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.

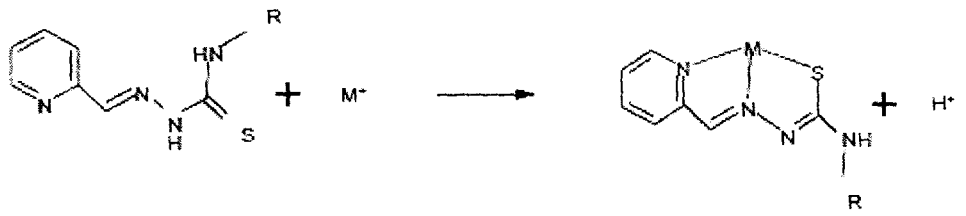
(iv) Nature of the solid support

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.



M+ = generic metal ion

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)

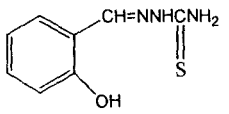


Figure2.3. 5- chloro salicylaldehyde thiosemicarbazone(2)

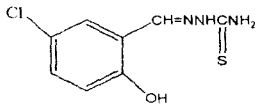


Figure2.4. pyridine - 2,5 – dicarboxylic acid(3)

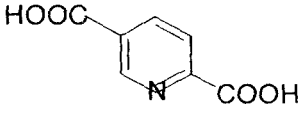


Figure2.5. 2- mercapto isothiocyanate(4)

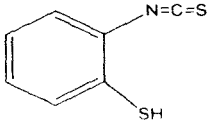


Figure 2.6. 2,4,6 - trihydroxy benzoic acid(5)

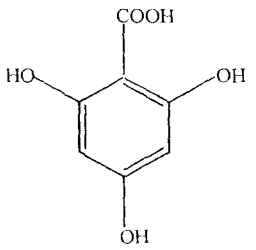


Figure 2.7. 2- hydroxy napthaldehyde thiosemicarbazone(6)

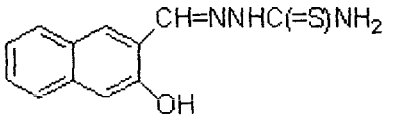


Figure 2.8. pyridine 1-carboxaldehyde thiosemicarbazone(7)

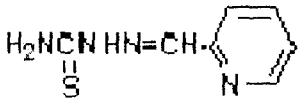


Figure2.9. 5- amino- 1,3,4- thiadiazole- 2- thiol(8)

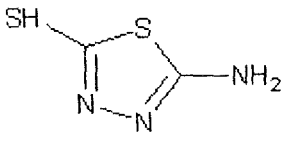
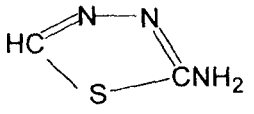


Figure2.10. 2- amino- 1,3,4- thiadiazole(9)



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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