18 – 3.1.19 SEM image of functionalized Cl-PSDVB (compound **8**) and cadmium metal sorbed on the surface of the functionalized resin **8.**

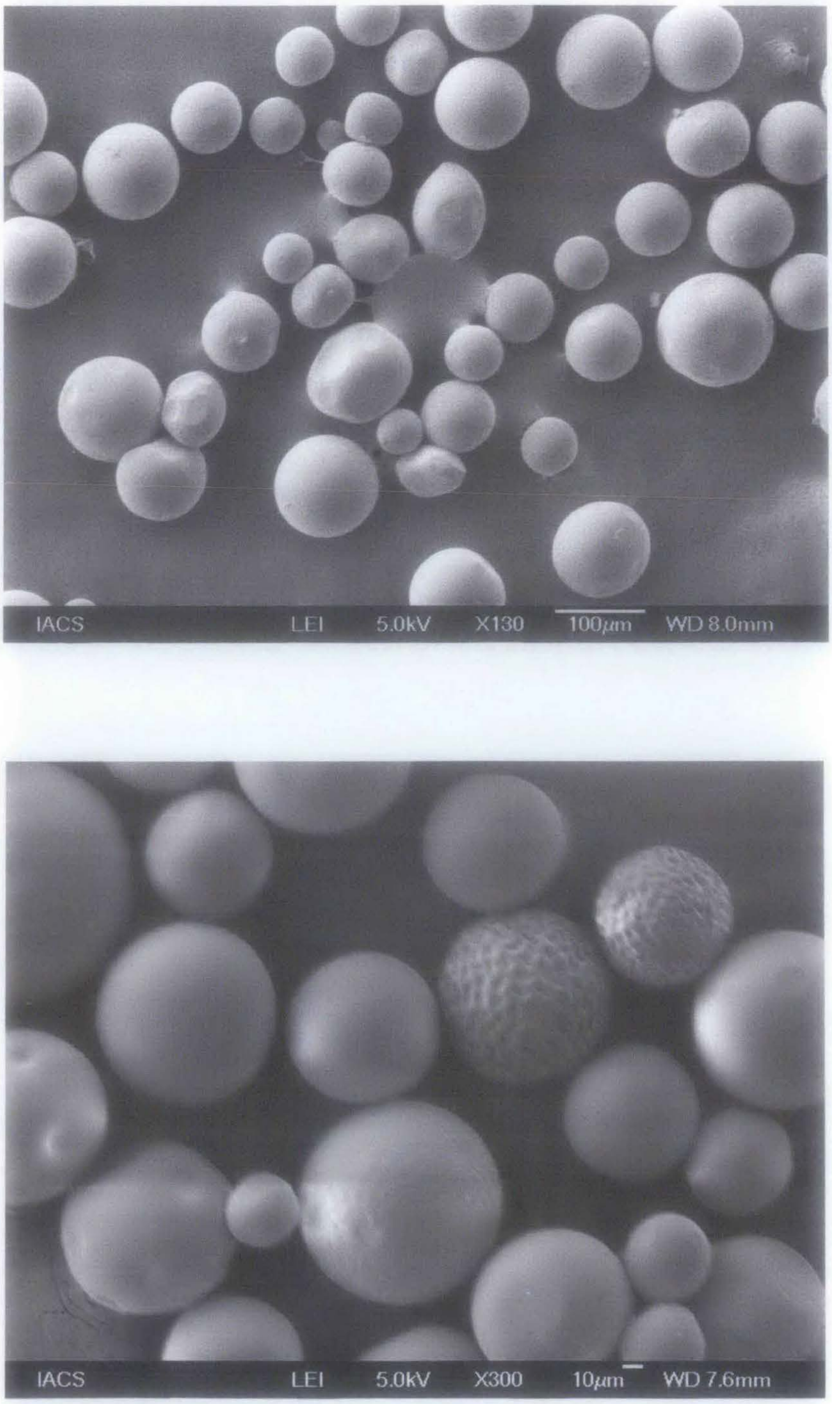
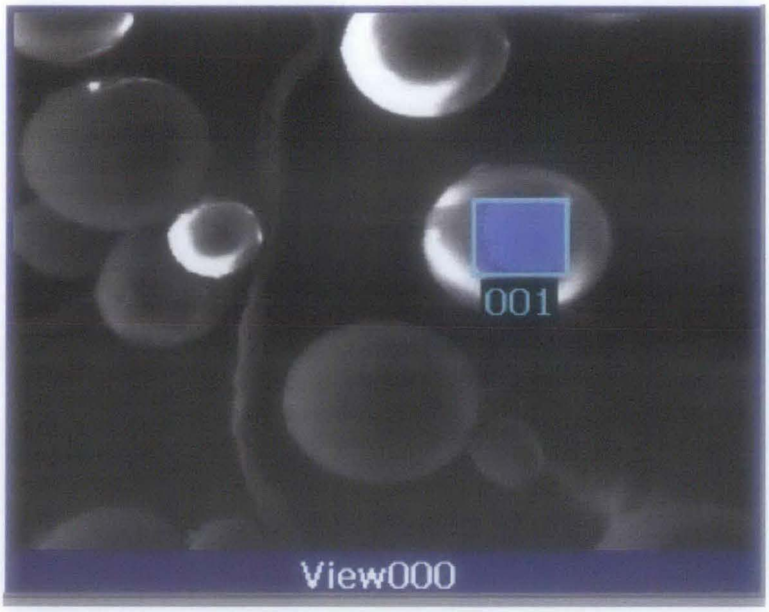
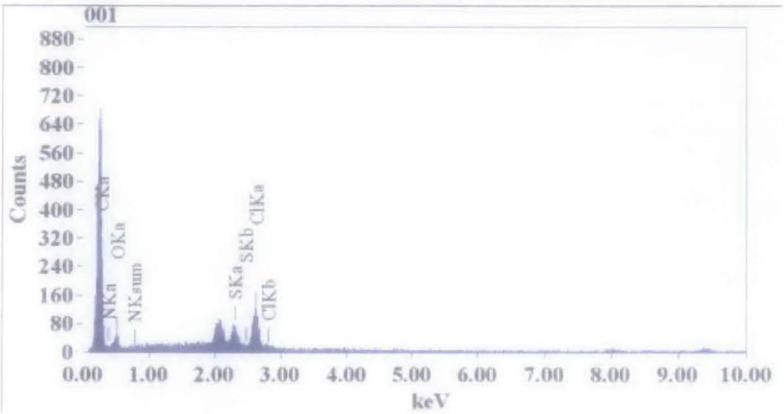
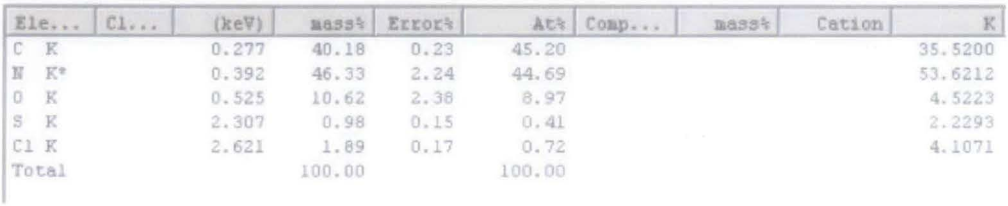


FIGURE : 3.1.20 SEM image of functionalized Cl-PSDVB (compound **6**)

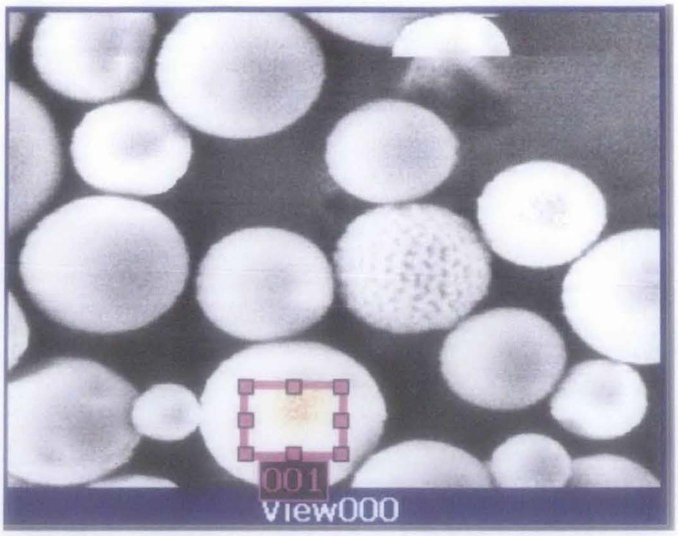


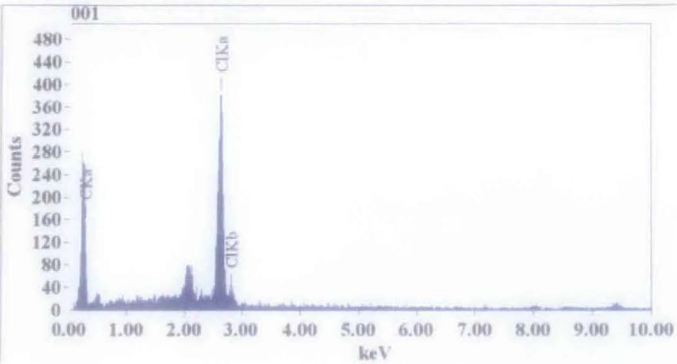


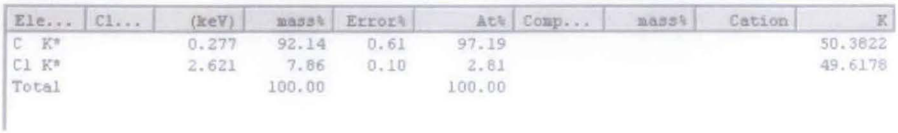


Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation	K
C K		0.277	40.18	0.23	45.20				35.5200
N K*		0.392	46.33	2.24	44.69				53.6212
O K		0.525	10.62	2.38	8.97				4.5223
S K		2.307	0.98	0.15	0.41				2.2293
Cl K		2.621	1.89	0.17	0.72				4.1071
Total			100.00		100.00				

FIGURE : 3.1.21 SEM image of Chloro-polystyrene divinyl benzene

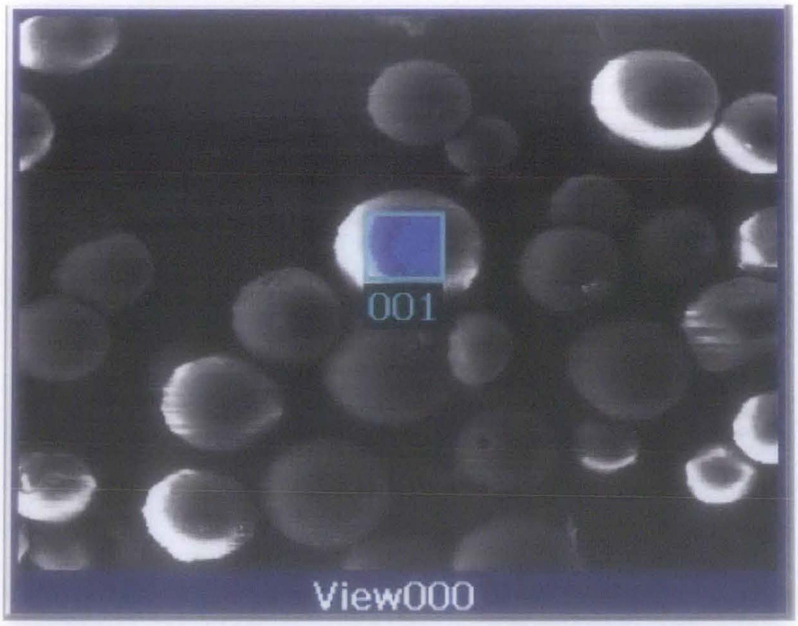


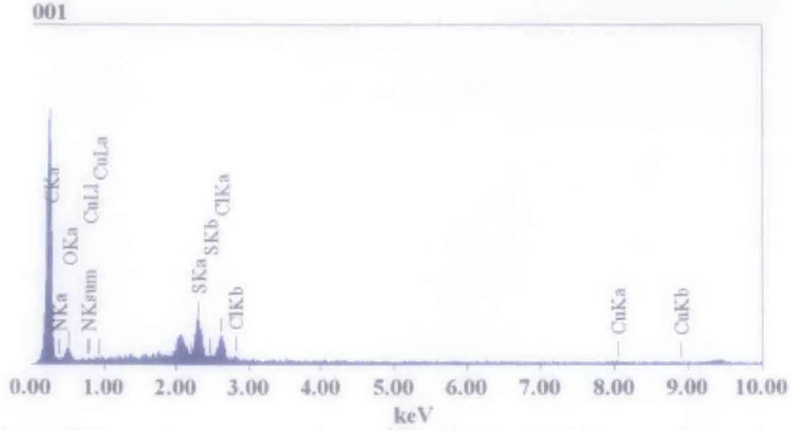


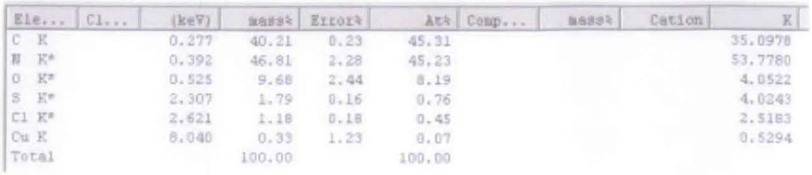


Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation	K
C K*		0.277	92.14	0.61	97.19				50.3822
Cl K*		2.621	7.86	0.10	2.81				49.6178
Total			100.00		100.00				

FIGURE : 3.1.22 SEM image of copper metal sorbed on the surface of the functionalized resin **6**.







Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation	K
C K		0.277	40.21	0.23	45.31				35.0978
N K*		0.392	46.81	2.28	45.23				53.7780
O K*		0.525	9.68	2.44	8.19				4.0522
S K*		2.307	1.79	0.16	0.76				4.0243
Cl K*		2.621	1.18	0.18	0.45				2.5183
Cu K		8.040	0.33	1.23	0.07				0.5294
Total			100.00		100.00				

3.8 Stability of resin compounds

The literature was followed [15]

3.8.1 Thermal stability was recorded. All the compounds are stable in air and moisture. However, it was found by TGA and differential scanning calorimetry (DSC) analyses that all the resin compounds were stable up to 230^{0}C.

3.8.2 Acid - Base Stability

The literature [16 - 18] were followed

Each of the functionalised resin compounds (**1-9**) (0.5g) was stirred with 100ml each of (i) 1-6(N) HCl (ii) 1-6(N) HNO_3 and (iii) 2N NaOH in a 150ml beaker and left for seven days. It was then filtered and the resin was washed with distilled water. After drying at room temperature the nitrogen content of the resins were determined. No significant change in nitrogen content of the resin compounds before and after treatment with the above three different solution was observed.

3.8.3 Stability of the resin compounds while remained in the column

During the entire period of investigation the columns of functionalized resins were left immersed in water for six months. After this period the resin compounds were recovered from the column, was washed with distilled water, dried and nitrogen content of each of the compounds were determined. No significant change in the analyses were observed.

3.8.4 Reusability of the resin

The resin compounds were used several times for sorption and elution cycles by batch as well as column process and it was observed that the exchange capacity remained constant after its use at least of fifty times.

3.9 Results and discussion

For the functionalisation of the resin, in all, five ligands (Figure 2.1,2.2,2.4,2.6 and 2.7) were synthesized by following standard literature methods [5 – 7]. Other four ligands (Figure 2.3,2.5,2.8 and 2.9) were obtained from the commercial sources and used without further purifications. All the synthesized ligands analysed satisfactorily and had the mp, IR and ^{1}H and ^{13}C spectra identical as reported previously [5 – 7]

The ligands were used to functionalise the chloromethylated polystyrene divenyl benzene resin (Merrifield polymer).This was carried out by heating under reflux for a considerable period (between 25 h – 42 h) the ligand and the resin in DMF solvent in presence of a base. To minimize the duration of the reaction heating by microwave irradiation was also carried out. The products of either processes were identical. The yield did not vary indicating that the microwave irradiation method to be a better option for the syntheses.

Each of the compounds were coloured solids(pale yellow – yellowish brown) insoluble in common organic or inorganic solvents. The compounds did not melt or decompose and were found to remain unchanged at least up to 230^{0}C.

Incorporation of the ligand to the resin were identified by the chemical analyses in which all of the compounds analysed for the presence of quite a high percentages of nitrogen in it.The presence of both nitrogen and sulfur was also indicated in the products by the conventional qualitative tests. The IR spectra on analyses showed the desired stretching frequencies for all the relevant groups which are presented in Table 3.4.

The strong stretching frequency attributable to ν_{CCl} (699cm^{-1}) of the parent chloromethylated polystyrene divenyl benzene resin (Merrifield polymer) was absent after functionalisation by the ligands. This indicates the involvement of the C-Cl bond of the resin in compound formation. The presence of both ν_{OH} and ν_{NH} stretching frequencies as a medium broad band indicated extensive hydrogen bonding [11] in them. For compounds **3** and **5** (Table 3.4) the ν_{COOH} appeared as a medium to strong stretching bands at around 1600 cm^{-1} consistent with the literature [11].In compounds **4** and **8,** the ν_{SH} were assigned tentatively at 2376 and 2319cm^{-1} respectively as weak bands.Whereas for compounds **8** and **9** the ν_{CS} could be tentatively assigned at670 and 675cm^{-1} respectively as weak vibrations.

Incorporation of the ligands on the resins were confirmed by the SEM micrographs of at least two of the newly synthesized resin compounds.

Interestingly, the SEM micrographs for the sorption of copper and cadmium ions on compounds **6** and **8** respectively showed the presence of both the metal ions on the surface. These further proved the extensive metal ion binding on the surface of the functionalized resins.

As far as the stabilities of the resin compounds were concerned these were found to be stable both in strong acids and in basic medium. These were also found to be stable in neutral aqueous conditions for several months rendering them very useful to use over and over again.

We would like to point out that it was possible for the ligands which contained more than one binding sites in it (eg.COOH,OH,NH_2 or SH) might of course be immobilized through more than one of these groups in the resin matrix. However, in absence of more precise tools, the identifications of these compounds as proposed were mainly based on IR data.

3.10 Conclusion

It is to note that several new functionalized resins shave been designed purposefully to study the sorption and desorption behavior of the toxic heavy metals which cause severe pollution problems. The methods for the syntheses are relatively simple, the yield of the desired products are high and all the compounds are found to be stable under experimental conditions which encourages their suitability for the removal of undesired toxic metal ions from water and soils in particular.

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CHAPTER IV

INVESTIGATIONS ON THE SORPTION-ELUTION BEHAVIOUR OF NEW FUNCTIONALIZED RESINS

Abstract

The pH dependence of metal sorption, sorption capacities, IR analysis, SEM analysis, stabilities of the resin compounds are examined. Sorption behaviour of metal ions are investigated by varying the flow rate of the metal solutions through the column. Electrolytic effect on sorption, selection of suitable eluting agents of the metal ions Cu(II), Zn(II), Pb(II), Cd(II), Cr(III) and Ni(II) for each functionalised resin compounds were investigated. Pre-concentration studies are carried out for a selection of resin compounds. Mutual separation of metal ions both by changing the eluting agent and varying the pH of the medium are examined, investigated and the results are described here.

4.1 Introduction

Accurate analyses of metal ions specially at trace level is one of the most difficult and complicated analytical tasks. Solvent extraction and solid phase extraction are the two most common methods for the pre-concentration and separation of metal ions present in trace quantities. Solvent extraction has some disadvantages due to the use of excess solvent which not only makes the method costly but also is in the direct contradiction of the idea of green chemistry. During the past two decades the use of chelating resins for metal ion pre-concentration and separation has been considerably increased. For this purpose ligands already reported are salicylic acid, pyridine, dithizone [1], thiourea [2], alizarin red S [3], salicylaldehyde, substituted thiosemicarbazone etc. [4, 5, 6].These are known to form stable complexes with transition and other heavy metal ions. Hence these ligands when immobilized on the polystyrene divinyl benzene and other similar resins constitute solid phase extraction system. For example Dev and Rao [7] synthesized bicine immobilized solid support to separate bivalent Cu, Fe, Ni, Co, Zn, Hg and Pb ions .Again 1-hydrazinophthalazine has been functionalized on XAD-4 resins by Pathak and Rao [8] to pre-concentrate the bivalent ions of Cu, Ni, Co, Zn, Cd, Pb and Fe(II) ion efficiently. Dutta and Das[9] reported the separation and pre-concentration of Cd(II) and Hg(II) in a mixture by solid support produced from polystyrene divinylbenzene and 2-aminothiazole.A deviation from the solid polystyrene divinylbenzene resin was indicated when Özcen et al [10]reported natural clay minerals as the solid support, the 8-hydroxy quinoline-immobilised bentonite to separate and pre-concentrate Pb(II) metal ions from aqueous solution. Metilda et al11] carried out extensive studies on U(VI) by using Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation.

Shah et al [12], on the other hand, utilized a convenient microwave irradiated syntheses for the pre-concentration studies of Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II) with a polymeric solid support produced from salicylic acid-formaldehyde-resorcinol (SFR-M). Sahana et al [13] produced a new chelating resin containing indole-methionine composite and determined lead and silver ions after pre-concentration in biological and environmental samples. A new chelating resin was prepared by coupling Amberlite XAD-4 with 1-amino-2-naphthole through an azo spacer by Panahi et al [14] and studied for pre-concentrating of Fe (II) using flame atomic absorption spectrometry (FAAS) for metal monitoring. In a remarkable nano material based solid support Shishehbore et al [16] reported a method for the pre-concentration of trace heavy metal ions in environmental samples. The presented method was based on the sorption of Cu(II), Cd(II), Ni(II) and Cr(III) ions with salicylic acid as respective chelate on silica-coated magnetite nanoparticles.

Therefore, the need for new functionalized solid support could not be over emphasized.There is a continuous search for the new ligands. One such ligand – the thiosemicarbazones, though are known to act as unidentate, bidentate and tridentate fashion have not been exploited extensively for metal ion separation and pre-concentration. A few literature reports are available on the ligands [4, 5]. XAD-2 and PSDVB[15] were used as the solid supports. The pre-concentration of late transition metal ions such as Pt(IV), Pd(II), Ru(III), Rh(III), Ir(III) were studied with thiosemicarbazone moiety immobilized on PSDVB support.This promted us to under take an extensive study on the separation and pre-concentration of early transition and other heavy metal ions by the functionalized PSDVB resins with the suitable derivatives of the thiosemicarbazones, the Schiff base, with a view to examine the applicability of these solid supports to remove toxic metal ions from the environment. Further investigations were also carried out on a few other (N,S),(N,O) and (O,O) containing ligands which were used to functionalise PSDVB and examine the produced solid supports for their environmental applications.

In the light of above discussion the present study embodies the investigations on the usefulness of nine new functionalized resin compounds synthesized by us as described in chapter III for the separation and pre-concentrations of some toxic heavy metals in details. The importance of such investigations could not be over emphasized. The results of such studies are presented herein.

4.2 Methodolgy

4.2.1 Instrumentation

pH of the solutions were measured by using Systronics MK-IV 5631 pH meter while the metal analyses were performed by atomic absorption spectrometer VARIAN model No. 55 with air-acetylene flame and spectra AA-50B. C, H, N analytical data were obtained either from (i) IACS, Kolkata, India or (ii) SAIF, NEHU, Shilong India. DSC used was of PYRIS 6DSC-Perkin Elmer model where as the TGA were done on SHIMADZU TG50/DT50. A domestic Samsung MW73V micro wave oven with a 2450 MHz frequency magnetron and 800 Watt maximum power and PTFE reactors (with 100ml internal volume, 1cm cell wall thickness and hermetic screw caps) were employed to synthesise the funtionalised resins.

4.2.2 Materials

The reagents were procured from

1) Sd fine - chem limited, India - $Pb(NO_3)_2$, $3CdSO_4.8H_2O$, $CdCl_2.2.5H_2O$, $CuSO_4$, $5H_2O$, $ZnSO_4$, $7H_2O$, $MnSO_4$, H_2O, $HgCl_2$, $Co(NO_3)$, $6H_2O$ and Thiosemicarbazide (all AR grade).
2) Merck-Inida - Sodium acetate (AR) and Isobutyl methyl ketone
3) HiMedia Lab. Pvt. Limited, India - $Cr_2(SO_4)_3$(AR)
4) Aldrich, USA - 5 - amino - 1, 2, 4 - thiadiazol-2-thiol (98%) and 2-hydroxy - 1-naphthaldehyde (technical grade) and 5-chloro salicydaldehyde
5) Across Organics, USA 2-Pyridine-carboxaldehyde (GR) and used as received.
6) Fluka,Switzerland - 2, 4, 6 Trihydroxy Benzoic acid

7) Lan Caster,USA - Pyrindine 2, 5 dicarboxylic acid

8) Merck, Germany - $Ni(NO_3)_2, 6H_2O$

All other chemicals used during the study were of reagent grade procured from commercial sources.

4.2.3 Effect of pH on metal uptake

The literature [17, 18] were followed

The effect of pH on metal uptake was examined by batch method in the pH range 1 - 6 adjustd either by 0.1 M HCl or 0.2 M sodium acetate buffer solution. 50mg of the functionalised resin was suspended in a stock solution of the metal ion ($200\mu g\ ml^{-1}$, total volume 30ml) and was stirred for 2h - the mixture was left for overnight and then filtered, washed thoroughly several times with distilled water until no metal ions was detected in the washings. The solid was collected from it and the absorbed metal ions were eluted using 0.5- 4 M HCl or HNO_3.The eluted metal ions were transferred to a 50ml volumetric flask - volume was then made up and was analysed for the metal ions quantitatively by atomic absorption spectrometer (AAS). The results are presented in Table 4.2.1 and Figure 4.2.1

Column Operation

A literature method [4, 18] was followed for column operation: A 160mm × 8mm glass column was used. Air dried functionalized resin (1g) was immersed overnight in distilled water for swelling. The column was then packed with these fully swollen beads. The resin bed was thoroughly washed with sodium acetate buffer solution to adjust the appropriate pH of the column. The sorption and recovery characteristics of

Cu(II), Zn (II), Pb (II), Cd (II) and Cr (III) Ni (II) and Co(II) were examined for all the nine compounds (**1-9**) by passing 0.2 - 20ppm respective metal ion solutions through the column at the flow rate 0.5 - 1ml min^{-1}.

Table 4.2.1.pH dependence of the uptake of the metal (ug g^{-1} of the resin)

Compound **1**

pH	metal ions uptake(ugg^{-1} of the resin)		
	Cu	Pb	Zn
1	37.2	141.3	120.5
2	85.2	231.9	152.7
3	122.1	486.8	190.9
4	160.0	609.9	210.9
5	212.8	645.6	259.2
6	12702.0	2052.7	348.9

Compound **2**

pH	metal ions uptake(ugg^{-1} of the resin)		
	Cu	Pb	Zn
1	292.0	71.2	163.6
2	396.0	1150.6	307.6
3	445.0	1994.6	320.4
4	348.0	1952.6	341.5
5	531.0	2068.7	346.1
6	597.0	2393.7	376.7

Compound **3**

pH	metal ions uptake(ugg^{-1} of the resin)			
	Pb	Cd	Co	Ni
1	947.7	144.4	BDL*	BDL*
2	797.4	56.6	BDL*	BDL*
3	912.0	122.4	2.1	BDL*
4	1601	190.0	BDL*	32.9
5	1552.2	118.0	19.1	22.5
6	1560.4	115.5	57.6	32.9

* BDL = below detection limit

Compound **4**

pH	metal ions uptake(ugg^{-1} of the resin)					
		Mn	Pb	Hg	Cd	Cu
	1	490	BDL*	20	39	30.5
	2	67	62	115	72.1	65.3
	3	80	386.9	45	167.5	285.5
	4	458	154.7	145	120.1	230.4
	5	86	400.0	3210	153.3	387.3
	6	93	980.0	730.0	126.0	530.0

* BDL = below detection limit

Compound **5**

pH	metal ions uptake(ugg^{-1} of the resin)			
	Cu	Cd	Ni	Zn
1	104.9	33.8	95.4	1.5
2	101.1	55.6	127.8	8.0
3	231.8	111.1	198.0	401.0
4	122.8	107.4	135.9	34.1
5	189.0	132.5	131.1	30.1
6	269.6	219.0	152.7	93.9

Compound **6**

pH	metal ions uptake(ugg^{-1} of the resin)		
	Cu	Cr	Zn
1	40.6	7.0	120.0
2	72.23	29.0	155.3
3	112.2	57.5	193.5
4	263.7	58.7	212.5
5	220.0	151.2	270.2
6	1089.9	1563.9	370.8

Compound **7**

pH	metal ions uptake(ugg^{-1} of the resin)		
	Cd	Cr	Pb
1	435.2	13.6	610.3
2	152.0	18.5	721.4
3	171.12	37.8	1025.5
4	116.4	49.7	864.7
5	154.9	187.6	1055.7
6	209.4	2255.3	1769.7

Compound **8**

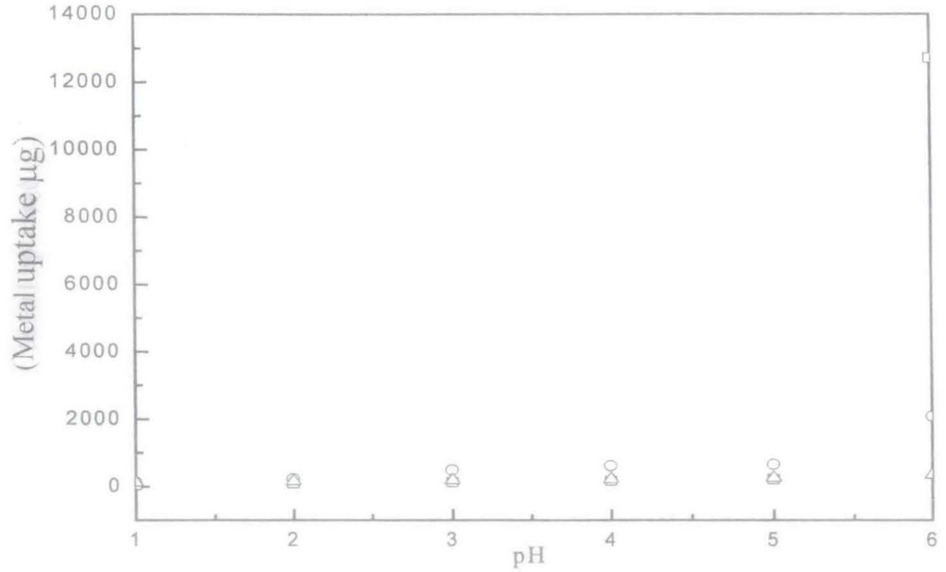
pH	metal ions uptake(ugg^{-1} of the resin)			
	Cu	Pb	Zn	Cd
1	26.6	270.0	162.1	56.9
2	72.3	414.9	197.3	88.5
3	151.9	716.1	309.7	103.8
4	146.3	748.4	384.5	429.5
5	215.4	724.4	338.6	158.1
6	424.6	1593.2	381.0	219.2

Compound **9**

pH	metal ions uptake(ugg^{-1} of the resin)		
	Pb	Cd	Zn
1	125.4	165.0	122.8
2	277.0	84.2	129.8
3	546.5	253.2	182.2
4	549.2	419.2	218.1
5	480.7	125.0	195.5
6	778.1	229.0	319.0

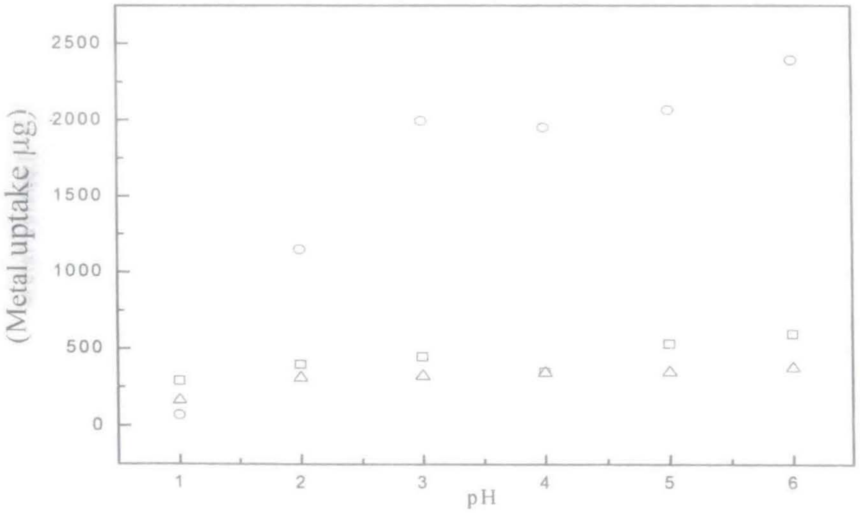
Figure 4.2.1 pH dependence of the uptake of the metal (ug g^{-1} of the resin)

Compound **1**



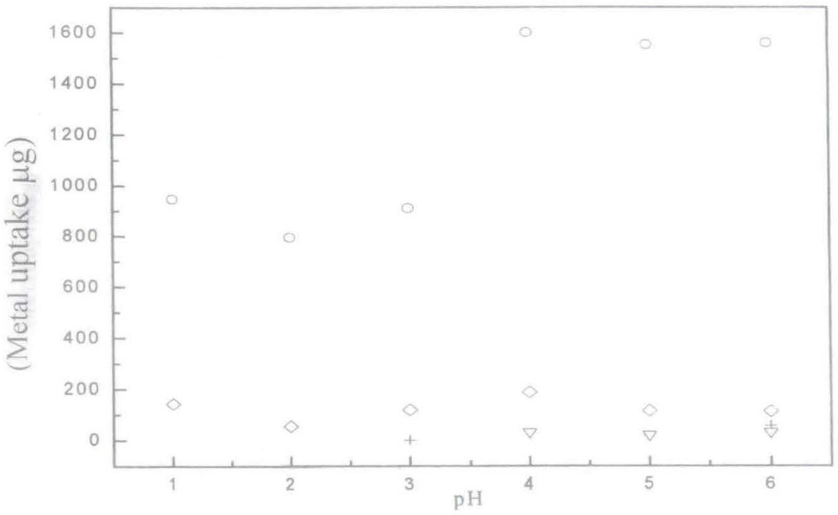
Graphical points: □, Cu; ○, Pb; Δ, Zn

Compound **2**



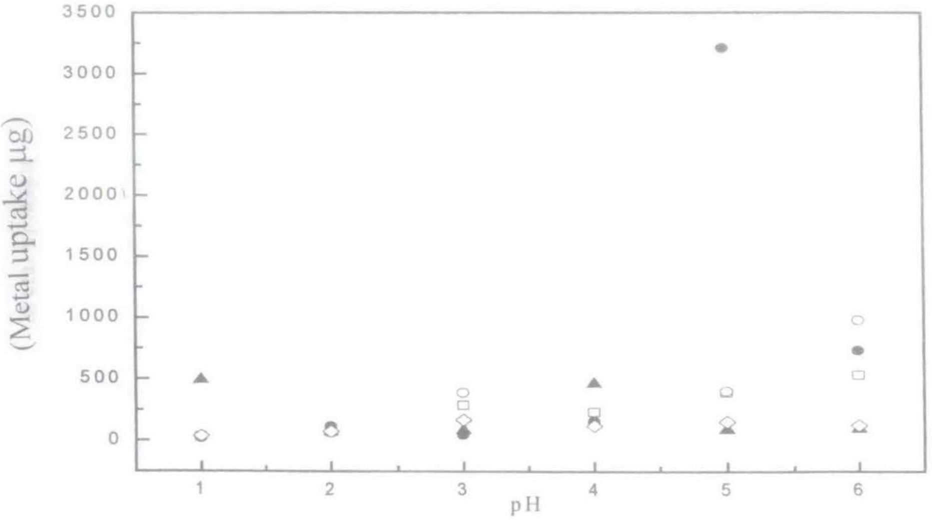
Graphical points: □, Cu; ○, Pb; Δ, Zn

Compound **3**



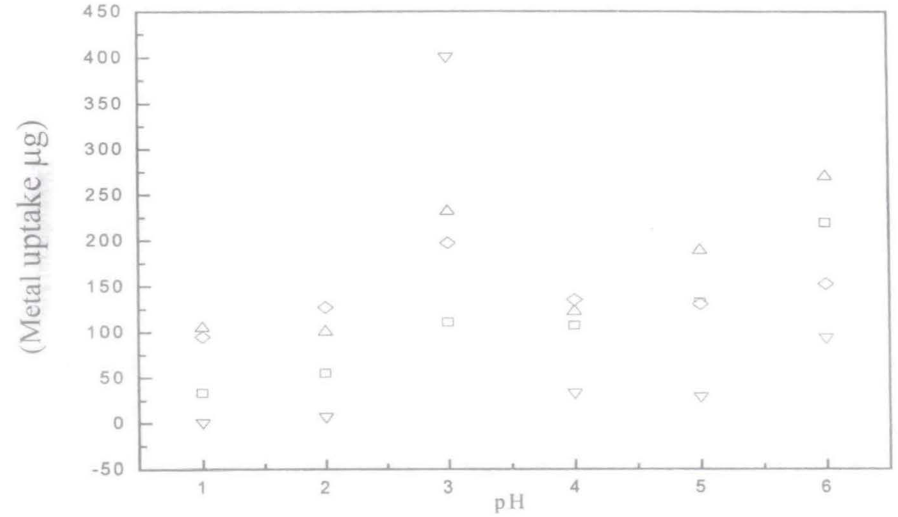
Graphical points: ◊, Cd; ○, Pb; +, Zn; ▽, Ni

Compound **4**



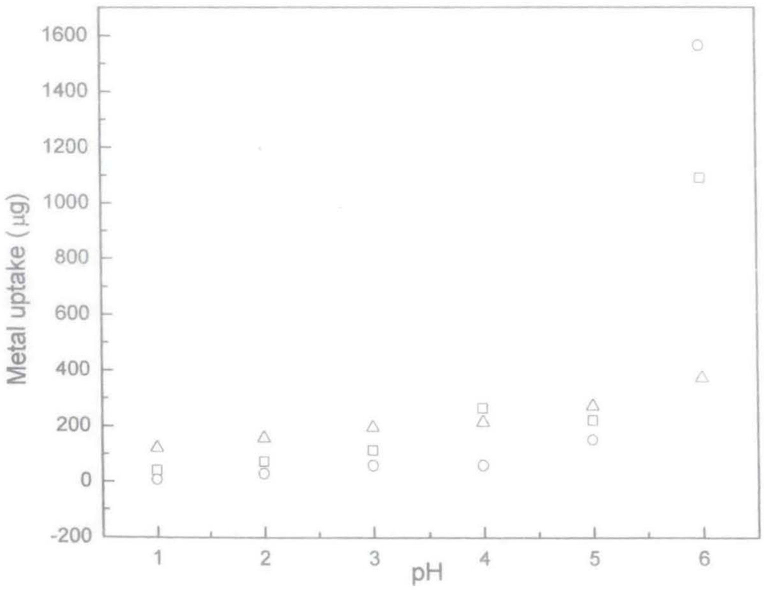
Graphical points: □, Cu; ○, Pb; ▲, Mn; ● Hg, ◇, Cd

Compound **5**



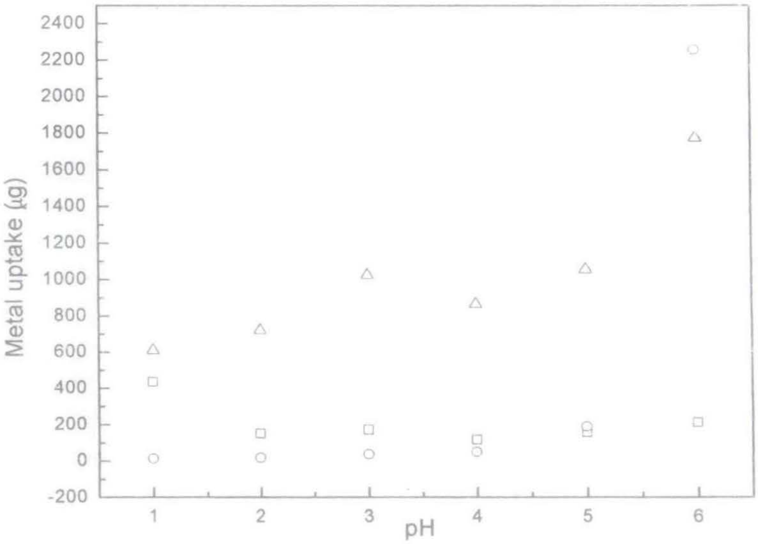
Graphical points: □, Cu; ▽, Ni; ΔZn, ◇, Cd

Compound **6**



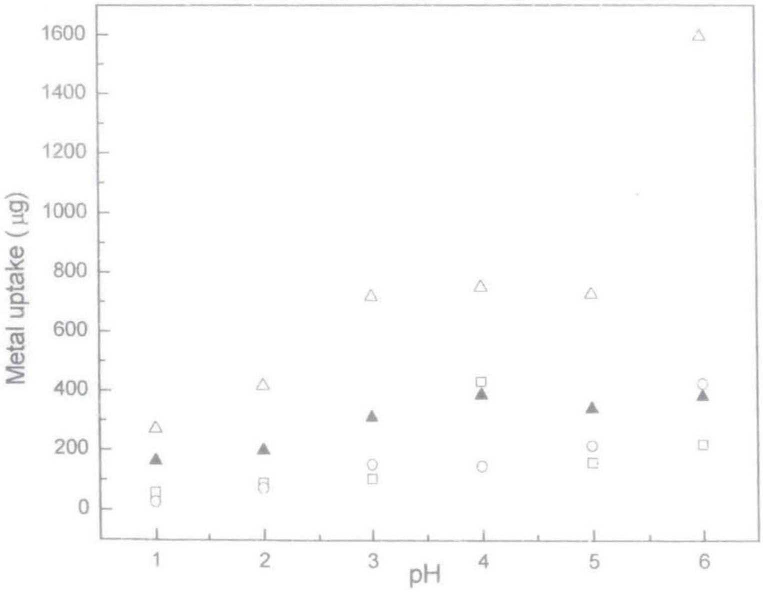
Graphical points: □, Cu; ○, Cr; Δ, Zn

Compound **7**



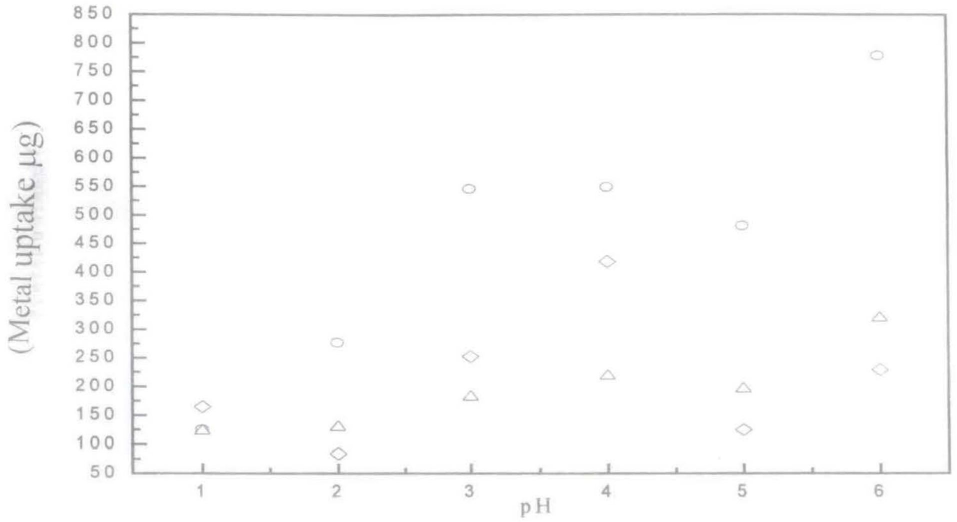
Graphical points: □, Cd; ○, Cr; Δ, Pb

Compound **8**



Graphical points: □, Cd; ○, Cu; Δ, Pb; ▲, Zn

Compound **9**



Graphical points: ○, Pb; ◇, Cd; ○, Δ, Zn

4.2.4 Selection of eluting agents

The literature [9, 18] were followed

In order to find out suitable eluting agent 0.5- 4M HCl or HNO_3 was passed through the column of functionalized resin compounds (**1-9**) in which the metal ions were already absorbed. The data on the suitability are presented in Table 4.2.2.

Table 4.2.2 Selection of eluting agents

Compound **1**

	% recovery of metal ions		
Eluting agent	**Pb**	**Cu**	**Zn**
0.5M HNO_3	80	NC	NC
1.0M HNO_3	50	100	50
2.0M HNO_3	100	80	NC
1.0M HCl	NC	NC	100
2.0M HCl	NC	70	80
3.0M HCl	20	NC	80
4.0 M HCl	NC	60	NC

NC = Not checked

Compound **2**

	% recovery of metal ions		
Eluting agent	**Pb**	**Cu**	**Zn**
0.5M HNO_3	50	NC	NC
1.0M HNO_3	100	80	50
2.0M HNO_3	80	100	NC
1.0M HCl	NC	NC	80
2.0M HCl	50	80	100
3.0M HCl	NC	NC	80
4.0 M HCl	NC	50	NC

NC = Not checked

Compound **3**

	% recovery of metal ions		
Eluting agent	**Pb**	**Cu**	**Cd**
0.5M HNO_3	NC	NC	30
1.0M HNO_3	NC	30	50
2.0M HNO_3	100	50	80
3.0M HNO_3	100	NC	100
1.0M HCl	80	80	NC
2.0M HCl	50	100	NC
3.0 M HCl	NC	NC	NC

NC= Not checked

Compound **4**

	% recovery of metal ions		
Eluting agent	**Pb**	**Cu**	**Cd**
0.5M HNO_3	NC	NC	NC
1.0M HNO_3	80	80	30
2.0M HNO_3	25	100	100
3.0M HNO_3	NC	NC	NC
1.0M HCl	50	60	50
2.0M HCl	100	80	80
3.0 M HCl	NC	NC	NC

NC= Not checked

Compound **5**

	% recovery of metal ions			
Eluting agent	**Cu**	**Cd**	**Ni**	**Zn**
0.5M HCl	NC	NC	NC	60
1.0M HCl	100	NC	BDL	80
2.0M HCl	80	50	30	100
4.0M HCl	NC	NC	100	NC
1.0M HNO_3	50	100	BDL	25
2.0M HNO_3	80	60	NC	NC
3.0 M HNO_3	NC	NC	NC	NC
4.0M HNO_3	NC	50	NC	NC

NC= Not checked

BDL= Below detection limit

Compound **6**

% recovery of metal ions			
Eluting agent	**Zn**	**Cu**	**Cr**
0.5M HCl	50	50	NC
1.0M HCl	NC	80	NC
2.0M HCl	100	100	NC
3.0M HCl	70	NC	25
4.0M HCl	90	80	100
1.0 M HNO_3	NC	NC	25
3.0 M HNO_3	NC	NC	75

NC= Not checked

Compound 7

% recovery of metal ions			
Eluting agent	**Pb**	**Cd**	**Cr**
0.5M HNO_3	NC	60	NC
1.0M HNO_3	100	100	NC
2.0M HNO_3	50	60	80
4.0M HNO_3	NC	80	NC
1.0M HCl	80	NC	50
2.0M HCl	50	NC	25
4.0 M HCl	NC	NC	100

NC= Not checked

Compound **8**

% recovery of metal ions				
Eluting agent	**Cu**	**Pb**	**Zn**	**Cd**
0.5M HNO_3	NC	80	NC	NC
1.0 M HNO_3	NC	25	NC	50
2.0 M HNO_3	80	100	NC	25
3.0 M HNO_3	50	60	NC	NC
0.5 M HCl	NC	NC	NC	100
1.0 M HCl	80	NC	60	80
2.0 M HCl	100	NC	50	NC
3.0 M HC 1	NC	NC	100	NC
4.0 M HCl	NC	NC	80	NC

NC = Not checked

Compound **9**

% recovery of metal ions			
Eluting agent	**Pb**	**Cd**	**Zn**
1.0M HCl	25	NC	80
2.0M HCl	50	NC	25
0.5M HNO_3	NC	100	NC
1.0M HNO_3	NC	80	NC
2.0M HNO_3	80	50	60
3.0 M HNO_3	100	25	100

NC= Not checked

4.2.5 Effect of Flow Rate

The literature was followed [20]

The degree of metal ion sorption on the functionalised resin compound was studied by varying the flow rate of the metal solutions. The solutions were passed through the columns packed up with resin compounds. Maximum sorption was found at a flow rate greater than 0.5 ml min^{-1} but less than 1ml min^{-1}

The results of flow rate measurements are presented in the Table 4.2.3.

Table 4.2.3. Flow rate data

Compounds	**Metal ions examined**	**Rate (minute -1)**	**Sorption (µg)**
3	**Cd(II)**	1ml	1.740
		0.5ml	1.455
		0.25ml	0.89
		2ml	1.35
4	**Cu (II)**	2ml	0.0526
		1ml	0.0269
		0.33ml	0.0715
		0.25 ml	0.0641
9	**Pb (II)**	0.5ml	0.1450
		1ml	0.1356
		0.25ml	0.0654
		2ml	0.0853

4.2.6 Effect of Electrolyte

The literature [6, 21] were followed

Each metal ion solution of Pb (II), Cu (II), Cr (III), Zn (II), Cd (II) respectively was mixed separately with a mixture of strong electrolytes containing Na^+, K^+, Ca^{2+}, Mg^{2+} ions in 100 fold greater concentration and then passed through the column of the compound **6** and compoud 7 adjusted to suitable pH. The data are presented in the Table 4.2.4.

Table 4.2.4. The effect of electrolytic ions at pH 6.

Ions added	**Added as Mixtures of**	**Compound**	**% of recovery of metal ions**				
			Pb(II)	**Cu(II)**	**Cr(III)**	**Zn(II)**	**Cd(II)**
Na^+, K^+ Ca^{2+}, Mg^{2+}	NaCl + KCl + $Ca(NO_3)_2$ + $MgSO_4$	6	NE	80	NE	80	NE
		7	100	80	100	NE	25

NE = not examined

4.2.7 Pre-concentration Study

The literature methods was followed [22]

200ml solution of Pb(NO$_3$), CuSO$_4$, ZnSO$_4$ in the concentration range of 0.02µg - 0.2µg were passed through the column of compound **1** (pH - 6), compound **3** (pH - 4), compound **6** (pH - 6) and compound **8** (pH - 4) for 3 hour and 20 minutes separately. The column was washed thoroughly by distilled water and the sorbed metal ions were desorbed by suitable eluting agent (presented in the table). The results are presented in the Table 4.2.5.

Table 4.2.5.Data showing percentages of pre-concentration

Column	Volume of Metal Solution (ml)	Metal(II) Ion	% of Recovery
Compound **1**	200	Cu	99
Compound **3**	200	Pb	98
Compound **6**	200	Zn	90
Compound **8**	200	Zn	90

4.2.8 Water Regain Value

The literature [22, 23] were followed]

A selection of functionalised resin compounds (compound **2**, compound **4** and compound **6**) were stirred in distilled water for 48 hour- then filtered and dried in air at room temperature – weighed and further dried at 100^{0}C overnight and reweighed. The water regain value is expressed as W = (mw-md) / md (where mw =weight of the air dried polymer and md = weight after drying st 100^{0}C).The results are presented in the Table 4.2.6.

Table 4.2.6. Water regain values.

Compound	Value obtained (mmolg^{-1} of the resin)
2	3.3
4	4.4
6	5.55

4.2.9 Mutual Separation of Cu(II), Cd(II), Cr(III), Pb(II), Zn(II) from binary and ternary mixture

The literature methods was followed [9, 24]

Two different metal ions were separated from the mixtures either by using different eluting agents or changing the pH of the medium.

Separation by changing eluting agents

a) When a solution of mixture of Cu(II) and Cr(III) ions was passed through the columsn of the compound **6** and compound **7** at pH - 6, both the metal ions were sorbed. The column were washed by distilled water, the Cu(II) ion was eluted sucessfully by 2M HCl and Cr(III) ion by 3M HNO_3.

b) The column of the compound **6** was adjusted to pH - 6 and a mixture of Zn(II) metal ion and Cr(III) metal ion was passed through the column. Both the metal ions Zn(II) and Cr(III) were separated quantitively using 2M HCl and 3M HNO_3 as eluting agents respectively.

c) Equal volumes of Cu(II) metal ions and Pb(II) metal ions in solutions were passed through the column of compound **3** adjusted to pH – 4 there was a total sorption of both the metal ions were. The sorbed Pb (II) metal ions was desorbed by 2M HNO_3 when the sorbed copper metal ion was eluted completly by 2M HCl.

d) The column of the compound **9** was adjusted to pH – 6. Then equal volumes of Zn(II) and Pb(II) metal solutions in a mixture was passed through the column. The sorbed Zn(II) metal ion was desorbed by 1M NaF and then the sorbed Pb metals ions were desorbed completely by 3M HNO_3.

Seperation by Changing the pH of the solution

a) The column of the compound 7 was adjusted to pH – 1. Then a mixture of equal volumes and same concentrations of Cd(II) metal ions and Cr(III) ions was passed through it. The portion of the metal solution which was not sorbed by the column was collected and the concentration of the metal ions present in it were determined. It was found that an insignificant amount of the Cr(III) ion was sorbed. The sorbed Cd(II) metal ion was eluted with 1N HNO_3.

b) Similarly a solution of a mixture of Cd(II) metal ion and Pb(II) ion was passed through the column of compound 7 adjusted to pH - 1. Insignificant amout of Pb(II) ion was found to be absorbed while only Cd(II) ion was left absorbed in the column.

c) In other case, a mixture of Pb(II) metal and Cd(II) metal was passed through the column of compound **8** adjusted to pH - 4. It was observed that all the Pb (II) ions were almost completely came out of the column without being significantly sorbed. The sorbed Cd(II) metal ion was then eluted by 2M HNO_3.

d) Further a ternary mixture of Cd(II), Cr(III) and Pb(II) ions was passed through the column of compound 7 at pH - 1, Interestingly, only Cd(II) metal ion was found to be sorbed. The results are presented in the Table4.2.7

Table 4.2.7. Mutual Separation of Metal Ions

Functionalised Resin Compound	**pH of the Medium**	**Metal Mixture**	**Dependence on pH or eluting agent**	**Eluting agent**
6	6	Cu(II) - Cr(III)	eluting agent	Cu(II) - 2M HCl Cr(III) - 3M HNO_3
7	6	Cu(II) - Cr(III)	eluting agent	Cu(II) - 2M HCl Cr(III) - 3M HNO_3
6	6	Zn(II) - Cr(III)	eluting agent	Zn(II) - 2M HCl Cr(III) - 3M HNO_3
3	4	Cu(II) - Pb(II)	eluting agent	Cu(II) - 2M HCl Pb(II) - 2M HNO_3
9	6	Zn(II - Pb(II	eluting agent	Zn(II) - 1M NaF Pb(II) - 3M HNO_3
7	1	Cd(II - Cr(III)	pH	Cd(II) - 1M HNO_3
7	1	Cd(II) - (Pb(II)	pH	Cd(II) - 1M HNO_3
8	4	Pb(II - Cd(II)	pH	Cd(II) - 2M HNO_3
7	1	Cd(II) - Cr(III) - Pb(II)	pH	Cd(II) - 1M HNO_3

4.2.10 Kinetics

The literature [10, 25] were followed

To investigate the rate of uptake of Cu(II) and Cr(II) ions by compounds **6** and **7**, a batch experiment was carried out with 0.50g of the compound stirred separately in 250ml solutions of Cu(II) and Cr(III) ions (200μgml^{-1} at pH 6) respectively at room temperature. At the time intervals of 30 minutes an aliquot of 10ml solution were taken out and transferred to 50ml volumetric flasks and the volume made up by adding distilled water.A similar procedure was followed for Cd(II)ions (200μgml^{-1} at pH 1) to study the kinetics during the sorption on compound **7**.

The same procedure was followed for the compound **3** and batch experiment was carried out with 0.1g of the compound with the metal ions Pb(II) and Cd(II) (200μgml^{-1} at pH 4).

Kinetic property of a functionalised resin compound depended on the nature and degree of cross linking of metal ion was controlled by intra-particle diffusion mechanism or by second order kinetics. The intra-particle diffusion equation could be written as follows.

$$q_t = K_p t^{1/2} + C$$

Where 'C' is the intercept and Kp is the intra-particle diffusion rate constant. According to intra-particle diffusion mechanism model, the plot of uptake, q_t versus the square root of time ($t^{1/2}$) should be linear if the intra-particle diffusion is involved in the adsorption process [10].The data are presented in Table 4.2.8 and Figure 4.2.2 and 4.2.3.

Table 4.2.8. Data on the kinetic studies of the metal sorptions

Compound 3

Metal ion	**time – t (minute)**	$t^{1/2}$	**Sorption (µg)**
Cd(II)	120	10.95	7.22
	240	15.49	2.5
	600	24.49	6.12
	1200	34.64	9.5
	1440	37.94	5.9
Pb(II)			
	120	10.9	47.385
	240	15.5	39.87
	600	24.5	45.6
	1200	34.65	80.07
	1440	37.95	77.76

Compound 6

Metal ion	**time - t (minute)**	$t^{1/2}$	**Sorption (µg)**
Cu(II)	30	5.45	304.4
	60	7.75	608.8
	120	10.95	640.0
	180	13.4	668.10

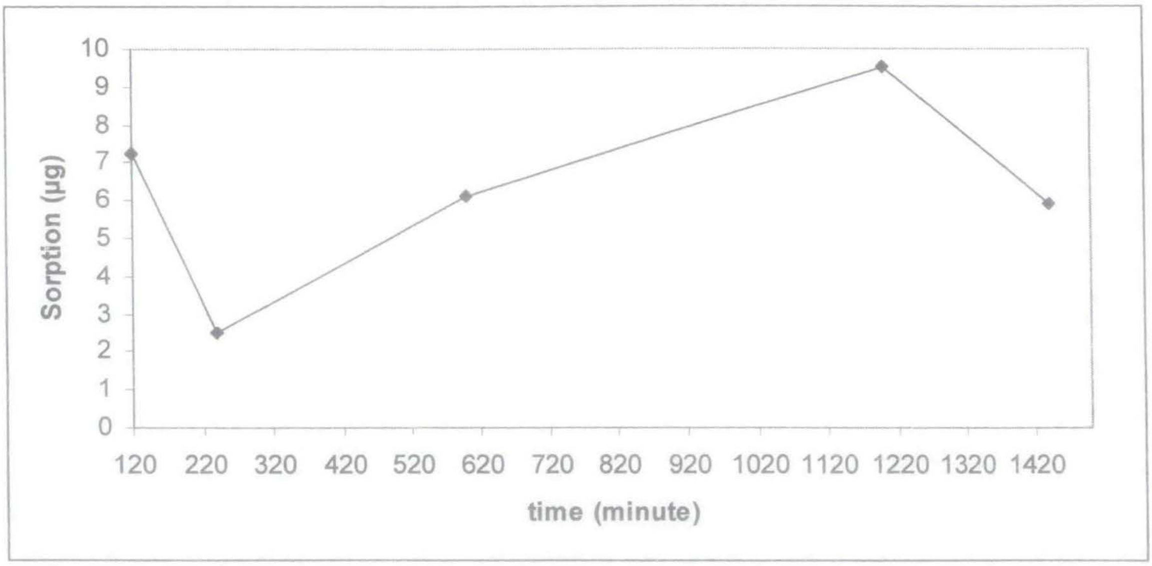
Compound 7

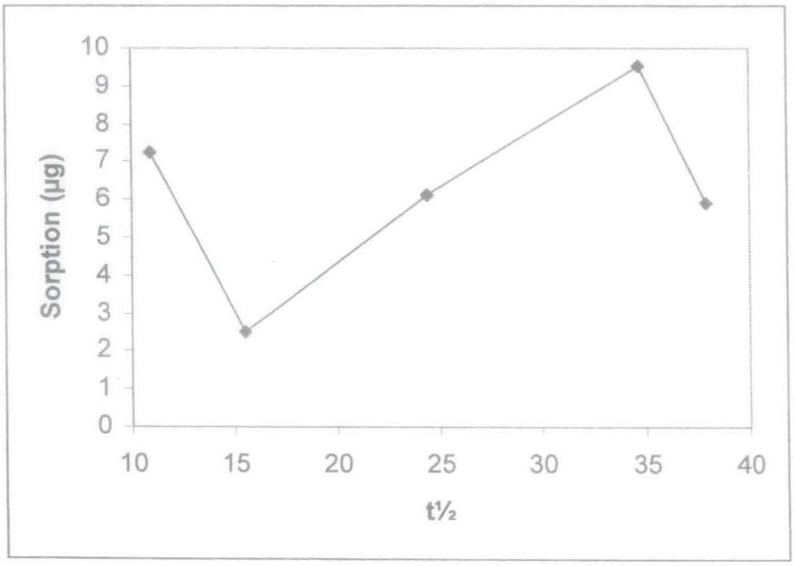
Metal ion	**time - t (minute)**	**t½**	**Sorption (μg)**
Cd (II)	30	5.45	340.4
	60	7.75	348.8
	120	10.95	439.5
	180	13.4	470.0

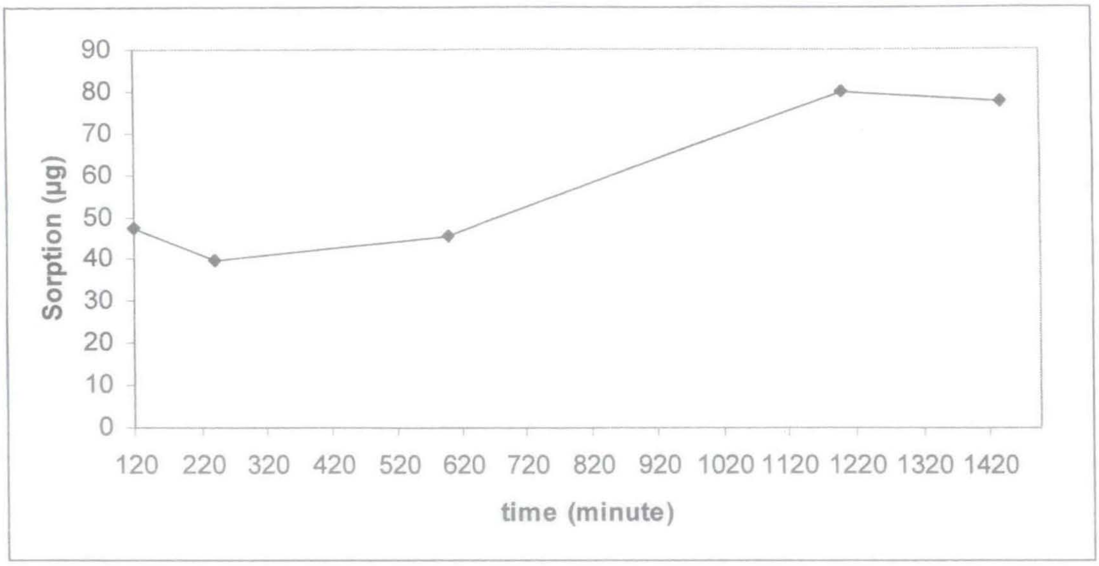
Metal ion	**time - t (minute)**	**t½**	**Sorption (μg)**
Cr (III)	30	5.45	340.4
	60	7.75	348.8
	120	10.95	439.5
	180	13.4	470.0

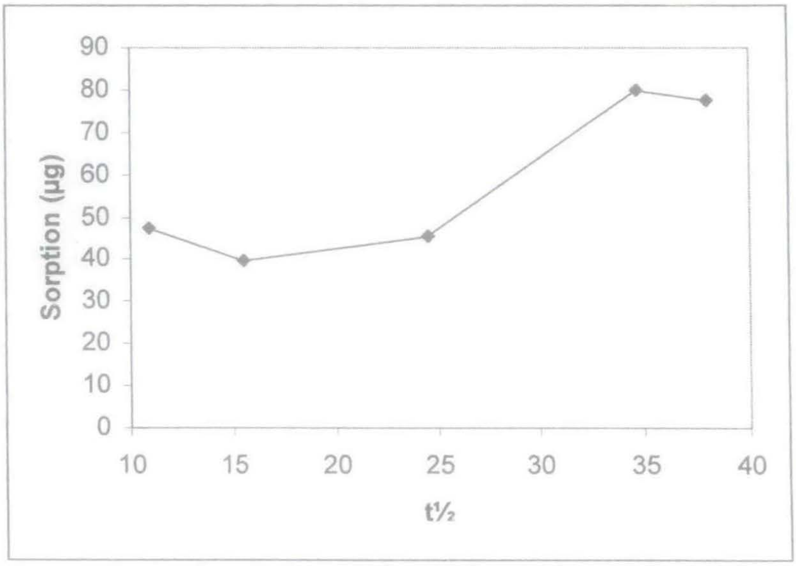
Figure 4.2.2 and 4.2.3. Data on Knetics Study

Compound **3**

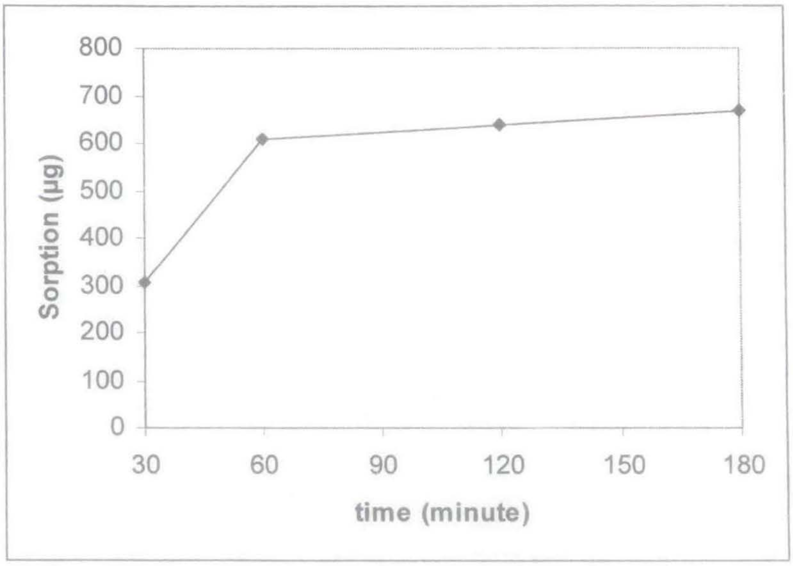


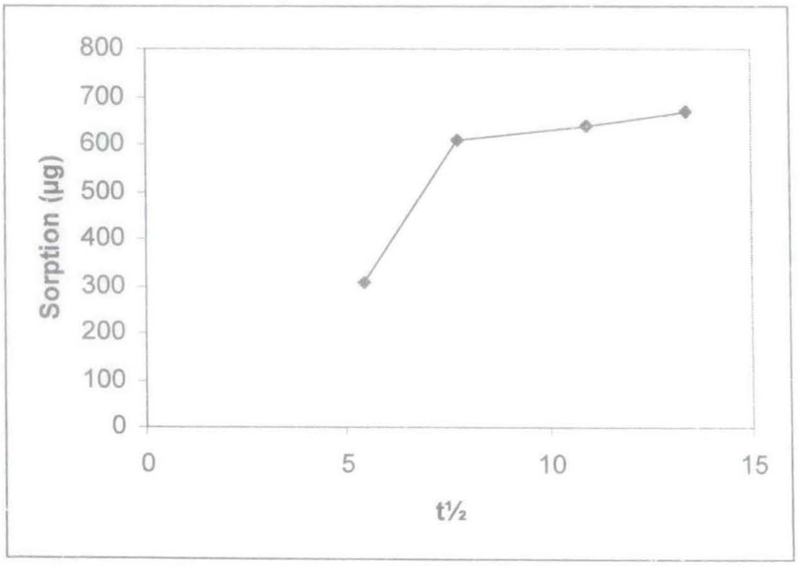



Sorption (μg)
90
80
70
60
50
40
30
20
10
0
120
220
320
420
520
620
720
820
920
1020
1120
1220
1320
1420
time (minute)

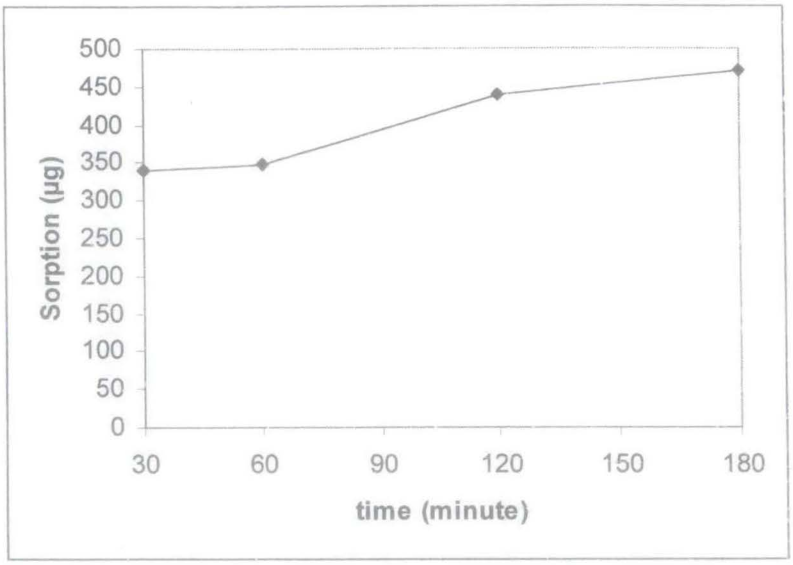

Sorption (μg)
90
80
70
60
50
40
30
20
10
0
10
15
20
25
30
35
40
t½

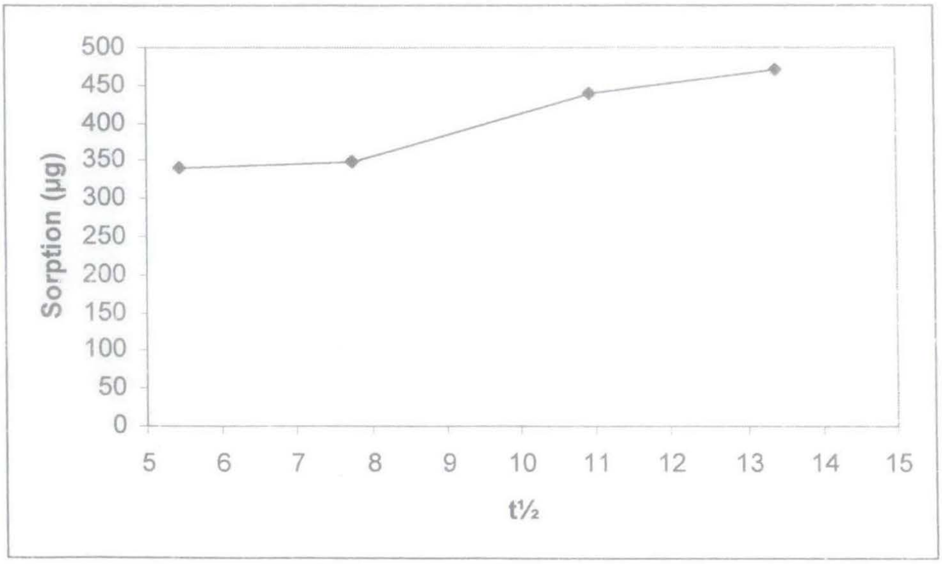
Compound **6**


Sorption (µg)
0
100
200
300
400
500
600
700
800
30
60
90
120
150
180
time (minute)

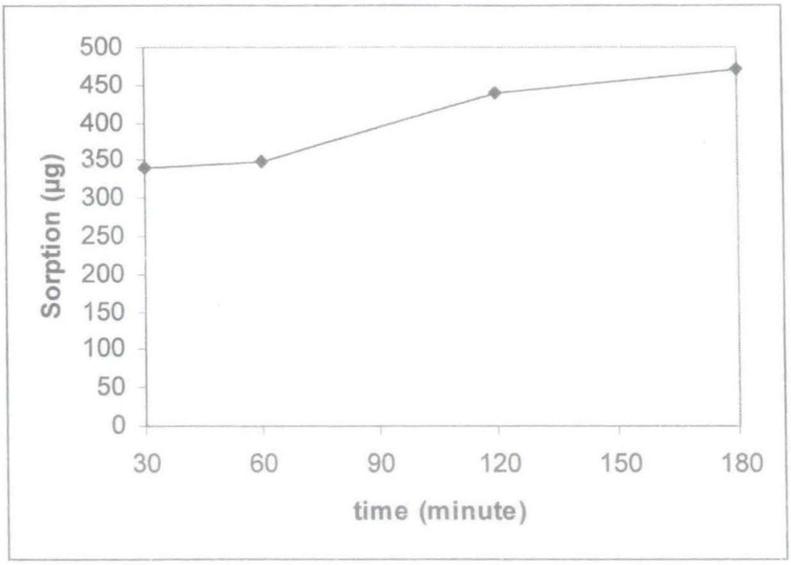

Sorption (µg)
0
100
200
300
400
500
600
700
800
0
5
10
15
t½

Compound 7


Sorption (µg)
0
50
100
150
200
250
300
350
400
450
500
30
60
90
120
150
180
time (minute)


Sorption (µg)
0
50
100
150
200
250
300
350
400
450
500
5
6
7
8
9
10
11
12
13
14
15
t½

Compound 7


Sorption (µg)
500
450
400
350
300
250
200
150
100
50
0
30
60
90
120
150
180
time (minute)

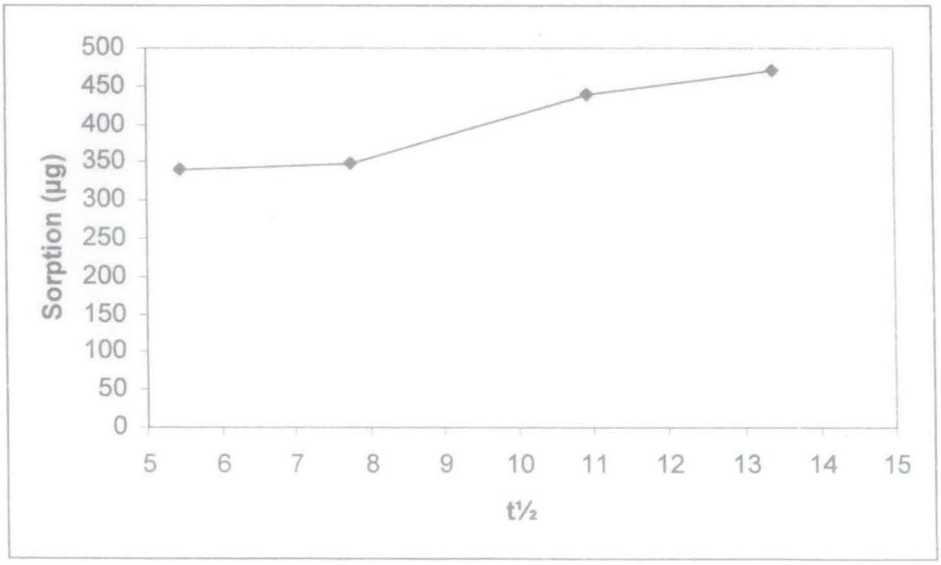

Sorption (µg)
500
450
400
350
300
250
200
150
100
50
0
5
6
7
8
9
10
11
12
13
14
15
t½

Figure 4.2.3. Differential Plot for the Compound 7

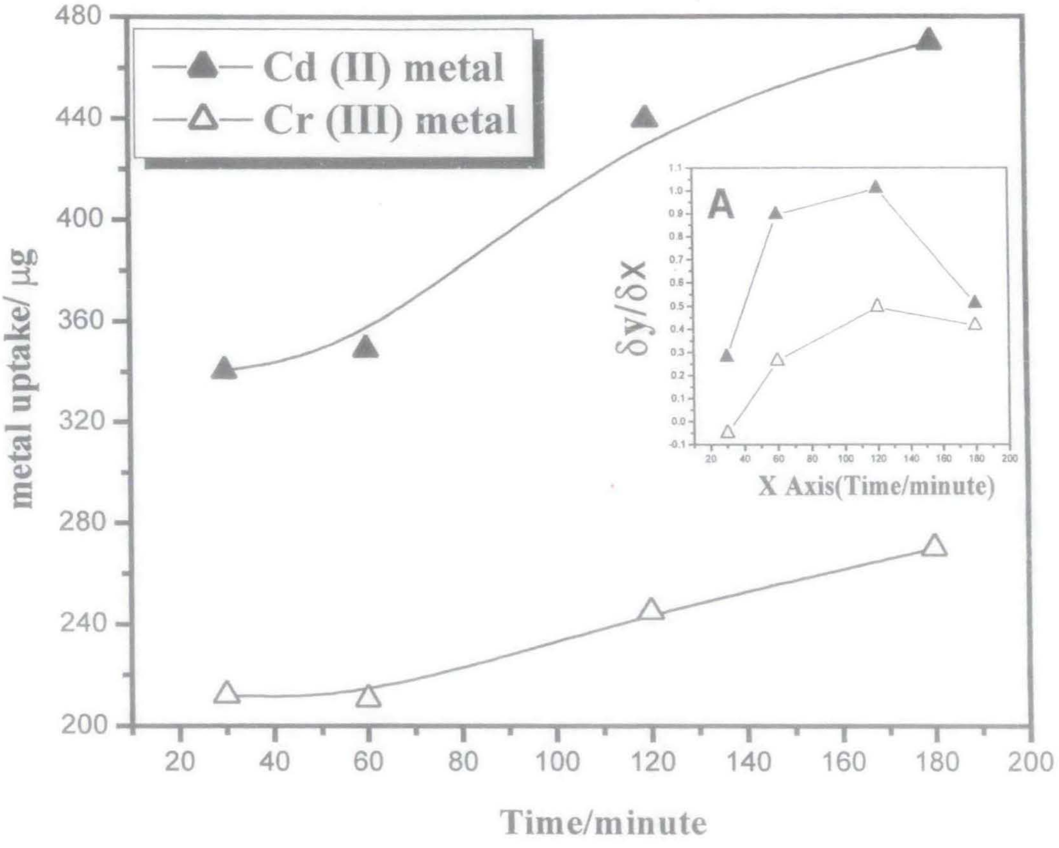


Table 4.2.9 Sorption Capacities by the nine (**1** – **9**) Functionalised Resin Compounds

Compound	**pH**	**Metal ion**	**Sorption of resin (µgg-1)**
1	6	Cu	12700
	6	Pb	2052
	6	Zn	348.2
2	6	Cu	597
	6	Pb	2393.7
	6	Zn	376.7
3	4	Pb	1601
	4	Cd	190
	6	Co	57.6
	6	Ni	32.9
4	1	Mn	490
	6	Pb	980
	5	Hg	3210
	3	Cd	167
	6	Cu	530
5	6	Zn	269
	6	Cu	219
	3	Cd	198
	3	Ni	401

Contd. Table 4.2.9 Sorption Capacities by the nine (**1 – 9**) Functionalised Resin Compounds

Compound	**pH**	**Metal ion**	**Sorption of resin (μgg-1)**
6	6	Cu	1089.9
	6	Cr	1563.9
	6	Zn	370
7	1	Cd	435.2
	6	Cr	2255.3
	6	Pb	1769.7
8	6	Cu	424.6
	6	Pb	1593.2
	4	Zn	384.5
	4	Cd	429.5
9	6	Pb	778.1
	4	Cd	419.2
	6	Zn	319.0

4.3 Results and discussion

It has been conclusively established during this investigation that all the functionalized resin compounds which constitute the solid support effectively separate and preconcentrate the metal ions like bivalent Cu, Pb, Zn, Cd, Co, Ni and Cr(III) in solutions. A good number of parameters have been examined and the results presented in appropriate section. The effect of pH on the metal uptake has been demonstrated clearly when it has been observed that – Cu(II), Pb(II), Co(II), Ni(II) and Cr(III) sorbed at higher pH for each compound studied as the adsorbants whereas Cd(II) was found to be srobed at very low pH at 1, Zn(II) has been found to be sorbed at intermediate pH between 3 and 4. Presumably because of the deprotonation of the complexing ligand present in the solid matrix allow the co-ordination of the lone pair of N atoms more effectively. On the other hand the highly protonated N atom at pH – 1 directs possibly the co-ordination of Cd(II) ion to the others co-ordinating sites e.g. S or O present in the ligand.

Further the complexing abilities of this ligand bound to the solid support may be explained on the baiss of the ionic radii of the metal under consideration. The sorption of metal ions by the resin compounds follow Pb(II) > Cu(II) > Zn(II). This may be explained on the basis of solvated cationic size, the larger the size of the unsolvated cation, lower will be degree of solvation. The ionic radius [15] of Pb(II)(2.1000132A) > Cu(II) (0.3554127A) > Zn(II) (0.3389701A).

Since Zn(II) has the smallest size, its solvated cationic size will then be the largest among the three ions under consideration which explains the order of absorption observed by the functionalized resin, The desorption behaviour has been found to be dependent on eluting agent. Thus elution were carried out with different molar concentration of HCl or HNO_3 e.g. for compound 1 maximum amount of desorption for Pb (II) ion has been observed fro 2M HNO3. Again with 1M HNO_3 desorption of Cu(II) is maximum (100%). All the data for all the compound 1 – 9 are tabulated in table 4.2.2 – which reflects clearly the dependence of the desorption on the eluting agents.

The variation in flow rate during the sorption of metal ions by the column is and important factor. However under the experimental condition there has been no regular trend observed for the optimization of flow rate. The corresponding table (table No – 4.2.3). For the flow rate indicate that on an average 0.5ml min^{-1} – 1 ml min^{-1} yield better sorption.

In different sources of water different types of electrolytes such as Na(I), K(I), Ca(II), Mg(II) ions are present in abundance. Therefore studies on the effect of added electrolytes on sorption behaviour in the laboratory condition is an important aspect. It has been demonstrated in table – 4.2.4 except for Cd(II) electrolytes have very small effect on the sorption of metal ion like bivalent metal ion Pb(II), Cu(II), Zn(II), Cr(III) when passed through the compound 6 and compound 7. It is interesting to note that very dilute solutions of Pb(II), Cu(II) and Zn(II) ions when passed through the column of compound 1, 3, 6, 8 be sorbed and therefore pre concentrated after desorption with 98-99% recovery.

The water regain value for the compound 2, 4, 6 are presented in the table indication the efficiency of the resin. The high efficacy of a selection of the new synthesized resin compounds in the selective separation of toxic heavy metal ions under study.

Amply demonstrate the usefulness of this compounds. In a mixture of Cu(II) and Cr(III) e.g. at pH – 6 the compound 6 can separate Cu(II) when eluted with 2M HCl and Cr(III) when eluted with 3M HNO_3. On the otherhand a pH dependent separation of Cd(II) from a ternary mixture of Cd(II), Pb(II) and Cr(III) with compound 7 is achieved when the sorbed ions are desorbed with 1M HNO_3. The other interesting separation under varying condition of pH, eluting agent and solid supports are presented in the table 4.2.7.

The kinetic studies of the sorption behaviour of the metal ions of Cu(II), Cr(III) and Cd(II) with compound 6, 7 and 3 demonstrates a expected linear co-relation of the sorption with the t½ (time) in table and figure. It also suggests an intra particle diffusion during the process.

The threshold amount of sorption by the compound 7 could also be determined as has been shown in the figure. 4.2.3.

4.4 Conclusion

The importance of the functionalized resin compounds synthesized in our laboratory (chapter III) has been established by thorough study on the sorption- desorption behaviour of the toxic heavy metal ions. Not only these compounds sorbed the ions under study but also the functionalized solid support could be reuse which has been demonstrated. Certain tuning of experimental condition produced hundred percent recovery of the sorbed metal ions. In short the quality of the solid support under study are very high for the separation and pre concentration of certain metal ions demonstrated here in.

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CHAPTER V

APPLICATION OF NEW FUNCTIONALISED CHELATING RESIN COMPOUNDS FOR PRE-CONCENTRATION AND SEPARATION OF Cu(II), Pb(II), Zn(II), Cd (II), Cr(III) AND Fe(II) METAL IONS FROM (I) RIVER WATER, (II) INDUSTRIAL WASTE WATER AND (III) AGRICULTURAL SOIL SAMPLES.

(i) Pre-concentration and separation of heavy metals of Mahananda river water (Siliguri, Dt. Darjeeling, WB, India) during the period of immersion of Durga idols : Studies on the sorptions on solid supports synthesized by functionalizing polystyrene divinylbenzene resins with 2-mercapto isothiocyanate and 2 - amino 1, 3, 4 - thiadiazole.

Abstract

In this chapter two functionalised chelating resin compounds (**4** and **9**) have been used to pre-concentrate and separate heavy metal ions like Pb(II) and Cr(III). River water contaminated by paints, colours and dyes from the immersed Durga idols are examined for the extent of pollution level.

5.1 Introduction

Balasan (its source is Lepchajagat having the altitude 7672 m) and Mahananda (its source is Mahaldiram having altitude 7312m) have joined together at their confluence on the new border of ward No. 31 of Siliguri Municipal Corporation (SMC), Figure 5.1.1. From this point it flows assuming the name as Mahananda river. As per the view of survey of India, it originates from Mahaldiram (260^{0}56'0" N – 88^{0}20’0"E) at an altitude of 7312m.

The catchment area of the Mahananda river looks like a leaf of the tree. Its small veins may be compared with the tributaries that come from the interfluves and join with main artery or stream (the Mahananda). At the latitude 24^0 49' 30" N it seems to be the beginning of the stem or base of single channel and from there it flows south-east and south over the plains in an anatomizing way. Sometimes it creates havoc in the life of the people by means of natural or artificial obstructions. From the southern border of Darjeeling district, (Northern part of West Bengal,India) (Figure 5.1.2) it flows south-west and then south-east in a circular way over Bihar (India) covering about 92km and enters in Malda District (West Bengal,India). The length of the river from source to mouth is about 275km. It flows about 55km over the Darjeeling district, 72km over Malda, 20km along the border between Bihar and North Dinajpur (West Bengal,India) and 56 km over Bangladesh till it joins the Ganga river ($24^0$28'0"N - $88^0$19'30"E).

Every year during the months of September and October Durga Puja Festival is celebrated. More than 300 Durga idols (made of clay- average frontal surface area of $12m^2$ for each idol) are used to be immersed in the Mahananda River near Lal Mohan Ghat, Siliguri,West Bengal, India. The river during winter season becomes almost a narrow stream when the depth of the river water is maximum 1m. Chemical paints which are used for idols generally are red, blue, orange and green in colours and are known to contain particularly chromium and lead in addition to some other heavy metals. During the period of immersion, the water gets contaminated by increased acidity, solid matters and compounds of heavy metals which are leached in the river water and the soil. Heavy metals like lead and chromium are easily assimilated in an aquatic environment and can lead to the massive damage of flora and fauna of river ecosystem [1]. Lead is very persistent and bio accumulates in the aquatic system and it has strong adhesion potential to soil particles [2- 4].

Under the circumstances we undertook the studies on the estimations of the levels of contaminations of the water and soil samples collected during the idol immersion period to investigate the concentrations of these heavy toxic metal ions present. The estimation is very important because the whole population (about six lakhs) depends on the Mahananda river water supplied by the Municipal corporation for domestic consumptions and drinking purposes. For this purpose we have used efficiently the functionalized resin compounds synthesized by us in the laboratory. We like to report herein the results of the investigation both for water and the soils.

5.2 Methodology:

All the required chemicals used were procured from commercial sources as mentioned earlier. The names of the instruments and their manufactures are mentioned in Chapter III.

5.2.1 Sampling :

For sampling the procedure described in literature [5] was followed.

2.5 litre water was collected from the river near Lal Mohan Ghat in a clean polythene bottle (sample - 1) on 17th October, 2010 at 1pm before the immersion of the idols. On the same evening after the immersion of about 240 (80%) Durga idols at 10 pm, 2.5 litre water sample was collected in a polythene bottle (sample - 2). The day after, on the 18th October at 9am in the morning (ie, after 12 hours of the immersions) - again 2.5 litre water was collected in a polythene bottle (sample - 3). The soil sample of 500gm was collected (in an open mouth polythene bottle) from the river bed where the idols were immersed and left. The spots for the sample collections are shown in the Figures 5.1.3.

All the analyses were carried out with these collected samples.

5.2.2 Digestion of the Sample:

500ml each of samples 1- 3 were filtered separately by using Whatman filter paper (No. 42). Three samples (1, 2 and 3) were then placed in three different 1 liter round bottomed flasks separately and distilled on heating mantles till the volume of the samples reduced to about 50ml. Then 50 ml of these filtered (and volume reduced) water samples were placed in three separating funnels.

An aqueous solution of 1ml ammonium pyrrolidine dithocarbamate (APDC) was added in each of the sample solution and was shaken for 30 seconds. Then 5ml methyl isobutyl ketone (MIBK) was added in each solution and was shaken vigorously for 1 minute and left standing till the two phases separate. After separation of organic layer from the aqueous layer, the organic phase was transferred to three 50ml conical flasks respectively. All the 3 conical flasks were left standing in open air for 48h for the slow evaporation of the solvent so as to obtain the solid organic materials containing metal ions as the residues.

The solid residues of the 3 samples thus obtained were digested on oil bath with 5ml acid mixture (HNO_3 : $HClO_4$ = 10 : 1).The digestions were carried out for 30 minutes. The temperature of the oil bath was maintained at 100-120^{0}C. After digestion the mixtures were cooled down to room temperature and diluted with distilled water. Then all the mixtures were transferred separately to three 50ml volumetric flasks and the volume of the contents were made up by adding distilled water.

5.2.3 Column Operation:

With compound **9**

The column of the compound **9** was adjusted to pH - 6. Now 10ml digested sample (sample 1) was passed through the column for 20 minutes. The column was washed by distilled water several times after the sorption. The sorbed metal ions were then desorbed by 20ml 2M HNO_3 for 20 minutes. The desorbed metal ion solution was collected in a 50ml volumetric flask and the volume made up. The concentration of metal ion present in it was estimated by AAS.

Other digested samples (sample 2 and sample 3) were sorbed similarly in the column of the compound **9** (pH - 6) and then desorbed by 2M HNO_3. The eluted metal ion solutions were collected in 50ml volumetric flasks and their concentrations were determined by AAS as before. The data are presented in Table 5.1.1

Table 5.1.1 water analysis (digested)

Sample	**Compound**	**Metal ion μgL^{-1} of water**	
		Pb(II)	**Cr(III)**
S1	9	2.25	BDL
S2	9	15.2	BDL
S3	9	38.4	10

BDL = Below Detection Limit

The experiments were further extended with water samples without concentrating the samples. The water samples for these experiments were also not digested. This procedure allowed us straightforwardly the determination of the amount of free metal ions present in the water samples collected from the river.

5.2.4 Experiments without digestion:

With compound **4**

250ml water sample (sample 2 *as described above*) was filtered through Whatman filter paper (No. 42) and the filtrate collected. 200ml of the filtrate was passed through the column through 3 hour 20 minutes period .The column was made up of compound **4,** and was adjusted to pH - 6. After complete sorption, the column was washed thoroughly with distilled water. The sorbed metal ion was then desorbed by 20ml 2M HCl and was transferred to a 50ml volumetric flask and the volume made up.

With compound **9**

250ml water sample (sample 3 *as described above*) was filtered through filter paper (Whatman No. 42).200ml of the filtrate was passed through the column of compound **9** adjusted to pH - 6 for 3 hour 20 minutes. The sorbed metal ions were washed by distilled water and then desorbed with 20ml 2M HNO_3 and transferred into a 50ml volumetric flask for subsequent determination of the concentration of the metal ions. All the results of estimations are presented in the Table 5.1.2

Table 5.1.2 water analysis (undigested)

Sample	**Compound**	**Metal ion μgL^{-1} of water**	
		Pb(II)	**Cr(III)**
S2	4	11.95	BDL
S3	9	15.2	16.25

BDL = Below Detection Limit

5.2.5 Soil digestion :

The literatures followed for the purpose were [6- 8].

5.2.5.1 *With HNO_3 : $HClO_4$ = 10 : 1 mixture*

The air dried and sieved 1.0g soil sample (soil was collected on 18th October, 2010, at 9.00 AM) in the morning from the bed of the river Mahananda at Siliguri after the immersions of the idols in the afternoon of the day before, was mixed with 10ml acid mixture (HNO_3 : $HClO_4$ = 10 : 1).The mixture was placed in a 50ml conical flask. Then the mixture was digested slowly on silicone oil bath at 200-220^{0}C for 30 minutes. It was cooled down to room temperature and diluted by distilled water (20ml) and filtered and washed. The filtrate and the washings were collected in a 50ml volumetric flask and the volume made up.

5.2.5.2 *With aqua regia*

In another experiment, 1.0g of soil sample was mixed with 30ml aqua regia and was placed in a 100ml round bottomed flask and heated. The mixture was refluxed for 2 hours. Then the mixture was allowed to evaporate slowly under a hood to dryness. The solid residue thus obtained was treated with 30ml water and was filtered. The filtrate was collected in a 50ml volumetric flask and the volume made up.

5.2.5.3 *Microwave assisted digestion* :

A mixture of 1.0g soil sample (dried and sieved) was treated with a mixture of 6ml conc. HCl and 2ml conc. HNO_3 was placed in a 100ml polytetrafluoro ethylene reactor (PTFE) inside a microwave oven. The mixture was irradiated for different power and time period. However, the total time period of irradiation never exceed 10 minutes. The mixture was then cooled down to room temperature, diluted and filtered. The filtrate was collected in a 50ml volumetric flask and the volume made up.

Column operation:

(a) 30ml of the sample solution as prepared via the procedure 5.2.5.1 was passed through the column of compound **4** (pH-6).The metal ions thus sorbed were desorbed by 20ml 2M HNO_3 and collected in a 50ml volumetric flask.

(b) 30ml each of the sample solutions as prepared via the procedures 5.2.5.2 and 5.2.5.3 respectively were passed through the column of compound **9** (pH-4).The metal ions thus sorbed were desorbed by 20ml 3M HNO_3 respectively for both the samples and collected them separately in two 50ml volumetric flasks. The data of the analyses are presented in Table 5.1.3.

Table 5.1.3 soil analysis (collected on 18th October, 2010)

Digestion medium	**Compound**	**Metal ion µg g^{-1} soil**	
		Pb	**Cr**
$HClO_4$, HNO_3 (oil bath)	4	1.43	5.00
Aqua regia (Reflux)	9	13.90	3.43
Aqua regia (microwave oven)	9	46.20	BDL

BDL = Below Detection Limit

Figure 5.1.1 Map of the Siliguri Municipal Corporation

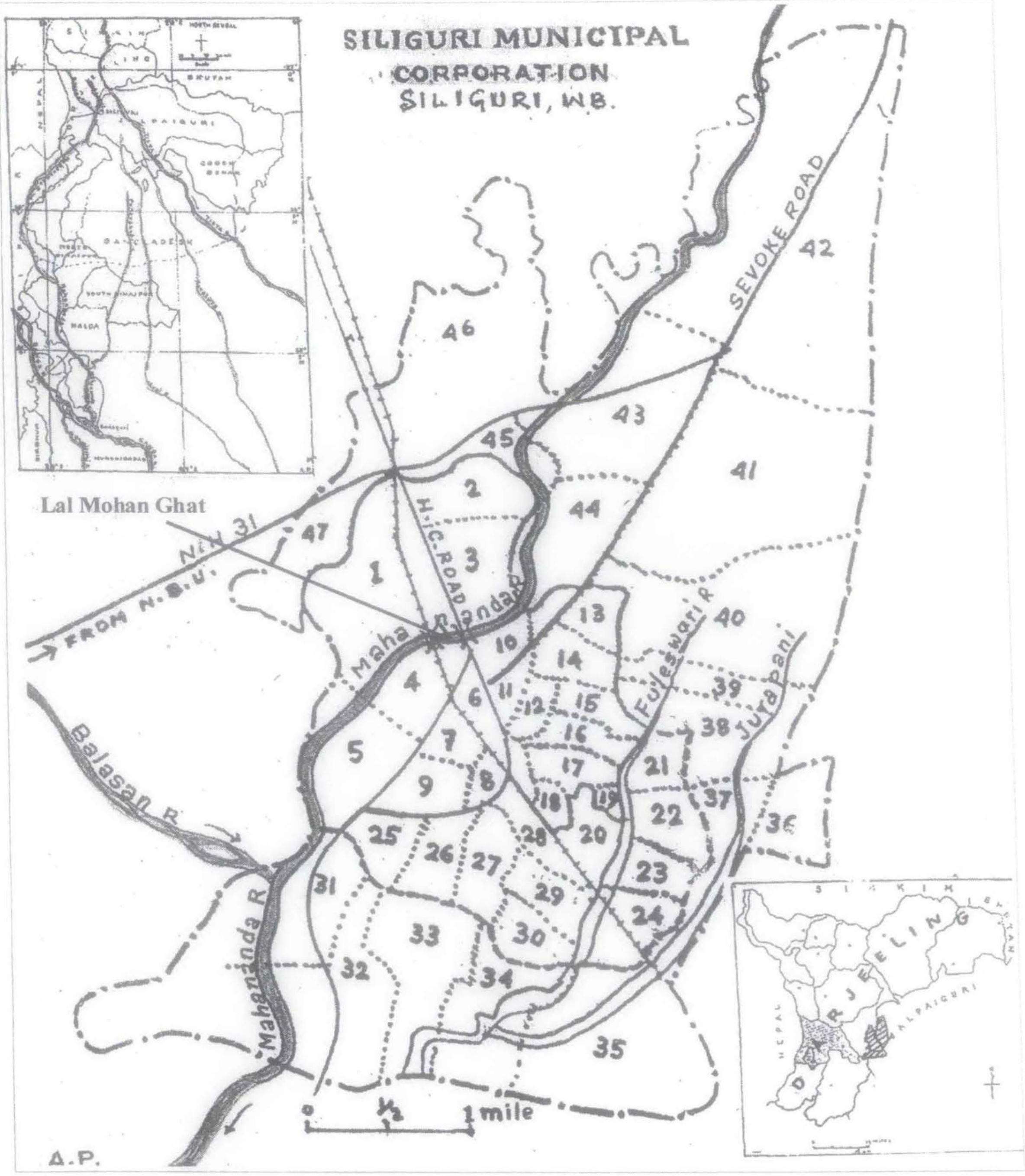


Figure 5.1.2 Map of the Northern Part of West Bengal

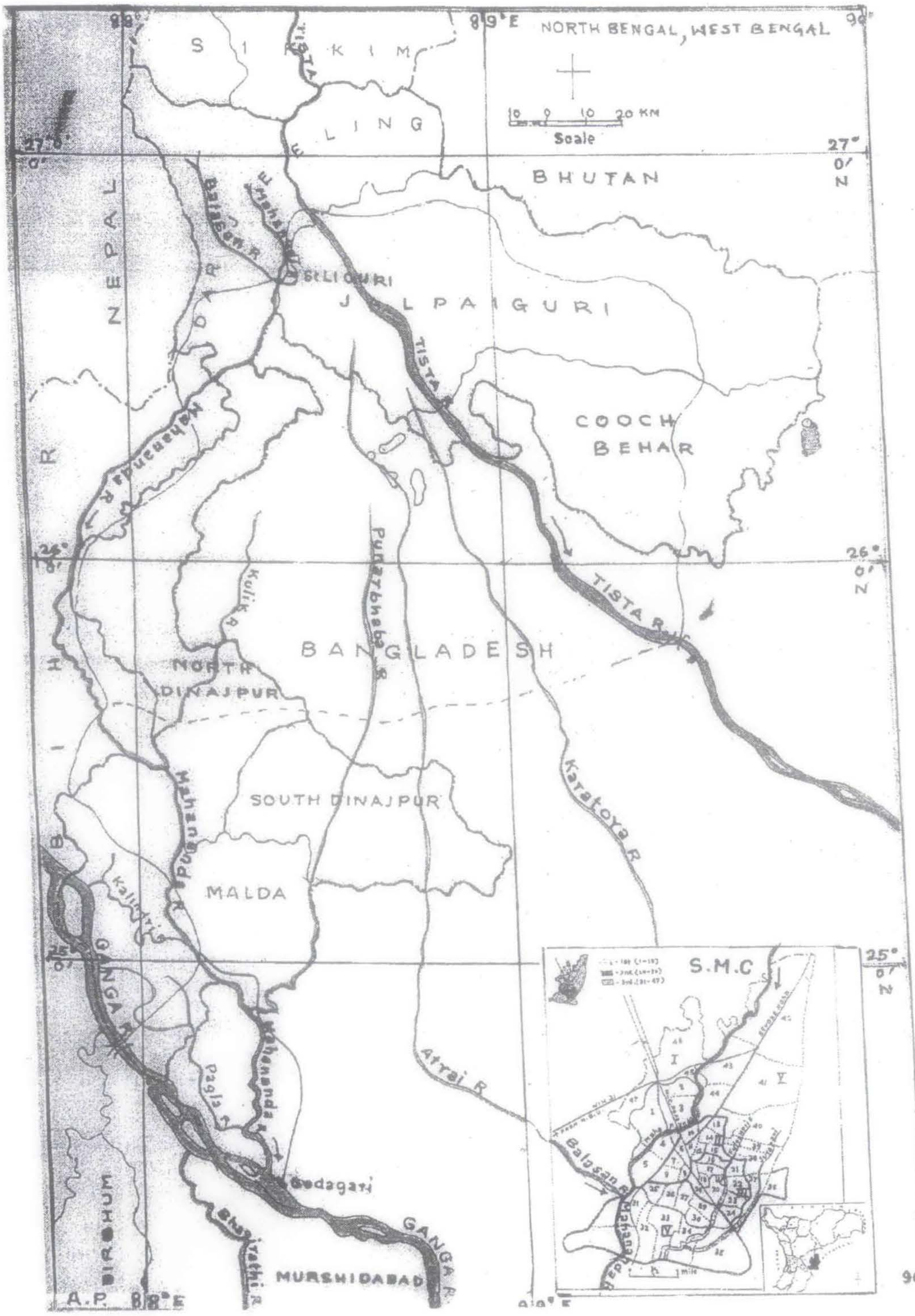
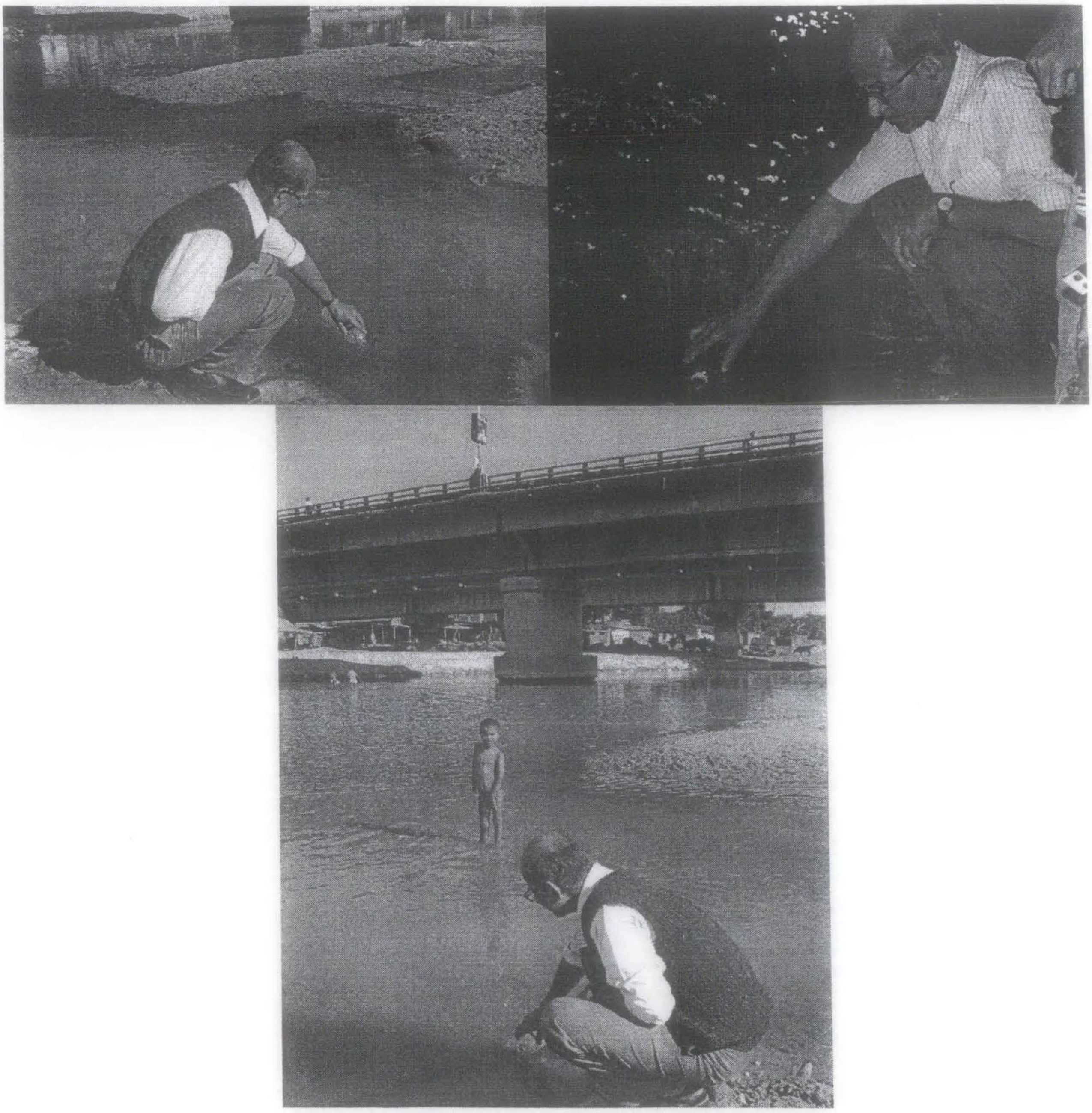


Figure 5.1.3 Water Collection on 17-10-2010 and 18-10-2010



5.3 Results and discussion:

The data obtained for water analyses (Tables 5.1.1 to 5.1.3) clearly brought about an indication of high levels of contamination after the immersions of the idols. Analyses with compound **9** for the sample 1, i.e, before the immersions – Pb(II) ions present was in low concentration (2.35 μgL^{-1})(Indian standard- 0.05 mg L^{-1}, drinking water, WHO – 0.01mg L^{-1}) whereas the Cr (III) ions (for Cr(VI)-Indian standard- 0.05 mg L^{-1}) was present below its detectable limit. However, for samples 2 and 3 the concentrations of both the ions were found to be considerably high indicating a risk of water pollution if the amount of pollution load continue to increase. When compared with the above results (Table 5.1.1) with the results presented in (Table 5.1.2) for water samples without digestion the concentrations of the free ions were found to be lower as expected.

The data on the soil analyses (Table 5.1.3) confirmed the presence in increased concentrations for both Pb (II) and Cr(III) in the soils of the river bed.

5.4 Conclusion:

The investigation indicated the real situation of Mahanada river in Siliguri during the Durga idol immersions. Both the soils and water got polluted though yet not alarming for a large population for heavy metal related problems. It is to be noted that the synthesized solid supports compounds **4** and **9** worked efficiently during these studies.

Industrial waste water analysis and separation of Pb(II) ions by Pyridine Carboxaldehyde thiosemicarbazone reisn, 5 -amino 1, 3, 4 - thiadiazole- 2-thiol resin and 2-hydroxy napthaldehyde thiosemicarbazone reisn.

5.5 **Introduction :**

Industrial waste water disposal has been a problem of heavily industrialized area. Many heavy metals are released in the environment through the waste water of industrial effluents. Metal industries such as electroplating, paints, dyes and lead battery industries released Cr, Cd, Pb metals into the environment through the effluent. Living organisms are damaged by these metals even at low concentrations for the various toxic metals and can affect human population in a large scale. Lead is particularly harmful to humans, plants and animals.

The lead poisoning can cause hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, learning disabilities, reading problems, development defects and language difficulties [9, 10]. As mentioned, major lead pollution has been through the manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings and radioactivity shields. Lead ions concentrations approach 200–500mg L^{-1} in the industrial waste waters. This value is very high in relation to the water quality standards and it should be reduced to a range of 0.1–0.05mgL^{-1}.

There are several methods for the separation and estimations of Pb ions. Among these methods, sorption using functionalized solid supports has proved to be one of the most feasible, simple, selective, cost-effective, ease of operation and high efficient process for the removal of heavy metals from polluted sources.

Therefore, an investigation was undertaken to determine the level of Pb (II) ion pollution in an adjoining industrial area of Siliguri township (West Bengal).In this industrial area several factories including lead battery factories are housed. Hence there is a possibility of Pb (II) hazard in the drinking water and the agricultural soils of the locality. We, therefore, have undertaken an investigation to study the level of Pb (II) pollution in the water collected from the drains of the industrial estate through which the discharges from all the factories flow.

5.6 **Methodology**:

All the required chemicals used were procured from commercial sources as mentioned earlier. The names of the instruments and their manufactures are mentioned in Chapter III.

5.6.1. **Sampling :**

To investigate Pb metal ion contaminations, water samples were collected in the month of May 2010 from three drains (5 liter from each location) where effluents were discharged from lead cells / battery and lead metal and other industries located at the Dabgram Industrial Growth Centre. Dist. Darjeeling, West Bengal, India.

Column operation :

Collected water samples (1 - 3) were filtered twice by using whatman filter paper (No. 42) and 10ml each of filtered sample 1 and sample 2 were diluted to 100ml by distilled water. These two samples (both of sample 1 and sample 2) were then passed through two separate columns of compound **7** which was pre-adjusted to pH- 6. The sorbed metal ions were eluted by 1M HNO_3 from the two columns. In another experiment 5ml of collected samples (sample 3) was diluted to 100ml by distilled water and then the total volume was passed through the column of compound **8**, the column was adjusted to pH- 6. After washing with distilled water the sorbed metal ion was eluted by 2M HCl. Similarly 100ml diluted sample 3 was passed through another column of compound **6** (pH adjusted to 6). The column was then washed with distilled water and the sorbed metal ions was desorbed by 2M HNO_3. All the eluted metal ion solutions were collected into four separate 50ml volumetric flasks.

Lead ion concentration was measured by the standard AAS method. The results are presented in the Table5.4.1

Table 5.6.1Concentration of Pb(II) ions in industrial water

Sample No. for Three locations	**Resin Compound Studied**	**Lead Metal ion found $\mu g\ L^{-1}$**
1	**7**	286.5
2	7	293.5
3	**8**	566.0
3	**6**	585.5

Figure 5.6.1 Main Entrance of Dabgram Industrial Growth Centre

5.7 Results and discussion

The results showed that the Pb(II) metal concentrations are much higher in the discharged water. The selected compounds worked well for the study. There is a trend of increasing level of water contamination which can be accumulated in the soil or water sources where it will be finally discharged.

Soil analysis of Khoribari and Haldibari Block area by Salicylaldehyde thiosemicarbazone resin, Pyridine carboxaldehyde thiosemicarbazone resin, 2-mercapto isothiocyanate resin and 2, 4, 6- tri hydroxy benzoic acid resin.

5.8 Introduction :

Metals like Cu, Zn, Fe, Co, Mo, Mn are essential components for normal growth of plant and fertility of soil. However, excess amount of these metals if accumulated in the soil can lead to a number of problems, such as soil contamination, surface and ground water contaminations etc. [6, 7]. Khoribari is a small block of Siliguri Mahakuma Parishad, Dist. Darjeeling, West Bengal [Figure 5.8.1]. This area cultivates many cash crops, vegetables like bringal, cauliflower, cabbages, cucumber, chili etc. for many years. The soil is very fertile not only for vegetable production but also for producing other agricultural crops.

Haldibari is a small area of Coochbehar District, West Bengal [Figure 5.8.1] and it is situated near Bangladesh Border area in the east.

The vegetables which are produced from this area are distributed throughout the northern part of West Bengal. The unique fertile character of the soil allows the production of many important crops throughout the year.

Besides natural cycle, metal concentrations are increasing many folds in the agricultural land for the indiscriminant use of chemical fertilizers, pesticides and insecticides. So it is an important area to investigate - the level of metal concentrations of the cultivable agriculture lands specially for preservation of soil fertility.

We under took a study to investigate the level of concentrations of Cu(II),Zn(II) and Fe(III) in the soils of these fertile areas of the North Bengal to enable to understand the conditions of soil fertility. We report here in the results of our studies.

5.9 **Methodology**

All the required chemicals used were procured from commercial sources as mentioned earlier. The names of the instruments and their manufactures are mentioned in Chapter III.

5.9.1 **Soil Sampling and Digestion :**

Top soil samples (from 0 – 10 cm depth) were collected from two spots of Khoribari and Haldibari area each during the month of October 2010.

1) The soil samples collected from paddy field of Haldibari was marked SH-1 and from cucumber field was marked as SH-2.

2) The soil samples collected from Khoribari were marked as follows:

SK – 1 Cauliflower cultivated land and

SK – 2 Cucumber cultivated land

The cultivated land for paddy and cucumber are shown in the figure [Figure 5.6.2]. After the collection of the samples foreign detritus and lithogenic shells were removed by hand picking. Then all the samples were air dried. 1gm each of soil samples was placed in four 50ml conical flasks. To this 10ml (10 : 1 $HClO_4$: H_2SO_4) acid was added and heated on an oil bath (200-210^{0}C) until the $HClO_4$ was evaporated off. All the mixtures were heated for 1 hour. The mixture were then cooled down - diluted and filtered. The filtrates were transferred to 100ml volumetric flasks for analysis of the metal ions (stock solutions), the white residues left for each of the samples was transferred and rejected.

Column operation

10ml of metal solution from the stock solutions of SK – I was passed through the column of compound **6** (pH – 6). The column washed by distilled water and the srobed metal ions were desorbed by 15ml 1M HCl.

In the another experiment 10ml metal solution from the stock solution of SK – 2 was passed through the column of compound **1** adjusted to pH – 6. The sorbed metal ions were desorbed by 15ml 1M HCl.

Further 10ml digested soil from the stock solution of SH -1 was passed through the column of compound **3** (pH – 4) – the sorbed metal ion was desorbed by 15ml 2M HCl.

Finally 10ml from the stock solution of the digested soil sample SH – 2 was passed through the column of compound **4** (pH adjusted to 6). After washing with distilled water, the sorbed metal ion was desorbed with 15ml 2M HCl. The concentrations of all the eluted metal ions of the two soil samples were measured by following standard AAS method. The results are tabulated in Table 5.9.1.

Table 5.9.1 Result of Soil analysis

	Place	Sample	Compound	Metal	(μg)g-1 of soil sorption
1	Khoribari	SK – 1	**6**	Cu	28.00
				Zn	99.50
				Fe	1690.0
		Sk – 2	**1**	Cu	18.52
				Zn	60.50
				Fe	1675.00
2	Haldibari	SH – 3	**3**	Cu	20.50
				Zn	65.50
				Fe	1570.0
		SH – 4	**4**	Cu	16.50
				Zn	50.50
				Fe	1605.00

Figure 5.9.1 The Map of West Bengal

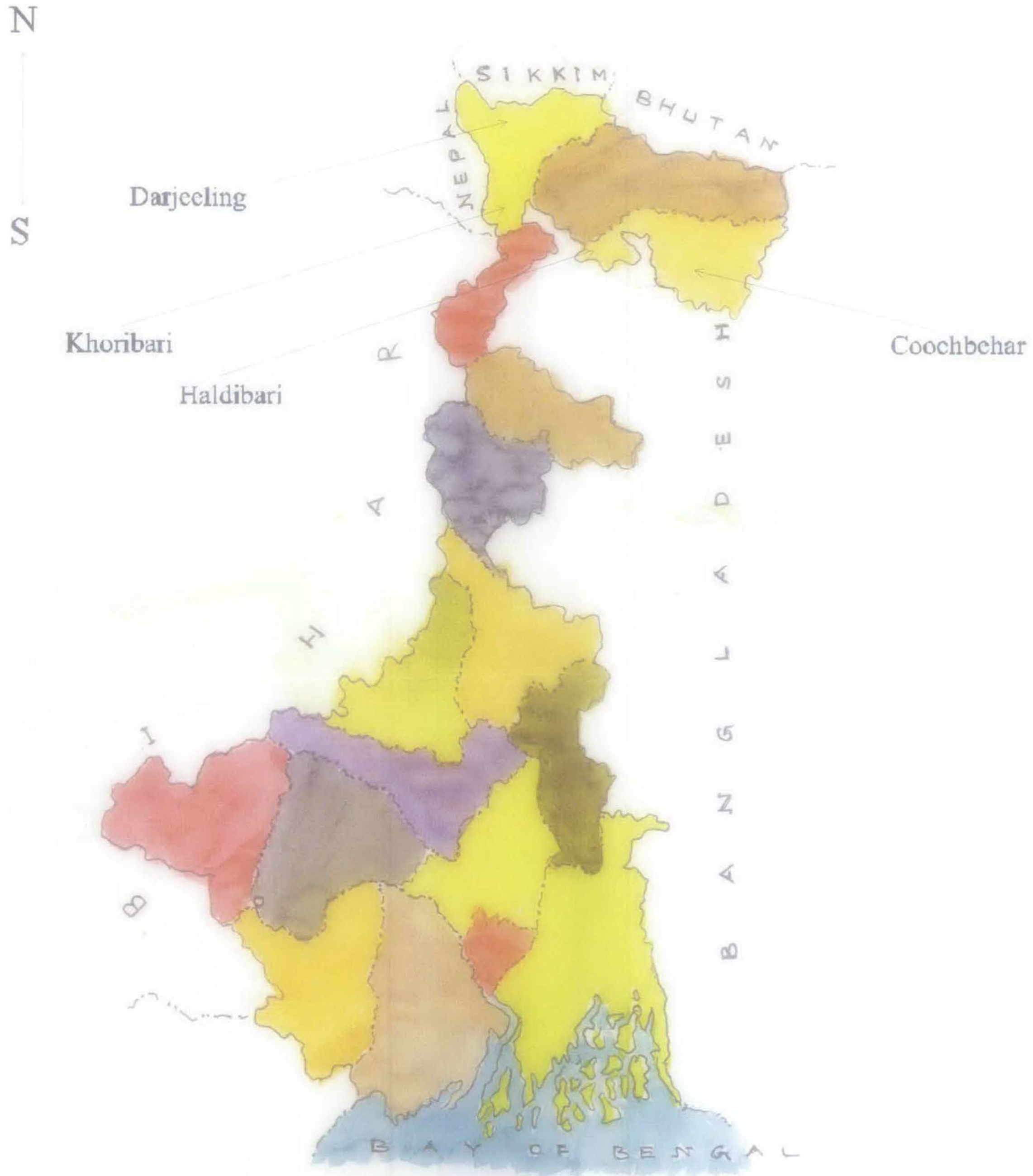


Figure 5.6.2 Cultivated land of Cucumber and Paddy land of Khoribari and Haldibari

5.10 Results and discussion

It is evident from the estimation and the obtained results that none of the metal ions under study are present in these soils in high concentrations. On the contrary the iron concentration is low than usual [6]. However, it is helpful if the concentrations of these metal ions in the soils be monitored at a regular interval of times.

5.11 Conclusion

A selection of the synthesized compounds from **1-9** may be effectively utillised to estimate the concentration levels of various metal ions in industrial waste water, river water and agricultural soils. The monitoring of such metal concentration should be an essential part which will ensure a safe and disease free environment to sustain.

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Publications and Seminar

1. G. C. Dey and A. Roy, Synthesis and Application of Functionalised Resins in the separation of Heavy Metal ions, Chemistry in North Bengal (Annual Journal) 1, (2007) 1.

2. G. C. Dey and A. Roy, Synthesis and Characterisation and application of a series of Functionalised Resins for separation and Pre-concentration of Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II), Mn(II) and Hg(II) metal ions, Chemistry in North Bengal (Annual Journal). 2, (2008) 1.

3. G. C. Dey and A. Roy, Application of Functionalised Resins for the separation and Pre-concentration of Cu(II), Zn(II), Pb(II), Cd(II), and Cr(III) metal ions, Chemistry in North Bengal (Annual Journal). 3 (2009) 1.

4. Seminar : Oral presentation :

   (i) West Bengal State Science and Technology Congress – 2008 at Bengal Engineering and Science University. "The Application of Functionalised Resins in Heavy Metal Separations."

   (ii) West Bengal State Science and Technology Congress – 2010 at West Bengal University of Animal and Fishery Sciences, Kolkata. "Application of Functionalised Resins in Heavy Metal Separations."

   (iii) West Bengal State Science and Technology Congress – 2011 at Ramkrishana Mission Residential College, Narendrapur, Kolkata. "Application of Functionalised Resins in the Pre-concentration and Separation of Heavy Metal ions discharged in the River Mahananda at Siliguri from paints and colours of immersed Durga idols."

5. G. C. Dey and A. Roy, Synthesis and characterization of Merrifield Resins Functionalized by N, S, O donor ligands – its application for the separation and Pre-concentration of Cu(II), Zn(II), Pb(II), Cd(II), and Cr(III) metal ions. Paper communicated to Journal of Hazardous Materials.