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SCIENCES

INVESTIGATION OF SORPTION CAPABILITIES OF CHELATING AGENTS LOADED AND UNLOADED POLYMERIC SORBENTS TOWARDS TRACE METAL IONS

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August, 2010

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INVESTIGATION OF SORPTION CAPABILITIES OF CHELATING AGENTS LOADED AND UNLOADED POLYMERIC SORBENTS TOWARDS TRACE METAL IONS

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ABSTRACT

Poly(styrene-divinylbenzene) (poly(Str/DVB), sulphonated styrene-divinylbenzene copolymer and polyester-styrene polymer were synthesized using high internal phase emulsion method and characterized by FT-IR and SEM analysis. 5,10,15,20-tetrakis (hydroxyl phenyl) porphyrin (THPP) and pyrocatechol violet (PCV) were loaded on poly(styrene-divinylbenzene) and sulphonated styrene-divinylbenzene copolymer and were characterized by FTIR. The amounts of attached THPP and PCV onto poly(Str/DVB) and sulphonated Str/DVB were calculated as 0.2840, 0.2993, 0.5716 and 0.4384 mmol g^{-1} polymer, respectively. Metal (Pb(II), Cu(II), Cd(II), Ni(II), Zn(II)) sorption capabilities of poly(Str/DVB) and sulphonated Str/DVB copolymers were much low in high acidity medium, moderate at pH 4-7. Polyester-styrene polymer has no tendency towards metal ions.

The sorption tendency of poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP polymeric sorbents towards studied metal ions were much higher than PCV loaded polymeric sorbents except Pb. By eluting with 2 or 4 mol L^{-1} HNO$_3$, the quantitative recovery of studied metal ions from poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP was obtained. The precision of sorption process as relative standard deviation (RSD%) for 2 µg mL^{-1} metal ion was between 0.02 and 5.12. The sorption capacities of poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP for Cu(II), Ni(II), Zn(II) and Pb(II) were found as around 5000 µg g^{-1} sorbent. The sufficient sorption capabilities of THPP based sorbent at pH 10 and PCV based sorbent at pH 8 (for only Pb(II)) was ≥ 8 µg metal ion g^{-1} sorbent. These synthesized polymeric sorbents loaded with THPP can be used for separation and preconcentration of the studied metal ions in aqueous solutions.

Keywords: polymeric sorbent, pyrocatechol violet, tetra hydroxy phenyl porphyrin, metal, sorption

ŞELATLAYICI REAKTİF YÜKLENMİŞ VE YÜKLENMEMİŞ POLİMERİK SORBENTLERİN ESER DÜZEYDEKİ METAL İYONLARINA KARŞI TUTUNMA KAPASİTELERİNİN İNCELENMESİ

ÖZ

Poli(stiren-divinilbenzen), sülfolu stiren-divinilbenzen kopolimeri ve poliester-stiren polimeri yüksek iç fazlı emülsiyon yöntemi ile sentezlendiler ve FT-IR ve SEM kullanılarak karakterize edildiler. 5,10,15,20-tetrakis (hidroksi fenil) porfirin (THPP) ve pirokatekhol moru (PCV) poli(stiren-divinilbenzen) ve sulfolu stiren-divinilbenzen kopolimeri üzerine yüklendiler ve FT-IR ile karakterize edildiler. Poli(Str/DVB) ve sülfolu Str/DVB üzerine yüklenen THPP ve PCV miktarı sırasıyla 0,2840, 0,2993, 0,5716 ve 0,4384 mmol g^{-1} polimer olarak elde edilmiştir. Poli(stiren-divinilbenzen) ve sülfolu stiren-divinilbenzen kopolimerinin metal (Pb(II), Cu(II), Cd(II), Ni(II), Zn(II)) tutma kapasiteleri kuvvetli asidik bölgede çok az, pH 4-7 arasında orta düzeyde elde edilmiştir. Poliester-stiren polimerinin metal iyonlarına karşı bir eğilimi belirlenmemiştir.

Poli(Str/DVB)-THPP ve sülfolu Str/DVB-THPP polimerik sorbentlerinin metal iyonlarına karşı tutma eğilimleri PCV yüklü polimerik sorbentlerden kurşun hariç çok yüksek bulunmuştur. Poli(Str/DVB)-THPP ve sülfolu Str/DVB-THPP den metal iyonlarının nicel geri kazanımı 2 veya 4 mol L^{-1} HNO_3 çözeltisi elüasyon yapılarak sağlanmıştır. Tutunmanın kesinliği 2 µg mL^{-1} metal iyonu için bağıl standard sapma, %BSS ile belirlendi ve 0,02 ve 5,12 arasında bulundu. Poli(Str/DVB)-THPP ve sülfolu Str/DVB-THPP sorbentlerinin tutunma kapasiteleri çalışılan metal iyonları için 5000 µg g^{-1} sorbent civarında bulundu. THPP bazlı sorbentlerin pH 10 da ve PCV bazlı sorbentlerin pH 8 de (sadece Pb(II)) metal iyonlarını tutma kapasiteleri gram sorbent başına 8 µg metal iyonu ve üzeri olarak belirlenmiştir. Bu çalışmada, THPP emdirilmiş yeni sentezlenmiş polimerik sorbentler sulu çözeltiden çalışılan metal iyonlarının ayrılması ve önderiştirilmesi için kullanılabilirler.

Anahtar Kelimeler: Polimerik tutucu, pirokatekol moru, tetra hidroksi fenil porfirin, metal, tutunma

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 Determination of Trace Metals

Many elements occur in a sample in such minute amounts that, at the beginning of the development of instrumental analytical methods in the 19th century, it was impossible with the existing techniques to determine their concentration quantitatively, although their presence could be detected qualitatively. To indicate such low and barely detectable concentrations the term ''trace'' was used and the elements were referred to as trace elements. Although nowadays very low concentrations determined accurately and precisely because of improvements to existing and development of new analytical techniques, the term ''trace element'' is in stil use. In general, one speaks of trace element when the concentration is below 100 $\mu g \ g^{-1}$. At extremely low concentrations, below 10 ng g^{-1}, one also speaks of ''ultra-trace'' elements. In spite of low concentration, these elements may play a very important role in many areas (biochemistry, medicine, environmental, industrial) (Vandecasteele & Block, 1993).

Trace metals play an important role in human metabolism and either excess or deficiency of them in the living organism can lead to biological disorder.

Cadmium, a metal with toxic effects, accumulates particularly in the liver and kidney and this accumulation is linked to metallothionein synthesis as well as to a disturbance in the metabolism of zinc and copper. The copper/zinc ratio is also imporrant for the diagnosis of cancer and cardiac activity as well as the determination of optimal nutrition. (Mondal, Das & K. Das, 2002).

Copper is an element essential for many biological systems, which plays an important role in carbohydrate and lipid metabolism. In general, copper at nearly 40

μgL^{-1} is required for normal metabolism of many living organisms; however, in higher levels it is considered to be toxic and severe oral intoxication will affect mainly the blood and kidneys

Zinc is an essential trace element of great importance for humans, plants, and animals. It is a co-factor in more than 200 enzymes and it is necessary for production of insulin in human. However, high concentrations of this metal can cause several damages to human body, such as disturbances in energy metabolism or increasing in oxidative stress.

Nickel is a moderately toxic element and it is known that inhalation of this metal and its compounds can lead to serious problems, including respiratory system cancer. (Silva, Roldan, & Giné, 2009)

Lead is a toxic metal, which accumulates in the vital organs of man and animals. Its cumulative poisoning effects are serious haematological damage, anemia, kidney malfunctioning, brain damage, etc. Lead is still emitted into the biosphere in considerable amounts owing to its application as a fuel additive, mainly as tetraethyllead and tetramethyllead. It is also present in many industrial streams. Due to the presence of lead in environmental samples at low levels, its separation from other elements present and the use of a preconcentration step prior to lead determination are usually necessary. (Zachariadis, Anthemidis, Bettas & Stratis, 2002; Tewari & Singh, 2002)

1.2 Preconcentration and Separation

The methods of analytical chemistry can be divided into two large groups: (1) methods of separation and preconcentration of components, (2) methods of determination of components of the material to be analysed.

Separation is a process in which the components constituting the starting mixture are separated from each other. Preconcentration is a technique by which the ratio of

concentration (or the amount) of trace components to the concentration (or the amount) of macrocomponent is increased. In separation, the components constituting the mixture may or may not differ in concentration from each other. In preconcentration, the components that have significantly different concentrations are treated.

Numerous methods are used for analytical preconcentration of trace elements. A large majority of them had previously been employed only for separation. Probably evaporation was first utilized for preconcentration; precipitation, extraction, electrochemical and other methods gained recognition at a later stage. Fire assay is one of the oldest methods of preconcentration.

By the nature of the separation methods used, they can be classified into 1) chemical and physico-chemical and 2) physical methods. With the first group may be classed extraction, sorption, precipitation and co-precipitation, partial dissolution of matrix, flotation, volatilization after chemical transformations, chemical transport reactions, fire assay, electrochemical methods and dialysis. The second group may include volatilization, crystallization, freezing out, filtration and gel filtration and ultracentrifugation.

The selection of a preconcentration method is dictated by (i) the practical problem being solved, the nature of the material to be analyzed, trace elements to be determined, the specified metrological parameters of the technique; (ii) the origin and previous history of the material to be analyzed; (iii) the combination of the selected method of preconcentration and subsequent method of determination of trace elements in a concentrate; (iv) the simplicity, the availability and the duration of the method; (v) the equipment available in the laboratory of the scientist and in those laboratories which will use the method; (vi) the specialization and qualification of the researcher developing the technique and of the analysts of the laboratories where this technique is to be employed; (vii) the need to ensure safe working conditions.

Solvent extraction is an effective and widely used method of preconcentration. It can be applied both for the removal of matrix and for the selective, group, or subsequent separation of trace elements. One of its variants extraction chromatography is an effective way of separating substances with almost similar properties and ensures high efficiency of preconcentration (Zolotov & Kuz'min; 1990).

Liquid-liquid extraction is a classical method for preconcentrating metal ions and/or matrix removal. Solid phase extraction is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years solid phase extraction has been successfully used for the separation and sensitive determination of metal ions (Camel; 2003).

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples (especially water samples). Additionally, since high levels of non-toxic components usually accompany analytes, a clean-up step is often required. Liquid–liquid extraction is a classical method for preconcentrating metal ions and/or matrix removal. Solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples. After outlining the theory of this technique, guidelines are given for the development of SPE-based methods for preconcentration of many trace elements (Camel; 2003).

1.3 Solid Phase Extraction

The principle of SPE is similar to that of liquid–liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible

liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After all of the sample has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent.(Liska; 2000; Poole; 2000)

1.3.1 Process of Solid-Phase Extraction

An SPE method always consists of three to four successive steps (Figure 1.1). First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent.

The nature of the conditioning solvent depends on the nature of the solid sorbent. Typically, for reversed phase sorbent (such as octadecyl-bonded silica), methanol is frequently used, followed with water or aqueous buffer whose pH and ionic strength are similar to that of the sample. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned.

Washing /
Conditioning   Loading   Washing   Elution
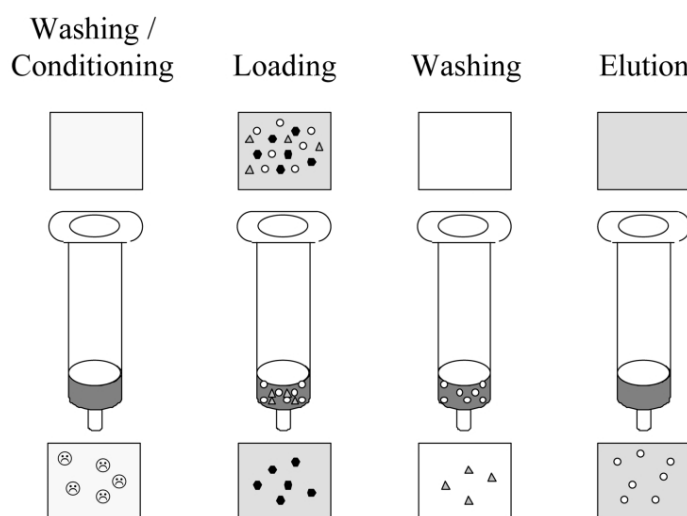
Figure 1.1 SPE operation steps

The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 mL to 1 L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation) of the sample.

The third step (which is optional) may be the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorbent. This will eliminate the presence of water in the final extract, which, in some cases, may hinder the subsequent concentration of the extract and/or the analysis.

The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent

low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorbent.

1.3.2 Advantages of Solid Phase Extraction

Solid-phase extraction has several important advantages over liquid-liquid extraction (Pyrzynska & Trojanowicz; 1999).

1. Faster and easier manipulation. A sample can be quickly passed through a SPE column or cartridge by means of a pump or with gentle pressure of suction. After a quick rinse, the extracted substances can be washed from the column by a small amount of appropriate eluent. However, simple solvent extraction requires a considerable amount of manipulation in adding the extractive liquid, shaking, waiting for the emulsion to break, and carefully separating the two liquid phases. Often a washing step and a back extraction are required.

2. Much smaller amounts of organic solvents are used. The large volumes of organic solvents used in analytical separations have become an important environmental concern. Aqueous samples have become contaminated with organic solvents and an evaporative concentration of the extracts pollutes the air with organic vapors. Proper disposal of used organic solvents has become troublesome and expensive. Today, analytical chemists are working to replace liquid-liquid extraction with solid-phase extraction in analytical procedure in control laboratories.

3. Less stringent requirements for separation. SPE is a multistage separation method and as such requires only a reasonable difference at least %80 in extractability to separate two solutes.

4. Higher concentration factor. The concentration factor is how many times more concentrated a substance is in the extract than it is in the original sample. In SPE,

concentration factors of 100 or more are possible. The concentration factor in liquid-liquid extraction depends in part on the volume ratio of the liquids.

1.4 Solid Sorbents

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for a solid sorbent are:

(1) The possibility to extract a large number of trace elements over a wide pH range (along with selectivity towards major ions);
(2) The fast and quantitative sorption and elution;
(3) High capacity;
(4) Regenerability;
(5) Accessibility.

Adsorbent properties that increase retention are a larger surface area and a high activity. Hydrogen-bonding functional groups are strongly retained (e.g. sulfonic acid, carboxylic acid, phenol and hydroxyl). Coating inorganic oxides with a complexing agent (e.g. silver nitrate, and caffeine) or an acid or base (an acid can be used for the selective isolation of bases and vice versa) can be used to modify selectivity for the isolation of target compound (Thurman, & Mills; 1998).

Various selective sorbents based on ion exchange, bioaffinity, molecular recognition, and restricted access material are used. Ion-exchange sorbents are usually classified as weak or strong, depending on the identity of the ionic group and whether its charge is independent of the sample pH (strong ion exchanger) or can be manipulated by changing pH (weak ion exchanger) (Poole, 2003).

Restricted access sorbents were initially developed for the isolation of low-molecular-mass drugs from biological fluids with minimum sample pretreatment and

now also find use in the isolation of herbicides from surface waters containing high levels of humic substance (Simpson; 2000).

Immunosorbents (or immunoaffinity sorbents) have long been used for sample pretreatment in medicine, biology and food science, but more general applications, such as to environmental samples. Immunosorbents are prepared by covalently bonding a suitable antibody to an appropriate sorbent (Delaunay, Pichon & Hennion; 2000).

1.4.1 Inorganic Based Sorbents

Inorganic based sorbents are mainly made of silica gel even though other inorganic oxides may be used, as discussed later. Silica-based, siloxane-bonded sorbents can be prepared with a wide range of bonding density, pore size and functional group types. Silica gels of high surface area, 500-600 m^2 / g, are generally used to prepare sorbents for the isolation of small molecules. Siloxane-bonded sorbents with high surface areas, long alkyl chains and high phase loading maximize retention of small molecules from aqueous solution, while wide-pore materials with a low phase loading short alkyl chains are used to isolate macromolecules.

The surface of silica gel is characterized by the presence of silanol groups, which are known to be weak ion-exchangers, causing low interaction, binding and extraction of ionic species [131]. In particular, silica gel presents high sorption capacity for metal ions, such as Cu, Ni, Co, Zn or Fe. (Sarkar, Datta & Sarkar, 1996).

Despite the large variety of bonded phases available, octadecylbonded silica (C_{18}-bonded silica gel) has currently become the most popular phase used.

Whereas SiO_2, due to its acidic properties, is expected to adsorb only cations, basic oxides (such as magnesia MgO) should adsorb only anions. As a matter of fact adsorption of ions on oxide surfaces is believed to proceed with participation of hydroxyl groups. These groups are negatively charged (deprotonated) under basic

conditions, thereby retaining cations and positively charged (protonated) under acidic conditions, thereby retaining anions. Consequently, on amphoteric oxides (namely titania TiO_2, alumina Al_2O_3, zirconia ZrO_2), cations are adsorbed under basic conditions while anions are adsorbed under acidic conditions (pH below the isoelectric point of the oxide). (Vassileva, Proinova & Hadjiivanov, 1996).

1.4.2 Organic Based Sorbent

Organic based sorbents may be divided into polymeric and non-polymeric sorbents. Polymeric sorbents have been, by far, the most used for trace element preconcentration having the advantage over bonded silica in that they can be used over the entire pH range. Their disadvantage is that the conditioning step is more time consuming as they require extensive cleaning before use. (Kantipuly, Katragadda, Chow, & Gesser, 1990).

Porous polymer sorbents are generally copolymers of styrene and divinylbenzene processed to enhance their properties for SPE. They are either similar in chemistry to porous polymers developed for HPLC and have moderate surface area (< 600 m^2 / g) or are biporous and highly crosslinked with surface areas of 700-1200 m^2/ g. The modern forms of carbon used for SPE are graphitized carbon blacks and porous graphitic carbon. Graphitized carbon blacks are (largely) non-porous with moderate surface area of 100-210 m^2 / g. (Poole, 2003).

1.4.2.1 Polystyrene-divinylbenzene Based Sorbents

The term "macroporous resin sorbents" in the literature can be found as polymeric resin, nonionic polymeric resin, macroporous resin, macroporous polymeric adsorbent, macroporous copolymer, organic adsorption polymer, synthetic adsorber polymer, polymeric sorbent, nonionic macroreticular polymeric resin, macroporous synthetic adsorbent, etc. The most common type of macroporous sorbent is styrene and divinylbenzene copolymer, which may be found as polystyrene, styrene-divinylbenzene copolymer or simply Str-DVB copolymer.
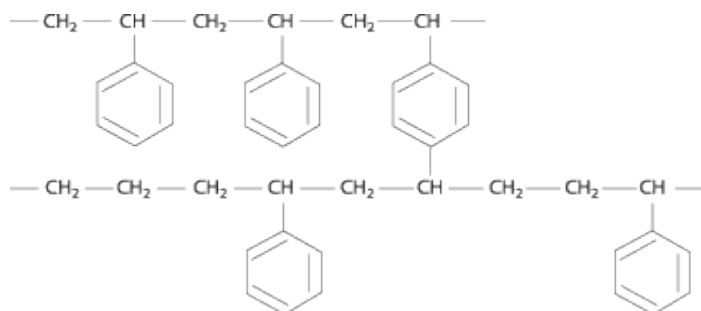
Figure 1.2 poly-(styrene divinylbenzene)

Polymeric adsorbents, which are sub-groups of low-specificity sorbents, are highly porous structures whose internal surfaces can adsorb and then desorb a wide variety of different species depending on the environment in which they are used. For example, in polar solvents such as water, polymeric adsorbents exhibit non-polar or hydrophobic behaviour and so can adsorb organic species that are sparingly soluble. This hydrophobicity is most pronounced with the styrenic adsorbents. In non-polar solvents, such as hydrocarbons, etc. most adsorbents exhibit slightly polar or hydrophilic properties and so will adsorb species with some degree of polarity. This polarity is most pronounced with the acrylic adsorbents and the phenolic adsorbents.The efficiency of the polymeric sorbents depends on various physico-chemical parameters such as particle size, surface area, pore diameter, pore volume, degree of crosslinking and particle size distribution. The highly porous materials have higher real activity surface available which allows higher π-π interactions and so higher adsorption capacity. The band broadening with highly porous sorbents is only slightly greater than with other sorbents because porosity minimizes band dispersion. Band broadening is also minimized when working with sorbents with a narrower particle size distribution (Puig & Barceló; 1996).

The most widely used polymeric sorbents are styrene-divinyl benzene copolymers with a hydrophobic surface (Prasada Rao, Praveen & Daniel; 2004). Polystyrene cross-linked with divinylbenzene with low cross-linkage developed by Merrifield in 1960 is the most commonly used polymer support for solid phase extraction because of the advantages such as good mechanical and chemical stabilities. Chelate

immobilized Merrifield chloromethylated styrene-divinyl benzene resin offer better retention capacities due to its small pore diameter and low bead surface area over Amberlite XAD resins (Praveen, Metilda, Daniel & Prasada Rao; 2005).

Macroporous hydrophobic resins of the Amberlite XAD series are good supports for developing chelating matrices. Amberlite XAD-1, XAD-2, XAD-4 and XAD-16 (Table 1.1) are polystyrene-divinylbenzene (PStr-DVB) resins with a high hydrophobic character and no ion-exchange capacity. The broader range of pH stability of these resins increases the flexibility of the method, and they have no silanol groups (Bouvier, Martin, Iraneta, Capparella, Cheng & Phillips., 1997).

XAD-1, XAD-2 and XAD-4 are PStr-DVB with a highly hydrophobic character. XAD-7 and XAD-8 are acrylic ester resin with a higher affinity for solutes. XADs based on PStr-DVB have some drawbacks including lack of selectivity, low breakthrough volumes for very polar compounds, and sampling rate, and they require extensive cleaning before use (Akerblom; 1995).

All those properties mentioned above make the macroporous polymers have higher capacities and be more highly selective than microporous resins. In addition; use of microporous matrix during preparation of polymers exhibit some problems, as the swelling of this kind of matrix is highly dependent on the consumption of the sample solution, thus making it difficult for data to be reproduced. However, macroporous resins are not affected by the concentration of the external solution or by the solvent.

Hypercrosslinked resin sorbents have also gained increasing interest. These sorbents are produced by crosslinking polymers of macroporous resin in a good solvent. The crosslinking tightens the structures and modifies the surface properties of the porous polymeric network.

One of the advantages of macroporous and hypercrosslinked resin sorbents is the possibility of controlling their resin structure, internal surface area, and pore size

distribution. This can be achieved by varying the polymerization conditions, the most crucial of which are the amounts of monomers and pore-forming agent used in the polymerization reaction.

Table 1.1 Some properties of Amberlite resins

Amberlite	Chemistry	Surface area (m^2/g)	Av. pore diameter ($\mathring{A}$)	Mean diameter (μ)	Applications
XAD-2	pStrDVB	300	90	500	Separation of metals, antibiotic recovery
XAD-4	pStrDVB	750	100	640	Removal of solvents and low MW species
XAD-16	pStrDVB	800	150	700	Small molecules, antibiotic recovery
XAD-1180	pStrDVB	500	400	530	Plant extracts, large MWproduct recovery
XAD-7	Aliphatic ester	500	450	560	Plant extract, enzyme purification, peptides

pStrDVB: polystyrene divinylbenzene

1.5 Preparation of Polymeric Sorbents Using High Internal Phase Emulsion (HIPE) Method

In 1985, Barby and Haq of Unilever successfully developed porous polymer structures that are distinct from macroporous polymers of prior decades. These materials are known as "high internal phase emulsions" ("HIPE"). HIPE structures had been of interest to chemists and materials scientists for many years, but they

were difficult to study because they were unstable. Unilever's methods of stabilizing these emulsions and finally, polymerizing them has lead to materials of unusual and useful properties. HIPE structures are characterized by the presence of very large pores of micrometer dimensions ("cavities") as opposed to pores associated with microporous or macroporous polymers having only Angstrom dimensions. Furthermore, these large cavities are interconnected by a series of smaller pores, thereby enabling each to communicate with those adjacent. (Benson, 2003).

1.5.1 Polymerized High Internal Phase Emulsion (polyHIPE)

A high internal phase emulsion (HIPE) has been defined as an emulsion in which the internal phase occupies more than 74 % of the volume. A polymerized HIPE (polyHIPE) is a highly cross-linked, porous polymer that results from polymerizing monomers and crosslinking comonomers in the external phase of a HIPE. Significant amounts of a cross-linking comonomer are used to prevent polyHIPE collapse during polymerization and drying.

A variety of polyHIPE and polyHIPE-based materials have been synthesized including copolymers, interpenetrating polymer networks (IPN) hydrogels, biocompatible polymers, organic-inorganic hybrids, and composites. Porous materials have numerous applications in such areas as catalysis, chromatography, and separation, where control over pore structure and pore size strongly influences the efficiency of the material.

PolyHIPE, with their high porosities, high degrees of interconnectivity, and unique micrometer- to nanometer-scale open-pore structures, have been investigated for such applications.

PolyHIPE are usually synthesized from monomers which yield amorphous homopolymers. Even monomers which could yield crystalline homopolymers are not likely to crystallize in polyHIPE, owing to the significant amounts of cross-linking

comonomer. The cross-linking comonomer disrupts the structural regularity of the polymer backbone, restricts polymer mobility, and limits the ability of the backbone to organize into an ordered, crystalline structure. (Livshin & Silverstein, 2008)
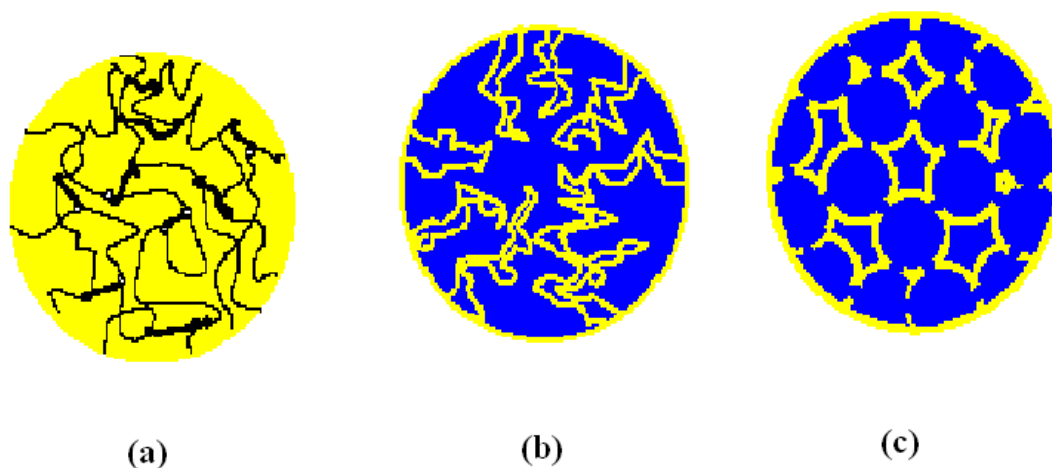
Figure 1.3 (a) Microporous,   (b) Macroporous and   (c) High Internal Phase Emulsion Polymers

Microporous polymer. These polymers are formed by cross-linking linear chains of monomer. Cross-links (shown as heavy lines above) create very small pores within the three-dimensional matrix. Known as "gels", these polymers are soft and compress under pressure.

Macroporous polymer. These materials have a high degree of cross-linking, preventing them from swelling in solvents. Pores are larger than gels, but are irregular and terminate inside the matrix. Total pore volumes are typically 50%.

High internal phase emulsion. HIPE polymers, illustrated above, contain extremely large cavities that are interconnected. Cavities are of micrometer dimensions, rather than angstrom dimensions of conventional polymers. Total pore volume can exceed 90%. (Benson, 2003).

1.6 Retention of Trace Elements on Sorbents

Adsorption of trace metals on the solid sorbent is required for preconcentration (Figure 1.4). The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, ion-exchange or chelation.
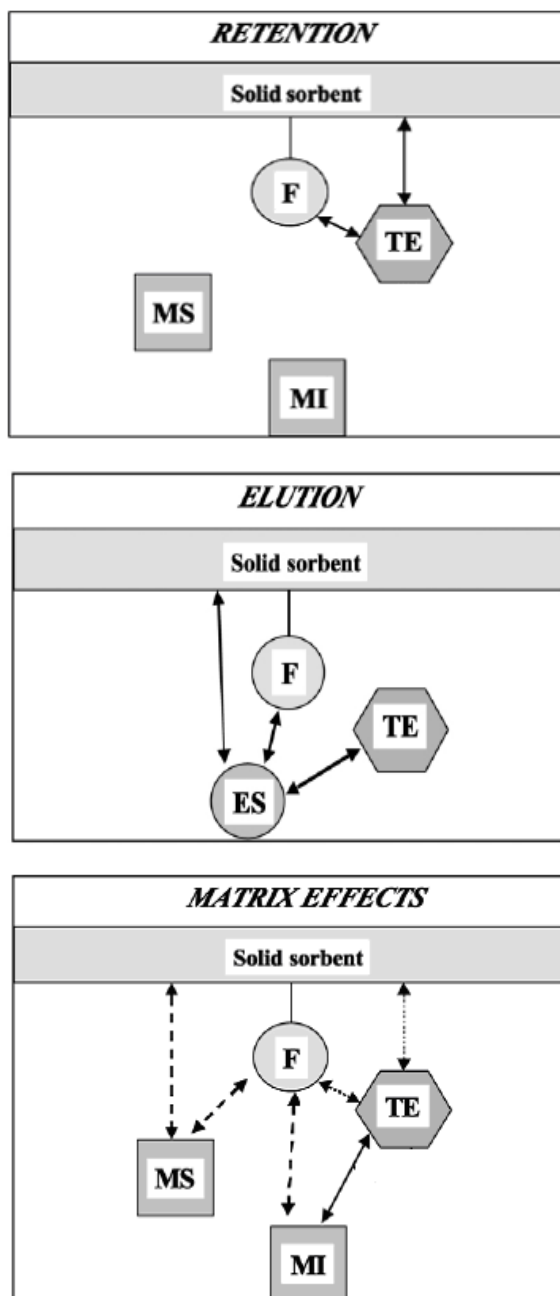

Figure 1.4 Interactions occuring at the surface of the solid sorbent. F, functional group; TE, trace element; MS, matrix solvent; MI, matrix ions; ES, elution solvent.

1.6.1 Adsorption

Trace elements are usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction. Hydrophobic interaction occurs when the solid sorbent is highly non-polar (reversed phase). The most common sorbent of this type is octadecyl-bonded silica (C_{18}-silica). More recently, reversed polymeric 18 phases have appeared, especially the styrene-divinylbenzene copolymer that provides additional π-π interaction when π-electrons are present in the analyte (Camel, 2003). Elution is usually performed with organic solvents, such as methanol or acetonitrile. Such interactions are usually preferred with online systems, as they are not too strong and thus they can be rapidly disrupted. However, because most trace element species are ionic, they will not be retained by such sorbents.

1.6.2 Ion Exchange

Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counter-ion. Strong and weak sites refer to the fact that strong sites are always present as ion-exchange sites at any pH, while weak sites are only ion-exchange sites at pH values greater or less than the pK. Strong sites are sulfonic acid groups (cation-exchange) and quaternary amines (anion-exchange), while weak sites consist of carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange).

Functional groups can be chemically bound to silica gel or polymers (usually a styrene-divinylbenzene copolymer), the latter allowing a wider pH range. An ion-exchanger may be characterized by its capacity, resulting from the effective number of functional active groups per unit mass of the material. The theoretical value depends upon the nature of the material and the form of the resin. However, in the column operation mode, the operational capacity is usually lower than the theoretical one, as it depends on several experimental factors, such as flow-rate, temperature, particle size and concentration of the feed solution. As a matter of fact, retention on ion-exchangers depends on the distribution ratio of the ion on the resin, the stability

constants of the complexes in solution, the exchange kinetics and the presence of other competing ions.

1.6.3 Chelation

Several functional group atoms are capable of chelating trace elements. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides and nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl and phosphor groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards trace metals (Camel; 2003).

In practice, inorganic cations may be divided into 3 groups:

Group I- 'hard' cations: These preferentially react via electrostatic interactions due to a gain in entropy caused by changes in orientation of hydration water molecules; this group includes alkaline and alkaline-earth metals (Na^+, Li^+ , Ca^{2+}, Mg^{2+}, etc.) that form rather weak outer-sphere complexes with only hard oxygen ligands.

Group II- 'borderline' cations: These have an intermediate character; this group contains Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}. They possess affinity for both hard and soft ligands.

Group III- 'soft' cations (*Soft acids or class b*): These tend to form covalent bonds. Hence, Cd^{2+} and Hg^{2+} possess strong affinity for intermediate (N) and soft (S) ligands.

For soft metals, the following order of donor atom increasing affinity is observed: O>N>S. A reversed order is observed for hard cations. For a bidentate ligand, affinity for a soft metal increases with the overall softness of the donor atoms: (O, O)>(O, N)>(N, N)>(N, S).

The order is reversed for hard metals. In general, the competition for a given ligand essentially involves Group I and Group II metals for O sites, and metals of Group II and Group III for N and S sites. The competition between metals of Group I and Group III is weak.

Chelating agents may be directly added to the sample for chelating trace elements, the chelates being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For that purpose, three different means are available:

(1) the synthesis of new sorbents containing such groups (new sorbents)

(2) the chemical bonding of such groups on existing sorbents (functionalized sorbents)

(3) the physical binding of the groups on the sorbent by impregnating the solid matrix with a solution containing the chelating ligand (impregnated, coated or loaded sorbents).

The last one remains the most simple to be used in practice. Impregnated resins have been proposed by Warshawsky and used successfully in the extraction of metals from a multicomponent mixture in various analytical applications (Cortina, Arad-Yellin, Miralles, Sastre & Warshawsky; 1998). Different ligands (dithizone, thiocarbamate, calixarene, resorcinarene, chromotropic acid, etc.) impregnated on a variety of solid matrices have been successfully used for preconcentration, separation and determination of trace metal ions. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent.

Due to their high capacity and operational efficiency ligand functionalized sorbents have been used for matrix isolation and preconcentration of trace metal ions prior to their determination by atomic spectrometric methods (Sabermahani & Taher;

2006). The application of functionalized resins has the additional advantage of controlling the capacity and selectivity of metal sorption by the appropriate choice of loading organic reagents, thus controlling the efficiency of the process.

Recently, chemically modified resins have been more used in the extraction of metals from a multicomponent mixture in various analytical applications. A number of chelating resins have been prepared by incorporating various functional groups (e.g. ethylenediamine tetraacetic acid, iminodiacetic acid, 8-hydroxyquinoline, dithiocarbamate, pyrocatechol, etc) and their analytical properties investigated. In this work, porphyrin and calixcrown have been used as functional group.

1.7 Chelating Agents

1.7.1 Porphyrins

A porphyrin is a heterocyclic macrocycle derived from four pyrroline subunits interconnected via their α-carbon atoms via methine bridges (=CH–). Each pyrrolenine ring is made up of a nitrogen atom and four carbon atoms . In the porphyrin ring, they are linked to each other by a carbon atom that bridges from the carbon atom nearest the nitrogen atom of one ring to the carbon atom nearest the nitrogen atom of the next ring (called the alpha carbon). The porphyrin ring is unsaturated, having alternating carbon-carbon single bonds and double bonds throughout the ring.

The class of porphyrin molecules is very large because the ring can be substituted at many positions. In biochemically derived porphyrins, the hydrogen atoms on the carbon atoms of each nitrogen-containing ring that are farthest from the nitrogen atom (called the beta carbon) are replaced by carbon-containing groups such as a methyl group ($-CH_3$), and ethyl group ($-CH_2CH_3$), a carboxymethyl group ($-CH_2COOH$), or one of a large variety of other groups. The substituents of porphyrins profoundly affect their solubilities and their interactions with other molecules. They also change the ease with which the porphyrin ring can be oxidized

or reduced. Substituents can greatly affect the oxidation-reduction properties of the metalloporphyrin complex. (Kong, Guo, Li & Pan, 2007).
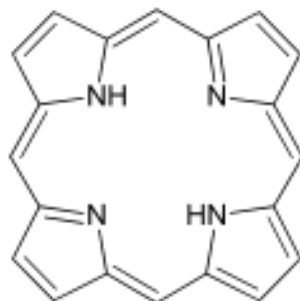
.

Figure 1.5 Porphyrin macrocyclic system

When cordination occurs, two protons are removed from the pyrrole nitrogen atoms, leaving two negative charges. The porphyrin ring system is very stable and exhibits aromatic characters. The porphyrin complexes with transition metal ions are very stable. (Biesaga, Pyrzyn´ska & Trojanowicz, 2000).
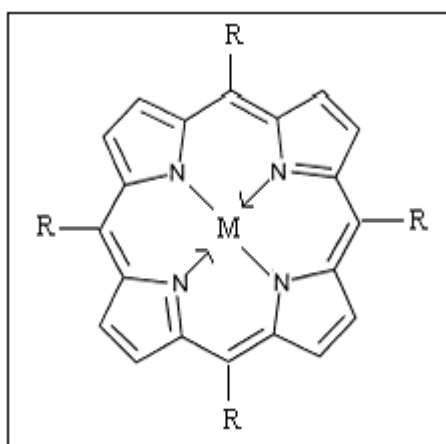
Figure 1.6 Porphyrin-metal complex

Almost all metals form complexes 1:1, although Na, K, Li complexes are 2:1 in which the metal atoms are incorporated slightly below and above the porphyrin macrocycle plane. When divalent metal ions (e.g. Co(II), Ni(II), Cu(II)) are chelated, the resulting tetracoordinate chelate has no residual charge. While Cu(II) and Ni(II) in their porphyrin complexes have generally low affinity for additional ligands, the chelates with Mg(II), Cd(II) and Zn(II) readily combine with one more ligand to

form pentacoordinated complexes with square-pyramidal structure. Some metalloporphyrins (Fe(II), Co(II), Mn(II)) are able to form distorted octahedral with two extra ligand molecules.

Porphyrin metal complexes play an important role in biological activities as for instance iron complex in the haemoproteins, magnesium complexes in the chlorophylls and a cobalt complex in Vitamin B_{12}. Complexes of many metals with various porphyrins have been extensively studied in order to understand the biosynthetic formation and biological activity of natural compounds.

It is well known that porphyrin is also a high sensitive chromogenic reagent. Porphyrins and their metal chelates generally exhibit characteristic sharp and intensive absorption bands in the visible region. The region from 400 to 500 nm, which is called the Soret band, shows the most intensive absorption and molar absorptivities of the order of 10^5 are often found. The Soret band is widely used for spectrophotometric determination of metalloporphyrins. (Pati˜no, Torres & Campos, 1999).

Due to strong complexing properties and catalytic behaviour of metalloporphyrins, these compounds have found numerous applications in chemical analysis. (Gupta & Agarwal, 2005).

1.7.2 Pyrocatechol Violet

Pyrocatechol violet is an often used chelating reagent with three hydroxyl groups an one sulphonate group:
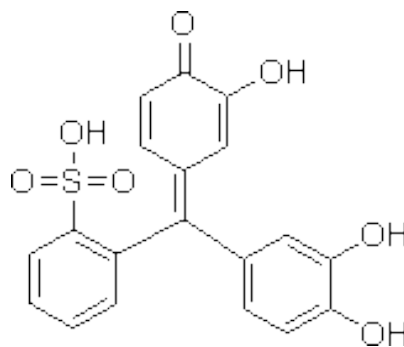
Figure 1.7 The structure of pyrocatechol violet

Pyrocatechol violet is freely soluble in water and aqueous alcohol, but less soluble in cold absolute alcohol. An aqueous solution of the reagent is yellow (pH 1-8), and colour of the solution changes to violet with increasing pH as a result of proton dissociation from the hydroxyl groups. Pyrocatechol violet forms coloured (often blue) chelates with many metals, (e.g. Be, Al, Co, Cu, Fe, Ga, In, Mn, Pb, Th, V, Zn, Zr) mostly in weakly acidic and basic solutions. (Marczenko, Z. 1986)

1.8 Atomic Absorption Spectrometer

Atomic absorption spectrometry is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level. Atomic absorption spectrometry has many uses in different areas of chemistry.

Atoms of different elements absorb characteristic wavelengths of light. Analysing of a sample to see if it contains a particular element means using light from that element. An atomic absorption spectrometer (Figure 1.8) needs the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed (Levinson, 1997).
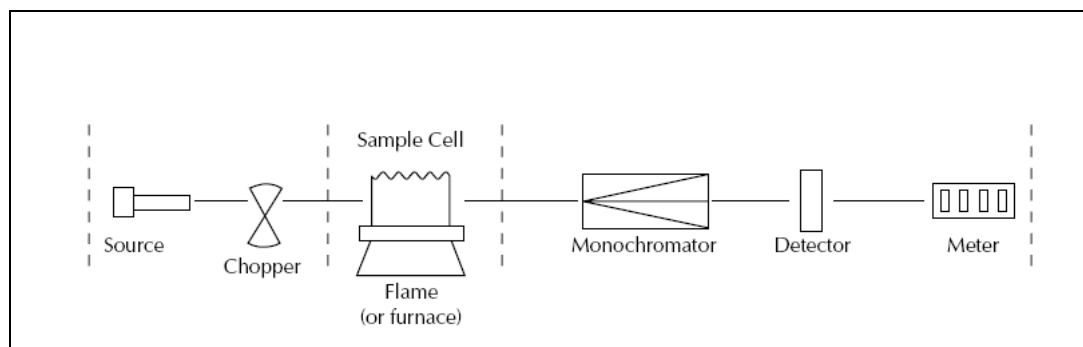
Figure 1.8 Atomic Absorption Spectrometer

1.8.1 Light Source

Common source of light is a hollow cathode lamp. This contains a tungsten anode and a cylindrical hollow cathode made of the element to be determined. These are sealed in a glass tube filled with an inert gas. The ionization of some gas atoms occurs by applying a potential difference of about 300–400 V between the anode and the cathode. These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called sputtering. Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state. A typical atomic absorption instrument holds several lamps each for a different element.

1.8.2 Optical System and Detector

A monochromator is used to select the specific wavelength of light – *i.e.* spectral line – which is absorbed by the sample, and to exclude other wavelengths. The selection of the specific light allows the determination of the selected element in the presence of others. The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube. This produces an electrical signal proportional to the light intensity.

1.8.3 Atomization of the Sample

Two systems are commonly used to produce atoms from the sample. Aspiration involves sucking a solution of the sample into a flame; and electrothermal

atomization is where a drop of sample is placed into a graphite tube that is then heated electrically. Some instruments have both atomization systems but share one set of lamps. Once the appropriate lamp has been selected, it is pointed towards one or other atomization system.

1.8.4 Sample Preparation

Sample preparation is often simple, and the chemical form of the element is usually unimportant. This is because atomization converts the sample into free atoms irrespective of its initial state. The sample is weighed and made into a solution by suitable dilution.

1.8.5 Calibration

A calibration curve is used to determine the unknown concentration of an element in a solution. The instrument is calibrated using several solutions of known concentrations. A calibration curve is produced which is continually rescaled as more concentrated solutions are used – the more concentrated solutions absorb more radiation up to a certain absorbance. The calibration curve shows the concentration against the amount of radiation absorbed. The sample solution is fed into the instrument and the unknown concentration of the element is then displayed on the calibration curve.

1.9 Related studies

Chelating agents as porphyrins and pyrocatechol violet have been used for metal determination in various analytical matrices by chromatographic, spectrometric and electroanalytic techniques. Chelating resins prepared by immobilisation of tetrakis(p-carboxylphenyl) porphyrin on anion exchange resin Amberlite IRA-401 and nonionic sorbent Amberlite XAD-2 were characterized and used for retention of some metals such as Cd, Cu, Co, Ni Ph and Mg by Kilian et al. . Their properties such as retention capacity and sorption kinetics were determined. The sorptions of metal complexes

were also investigated (Kilian & Pyrzynska, 2002).

By Kilian & Pyrzynska, Cd(II), Pb(II), Hg(II) and Zn(II)-5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin complexes were obtained and also their spectrophotocemical properties were investigated. Within these elements, Zinc having large radius was highly incorparated with the studied porphyrin reagent (Kilian & Pyrzynska, 2003).

In 2003, By Wang et al. a method for the simultaneous determination of lead, cadmium, and mercury ions as metal tetra-(4-chlorophenyl)-porphyrin (T4CPP) chelates was developed using reversed-phase-high performance liquid chromatography (RP-HPLC) and combined with on-line enrichment technique. The complexation pH was pH 10, pyrrolidine-acetic acid buffer solution. The linearity ranges are 0.01 - 120 μg L^{-1} for each metal chelate. This method was applied to the determination of the μg/L level of lead, cadmium, and mercury ions in a water sample with good results (Wang et al., 2003)

Simultaneous determination of copper, nickel, cobalt, silver, lead, cadmium, and mercury ions in water by solid-phase extraction and reversed-phase high-performance liquid chromatography (RP-HPLC) using tetra(m-aminophenyl) porphyrin at pH 10 was developed by Hu and co-workers. The detection limits of copper, cobalt, nickel, silver, lead, cadmium, and mercury are 2, 2, 3, 4, 3, 3, and 3 ng L^{-1}, respectively, in the original sample (Hu, Yang, Zhao & Yin, 2003).

In 2004, an ionselective electrode for silver has been progressed using meso-tetraphenylporphyrin as complexing agent by Ardakani. This linearity of this electrode was in range of 1.0 x 10^{-7} - 1.0 x 10^{-1} M silver ion. The silver-selective electrode exhibited good selectivity for Ag(I) with respect to alkali, alkaline earth and heavy metal ions (Ardakani, Dehghani, Jalayer & Zare, 2004).

By Pyrzynska & Wierzbicki, silica loaded with tetrakis(4-carboxyphenyl) porphyrin by physically and chemically was used for preconcentration and separation

of vanadium prior to its determination by atomic absorption spectrometry. Speciation types of vanadium, V(IV) and V(V) ions, were investigated (Pyrzynska & Wierzbicki, 2005).

In 2007, Pyrzynska and co-workers proposed an on-line preconcentration procedure for the determination of manganese depending on complexation with tetra carboxyphenyl porphyrin using flow-injection flame atomic absorption spectrometry. In this method, enrichment of manganese was studied by two methods; formation of metal complex in a solution followed by its retention on sorbent and sorption of metal onto ligand immobilized resin. With the first method reported that they obtained better results (Knap, Kilian & Pyrzynska, 2007).

By Asano et al., porphyrin–incorporated polymers were synthesized for spectrophotometrical determination of metals (Bi(III), Co(II), Cu(II), Mn(II), Pb(II), and Zn(II)). In these polymer synthesis, by free radical copolymerization vinyl monomers were reacted with protoporphyrin IX disodium salt multimetal. This proposed method was applied to several water samples (Asano, Wang & Iwasaki, 2010).

In 1989, Amberlite XAD-2 loaded with Pyrocatechol Violet as sorbent was used for separation and preconcentration of zinc and cadmium at pH 7.0–7.5 and 8.0–8.5. The linearity of concentration is in range of 0.1-1.5 and 0.05-1.0 $\mu g\ L^{-1}$ for Zn and Cd, respectively (Singh & Kumar, 1989).

Singh & Rita prepared Amberlyst A-26 resin loaded with pyrocatechol violet for preconcentrating of cadmium and lead before their flame atomic absorption spectrophotometric determination. The optimum sorption pHs are 7.0–7.8 and 7.0–7.5 for Cd and Pb, respectively. The absorbance varies linearly in the concentration ranges of 0.1–1.0 for Cd and 1.5–7.5 $\mu g\ L^{-1}$ for Pb (Singh & Rita, 1991).

By Saxena & Singh, pyrocatechol violet was chemically bound to Amberlite XAD-2 resin and used for preconcentration of Zn(II), Cd(II), Pb(II) and Ni(II) ions.

The effect of F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and PO$_4^{3-}$ on the sorption of these four metal ions has been investigated. The sorption capacity of the resin is 1410, 1270, 620 and 1360 μg g^{-1} resin for Zn, Cd, Ni and Pb, respectively (Saxena & Singh, 1996).

In 2000, trace metal ions (Cu, Mn, Co, Cd, Pb, Ni and Cr) complexed with pyrocatechol violet at pH range of 4-8 were passed through column filled with active carbon and determined by flame AAS after desorption with nitric acid-acetone solution (Narin, Soylak, Elci & Dogan, 2000).

By Narin et al., aluminum determination by atomic absorption spectrometry was succeeded using pyrocatechol violet immobilised on an Amberlite XAD-1180 support at pH 8-9 . The capacity of sorbent was 6.45 ± 0.59 mg g^{-1} A l (Narin, Tuzen & Soylak, 2004).

In 2009, a column method based on sorption of copper by pyrocatechol violet loaded Chromosorb 105 resin at pH 5-8, elution with nitric acid and determination by flame AAS. The present method was found to be applicable to the preconcentration of Cu(II) in natural water samples (Buke, Divrikli, Soylak & Elci, 2009).

By Sonmez and co-workers, polypyrrole-chloride as sorbent was used for preconcentration of copper(II) ion using solid-phase extraction technique prior to determination by flame atomic absorption spectrometry. The sorbent showed an extremely high selectivity towards copper(II) as an anionic chelate, i.e Cu(pyrocatechol violet)$_2$ $^{2-}$ in the pH range of 4–7. The working range is linear up to 50 μg L^{-1} (Sonmez, Divrikli & Elci, 2010).

1.10 Aim of This Work

The determination of heavy metal ions in the aquatic environment is of tremendous interest, because clean water will become rare in the future, not only in countries with a hot climate. Copper, cadmium, zinc, nickel and lead are heavy metals which are, on the one hand, essential for life but on the other, highly toxic to

organism, e.g. certain algae, fungi, and many bacteria or viruses. Although it was thought that these metals are harmless to man, infant liver damage is connected to a high concentration of heavy metal in drinking water. With spectrophotometry, electroanalytical chemistry, chromatography and radioactive analysis, many new and modified techniques that can be used to determine metal ions in real samples have been studied.

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry or atomic emission spectrometry there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples.

Solid phase extraction (SPE) is of importance due to the advantages such as the shorter analysis time, the less solvent usage. SPE also allows the achievement of high recoveries for metal ions. SPE can be interfaced on-line with analytical techniques, such as liquid chromatography or atomic absorption spectrometry. Thus, its application for preconcentration of trace metals from different samples is very convenient.

Because of the importance of the selection of the sorbent in SPE technique, one of the aims of this study is firstly to develop new chemically bound sorbents and then to examine the use of these sorbents for the preconcentration and separation by SPE of some metal ions in several analytical matrix. For this:

Firstly, poly(styrene-divinylbenzene), sulphonated styrene-divinylbenzene copolymer and styrene-polyester polymer will be synthesized using HIPE method. The obtained polymers are characterized by FTIR and Scanning Electron Microscopy (SEM).

Secondly, 5,10,15,20-tetrakis (hydroxyl phenyl) porphyrin (THPP) and pyrocatechol violet (PCV) will be loaded on poly(styrene-divinylbenzene) and sulphonated styrene-divinylbenzene copolymer and were characterized by FTIR.

Finally, all prepared sorbents are used to preconcentrate metals such as Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) in aqueous solutions and to compare the efficiencies of sorbents against metals. The determination of metal concentration will be carried out using flame atomic absorption spectrometer (FAAS).

CHAPTER TWO

MATERIAL AND METHOD

2.1 Apparatus

Concentrations of complexing agents were detected with an UV-1601 model Schimadzu spectrophotometer with background corrector. Barnstead/Lab-line shaker were used for batch sorption metals. All pH measurements were performed on a P-Selectra 2001 model digital pH meter. Polyethylene column (Varian cartridge (CA, USA), $0.7 \, cm \times 10.0 \, cm$, $20 \, \mu m$ polypropylene frits and Alltech model vacuum manifold were used for column studies.

2.1.1 Fourier Transform Infrared (FTIR)

FTIR spectra were recorded with Perkin Elmer Spectrum (Minnesota, MN, USA) BX Fourier Transform IR spectrometer using KBr discs in the range 4000-400 cm^{-1} at a resolution of 4 cm^{-1} and 24 scan. Sample as 1 mg was mixed with about 100 mg of dried potassium bromide powder (Merck) using an agate mortar. The mixture was then pressed into pellets under pressure. The pellet was investigated by FTIR.

2.1.2 Scanning Electron Microscope (SEM)

The structures of polymeric sorbents were investigated by scanning electron microscopy (SEM) using a JEOL JSM-6060 microscope with gold coating at an acceleration voltage of 20 kV.

2.1.3 Flame Atomic Absorption Spectrometer (FAAS)

Metal concentrations were determinated using Perkin Elmer AAnalyst 700 model flame atomic absorption spectrometer with deuterium background correction. The

radiation sources were hollow cathode lamps. The instrumental conditions were selected as suggested by manufacturer and given in Table 2.1. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal.

Table 2.1 Instrumental parameters for metal determination by FAAS

Element	Wavelength (nm)	Slitwidth (nm)	Lamp current (mA)
Ni(II)	341.5	0.2	30
Cu(II)	324.8	0.7	30
Cd(II)	228.8	0.7	15
Zn(II)	213.9	0.7	25
Pb (II)	283.3	0.7	10

2.2 Reagents and Solutions

Divinylbenzene, styrene, polyester (80 % vinyl chloride, 5 % vinyl acetate, 15 % hydroxypropyl acrylate), sorbitan monooleate (span 80) for polymerization process, pH 10 buffer solution (boric acid/potassium chloride/sodium hydroxide and pyrrolidine/acetic acid) and pH 8 buffer solution (boric acid/sodium hydroxide/hydrogen chloride), sulfuric acid (95-98 % extra pure) were supplied from Merck or Fluka.

0.10 % reactive reagent solution was prepared by dissolving suitable amount of pyrocatechol violet (PCV) / 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (THPP) (Sigma-Aldrich) in 250 mL of ethanol (Riedel-de Haën).

Standard stock metal solutions (100 mg L^{-1}) were prepared by dissolving the required amount of $NiCl_2$, $CuSO_4.5H_2O$, $ZnCl_2$, $CdCl_2.H_2O$ and $Pb(NO_3)_2$ salts (Merck) in deionized water and working solutions were freshly prepared by dilution of the stock solutions.

All other reagents and solvents used were of analytical grade. The materials and vessels used for trace analysis were kept in 4 M nitric acid solution for at least 24 h

and subsequently rinsed four times with deionized water. Hydrochloric and nitric acids used were suprapur from Merck. Water was distilled and de-ionized with a Milli-Q system.

2.3 Synthesis of Polymeric Sorbents

Poly(styrene-divinylbenzene), sulfonated styrene-divinylbenzene copolymer and styrene-polyester polymers were synthesized using HIPE method for sorption of metal ions.

2.3.1 Synthesis of Poly(styrene-divinylbenzene)

40 mL of aqueous phase were added in 10 mL of organic phase drop by drop and they were mixed in polyethylene bottle for about 30 minutes and polymerized for 3 h at 60º C. Then, the obtained polymer was washed with isopropanol and dried for 24 h at 60º C.

Organic phase: 56 % styrene
26 % divinylbenzene
18 % span 80
Aqueous phase: 0.5 g of potassium peroxodisulfate
40 mL of deionized water

2.3.2 Synthesis of Sulfonated Styrene-Divinylbenzene Copolymer

40 mL of aqueous phase were added in 10 mL of organic phase drop by drop and they were mixed in polyethylene bottle for 30 minutes and polymerized for 5 h at 60º C. Then, the obtained polymer was washed with isopropanol and dried 24 h at 60º C.

Organic phase: 56 % styrene
26 % divinylbenzene
18 % span 80

Aqueous phase: 0.5 g potassium peroxodisulfate

2 mL of 2.5 M H_2SO_4 solution

38 mL of deionized water

2.3.3 Synthesis of Styrene-Polyester Polymer

While 10 mL of organic phase was stirring at 40-50º C, 40 mL of aqueous phase were added drop by drop and they were reacted in polyethylene bottle for 3 h at 40-50º C and polymerized for 5 h at 60º C. Then, the obtained polymer was washed 24 h in soxhlet apparatus with ethanol and water.

Organic phase: 56 % polyester (80 % vinyl chloride, 5 % vinyl acetate,

15 % hydroxypropyl acrylate)

26 % styrene

18 % span 80

Polyester solution was prepared dissolving 100 mg of polyester in 3 mL of tetrahydrofuran and 100 mL of toluene.

Aqueous phase: 0.5 g of potassium peroxodisulfate

1.082 g of NaCl

40 mL of deionized water

2.4 Preparation of Sorbents Loaded with Reactive Reagents

A 1 g of Str/DVB or sulphonated Str/DVB was refluxed with 0.1% THPP / PCV ethanolic solution for 24 h at room temperature. The impregnated sorbents were separated through a porous filter on a vacuum pump. The impregnated sorbents were washed with water and were dried under vacuum. The amount of reactive agent on the organic phase was determined by UV spectrophotometer at 419.5 nm for THPP and 297 nm for PCV, respectively. Also, the reagents were stripped from the sorbent with pure ethanol to verify the mass balance. The amounts of attached THPP onto Str/DVB and sulphonated Str/DVB were found to be 0.2840 mmol g^{-1} and 0.2993

mmol g^{-1} polymers, respectively. The amounts of PCV onto Str/DVB and sulphonated Str/DVB were found to be 0.5716 mmol g^{-1} and 0.4384 mmol g^{-1} polymers, respectively.

2.5 Procedure for the Sorption of Metals on Column

Loaded sorbent as 0.025 g was firstly wetted with 5 mL methanol and stirred for 10 min, then 5 mL of doubly distilled water was added and stirred for 10 min again. Lastly, the mixture was transferred to the polyethylene column and 5 mL of methanol:water (10:90) was passed through the column. A sample solution (10 mL) containing 20 µg of metal ion was taken at optimum pH and passed through the column at a flow rate of 1.0 mL min^{-1}. Then, the loaded column was washed with 10 mL of deionized water. Finally, stripping was carried out by different concentration of HNO$_3$ solution for eluting. The concentration of metal ion in stripping solution was analyzed by flame AAS. The dilution with deionized water was made before aspiration, if necessary in the case of concentrated elutes. All runs were carried out at ambient temperature (23–25 °C). All studies were replicated two times.

2.6 Procedure for the Sorption of Metals by Batch Technique

25 milligrams of loaded sorbent was equilibrated with a sample solution containing 20 µg metal ion in a volume of 10 mL in a 50 mL well-stopped reagent bottles at 200 rpm for 60 min using a mechanical shaker, under optimized conditions. The impregnated resin containing metal ions were filtered and then metal ions were desorbed as given in column method and were determined by flame AAS.

DISCUSSION

3.1 Characterization of Synthesized Polymers

FTIR spectra of poly(styrene-divinylbenzene) and sulphonated styrene-divinylbenzene copolymer was shown in Figure 3.1. The bands were summarized as 3434 cm^{-1} water absorption band; 3022 cm^{-1} aromatic C–H stretching; 2922 and 2851 cm^{-1} aliphatic C–H stretching; 1601, 1491 and 1451 cm^{-1} aromatic C=C stretching; 904 cm^{-1} aromatic C–H in-plane bending; 834, 759 and 699 cm^{-1} aromatic out-plane bending. After sulphonation, resin swell in polar solvents which indicate the presence of hydrophilic groups (–SO$_3$H) (Oliveira, Aguiar, Aguiar & Santa Maira, 2005). FTIR spectrum of Str/DVB was different from FTIR spectrum of sulphonated Str/DVB.   On sulphonated polymer, the asymmetric and symmetric streching vibrations of S=O at 1250-1160 cm^{-1}, 1080-1000 cm^{-1}, respectively and symmetric streching vibrations of OH group at 3436 cm^{-1} were observed.
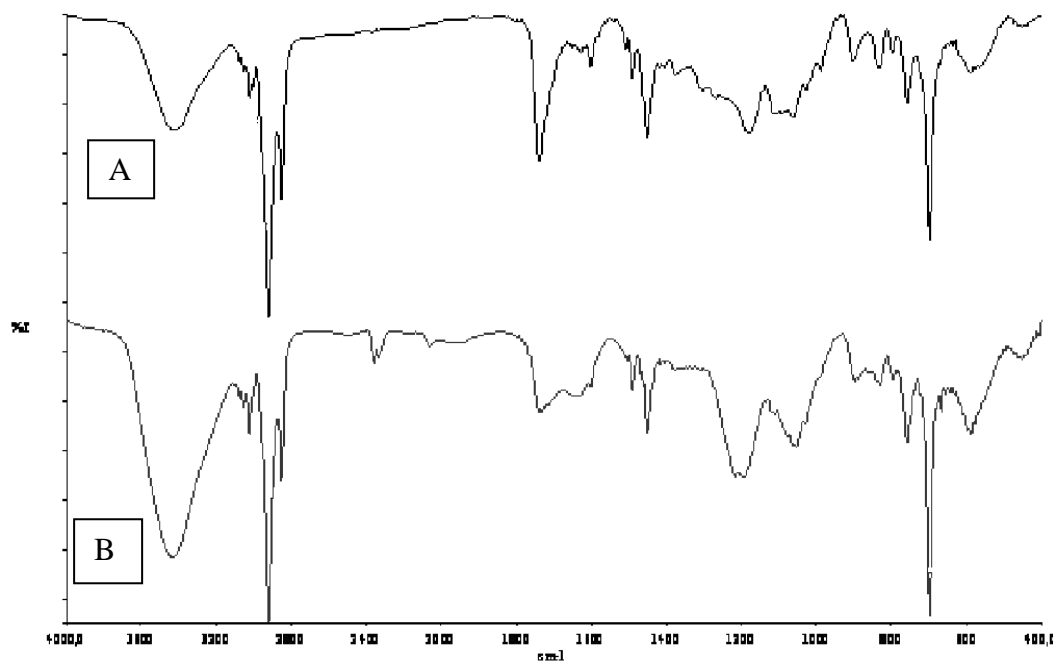

Figure 3.1 FTIR spectra of Str/DVB (A) and sulphonated Str/DVB (B).

The infrared spectrum of polyester-styrene polymer was compared with starting material, polyester (Figure 3.2). The peaks around 3061-3025 cm^{-1} and 2920-2850 cm^{-1} belong to stretching vibration of aromatic and aliphatic C–H groups, respectively. The bands between 1601 and 1436 cm^{-1} assigned to ring vibration of benzene rings, which also contain contribution due to bending observed at 906, 839, 756 and 709 cm^{-1}, assigned to out of plane ring C–H bending vibrations. The band at 1733 cm^{-1} shows the presence of Ø–C=O–OR group.
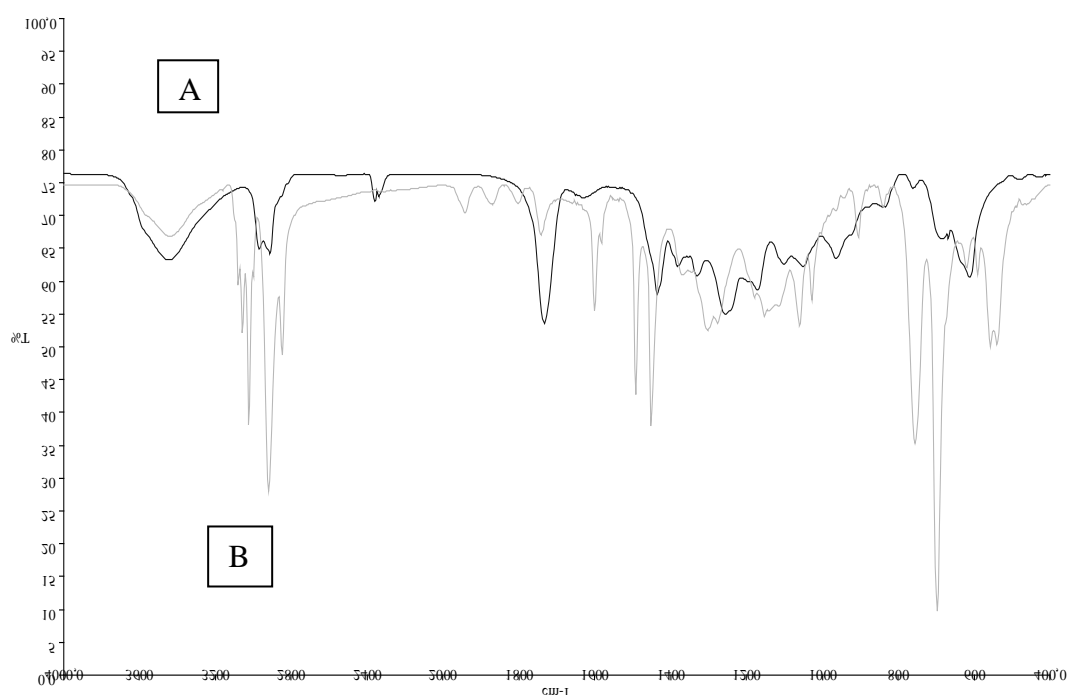

Figure 3.2. FTIR spectra of polyester (A) and polyester-styrene (B)

SEM micrographs of poly(Str/DVB), sulphonated Str/DVB copolymer and polyester-styrene polymer were shown in Figures 3.3 - 3.5. It is a typical polyHIPE structure consisting of voids and connecting pores (Dizge, Keskinler & Tanrıseven, 2009). As seen in the SEM image of sulphonated Str/DVB, porosity and pore diameter were higher than poly(Str/DVB). Polyester-styrene has equal microsphere structure.
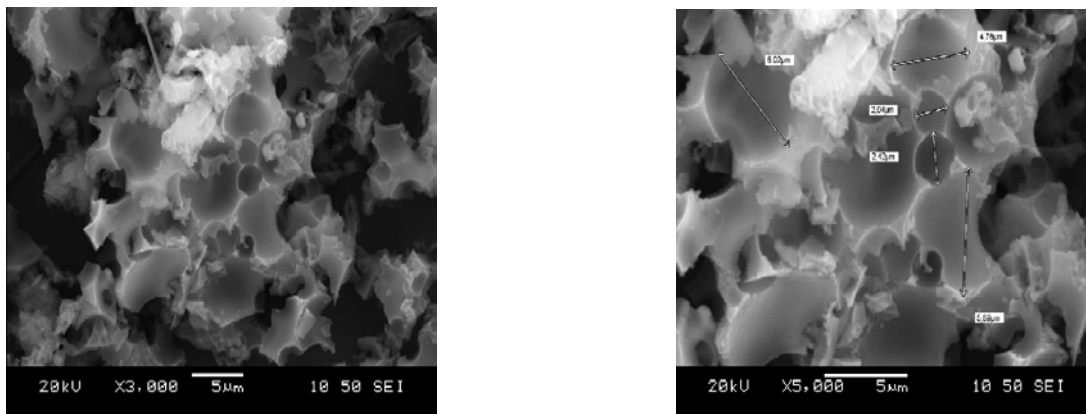
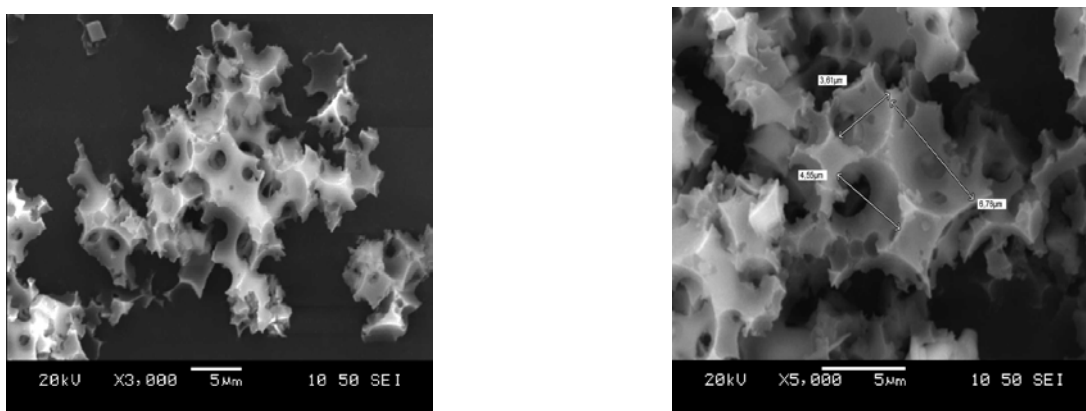Figure 3.3 SEM micrographs of poly(Str/DVB). (size 5 µm, magnifications are 3000x and 5000x)

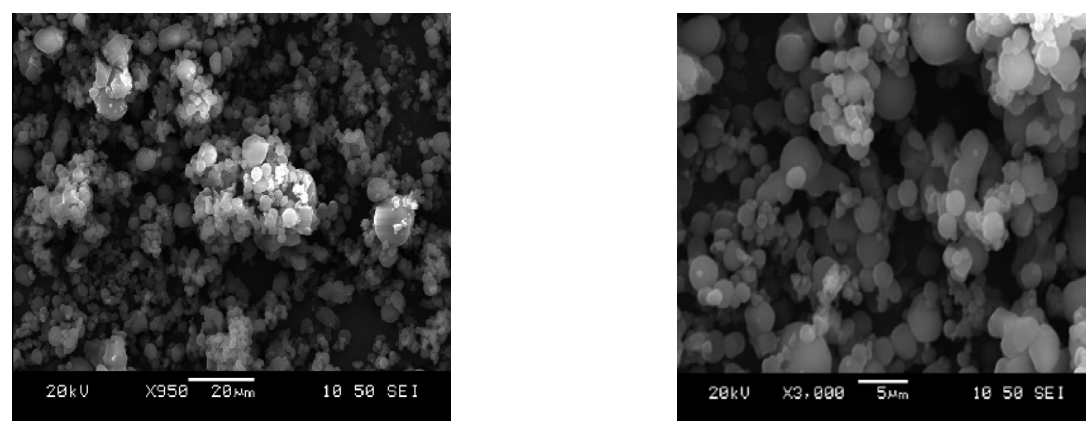Figure 3.4 SEM micrographs of sulphonated Str/DVB copolymer. (size 5 µm, magnifications are 3000x and 5000x)

Figure.3.5 SEM photographs of styrene-polyester polymer. (sizes are 5 and 20 µm, magnifications are 950x and 3000x)

3.2 Characterization of Sorbents Loaded with Chelating Agents

3.2.1 By THPP

The FT-IR spectra of THPP and THPP loaded resins (poly(Str/DVB) and sulphonated Str/DVB) were illustrated in Figure 3.6. The basic FT-IR peaks seen in the spectrum of THPP are: 804 cm^{-1} for γ C–H$_{pyrrol}$, 1169 cm^{-1} for δ C–H$_{pyrrol}$, 1232 cm^{-1} for ν C–O–H, 1345 cm^{-1} for ν C–N, 1435 cm^{-1} for ν C=N, 1502 cm^{-1} and 1585 cm^{-1} for ν C=C$_{pyrrol}$, 3187 cm^{-1} for ν N–H. In the FTIR spectra of poly(Str/DVB) and sulphonated Str/DVB loaded with THPP, the extra bands which belong to THPP given above were seen. THPP has indole N–H band at 2800-3600 cm^{-1}. Because of interrupting O–H stretching vibration at 3400-3600 cm^{-1} N–H band didn't observed sharply.
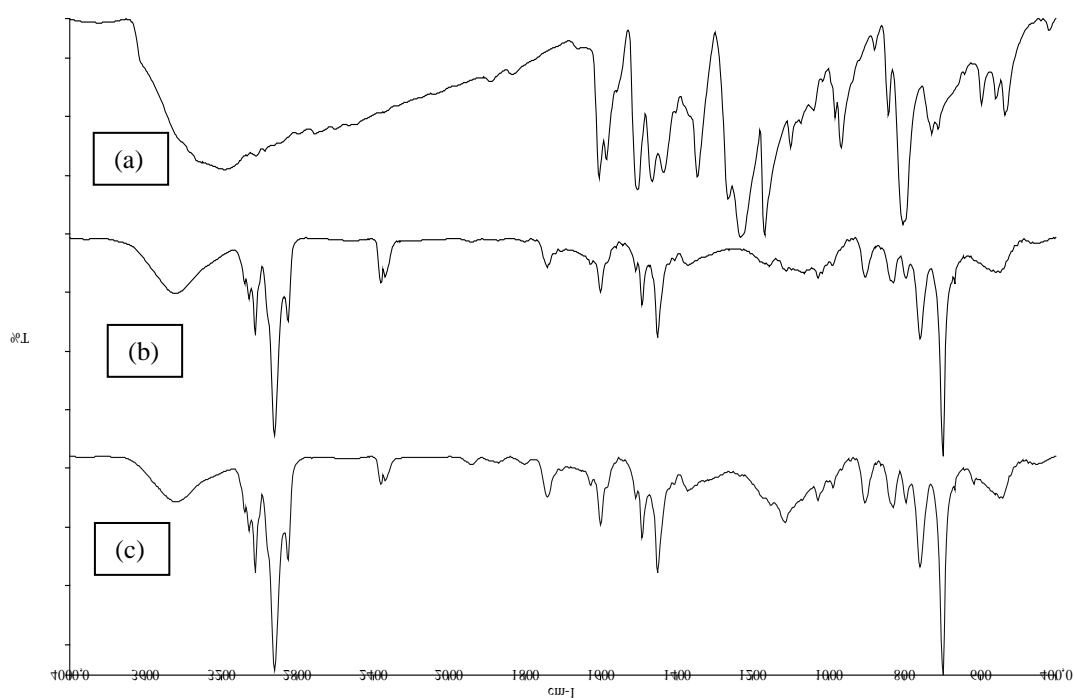

Figure 3.6 FTIR spectra of THPP (a), poly(Str/DVB) (b) and sulphonated Str/DVB (c) loaded with THPP

3.2.2 By PCV

For characterization, FT-IR bands of PCV and PCV loaded resins (poly(Str/DVB) and sulphonated Str/DVB) were given in Figure 3.7. The basic FT-IR peaks seen in the spectrum of PCV are: 1719 cm^{-1} for C=O, 1583 cm^{-1} for –N=N– , 1370 cm^{-1} for –C–OH, 1158 cm^{-1} for –S–O–, 1120 cm^{-1} for –C–N. In the FTIR spectra of poly(Str/DVB) and sulphonated Str/DVB loaded with PCV, the given peaks above were seen.
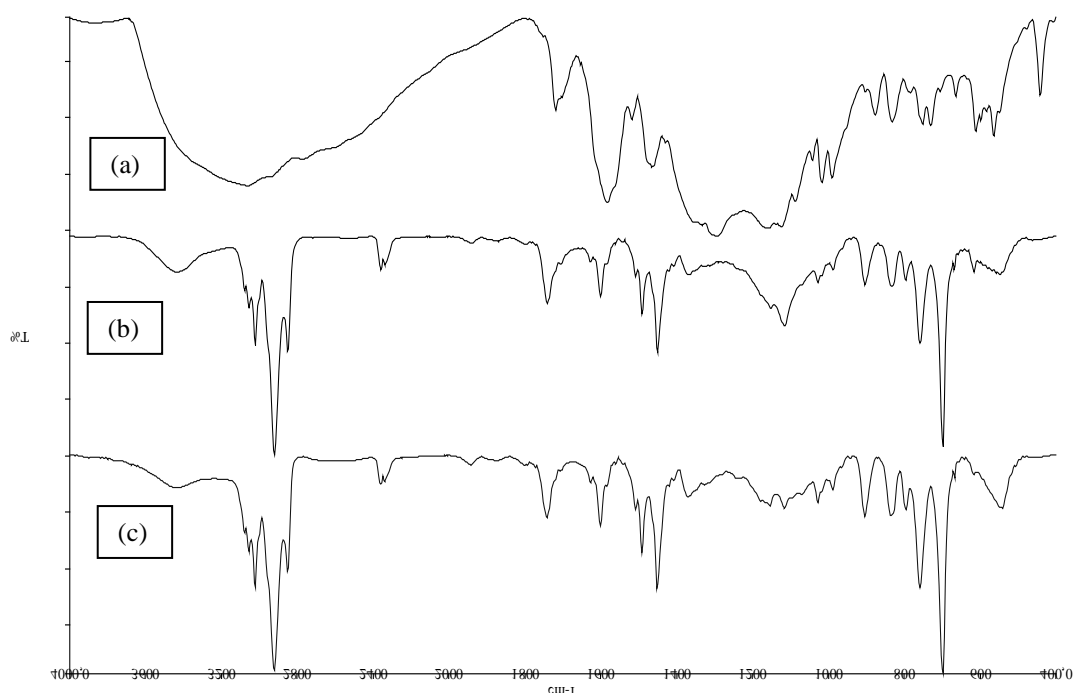

Figure 3.7 FTIR spectra of PCV (a), poly(Str/DVB) (b) and sulphonated Str/DVB (c) loaded with PCV

3.3 Sorption of Metal Ions

pH is the main parameter for the metal ion sorption onto the complexation-ligand modified resin. Mainly at low pH values, the metal ion-ligand complexes are unstable because of the protonation of some functional groups onto the chelating ligands. Also, at low pHs, removal of toxic metal ions from some aqueous medium is not feasible consuming high amount of acidic reagents.

A polypropylene column was packed with 25.0 mg of the synthesized polymers. A 10 mL solution containing 2.0 µg mL^{-1} of Pb(II), CdII), Ni(II), Cu(II), Zn(II), was passed through a column with a flow rate of 1.0 mL min^{-1} and the effect of pH on sorption of metal solutions was investigated in the pH interval of 1-7. The amount of Pb(II), Cd(II), Ni(II), Cu(II) and Zn(II) left in the solution after sorption and desorption were determined by FAAS.

On poly(Str/DVB), Ni(II) ion was not sorbed within pH range 1 to 7. The sorption levels of other studied ions were lower in high acidity medium. At moderate acidity, the percentages of sorption of Cu(II), Cd(II), Zn(II) and Pb(II) ions were varied from 30% to 50% as given in Figure 3.8. The sulfonated Str/DVB sorbent exhibited similar sorption behaviour as poly(Str/DVB) for studied metal ions. Only sorption of Cu(II) ion was slightly higher as given in Figure 3.9. Unfortunately, polyester-styrene showed no attraction to copper, zinc, cadmium, nickel and lead. As a consequence, it could be summarized that the synthesized polymers have less trend for the sorption of studied metal ions.
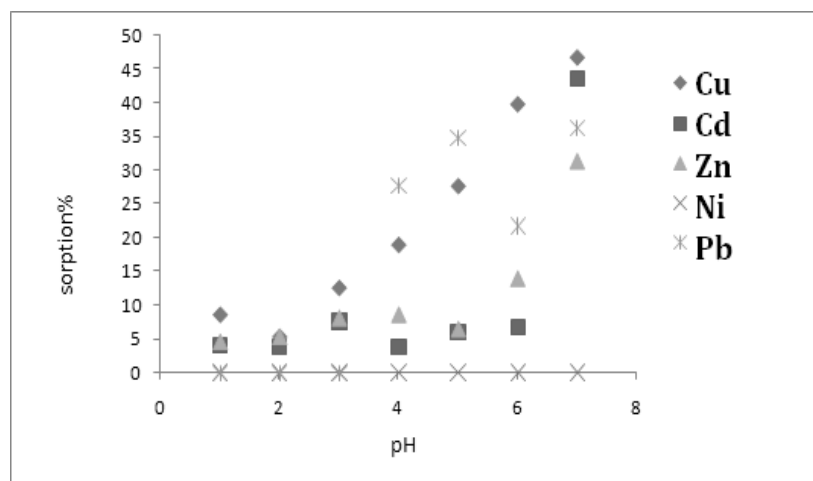

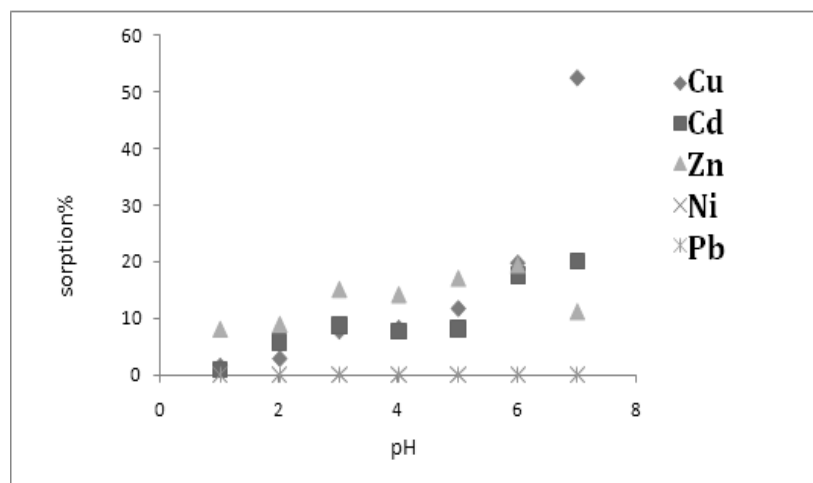Figure 3.8 Metal sorption onto poly(Str/DVB) as a function of pH

Figure 3.9 Metal sorption onto sulphonated Str/DVB as a function of pH

High sorption of metals can be accomplished by loading chelating agents physically or chemically onto sorbents such as inorganic sorbents or organic sorbents. Pyrocatechol violet and porphyrin as chelating agents have been used in removal, separation and preconcentration of metals in various analytical matrices. Therefore, in this study these ligands were loaded physically onto polymeric resins. In sorption studies, the optimum pH for each metal-complex was selected depending on the literature data (Narin, Soylak, Elci & Dogan, 2000; Buke, Divrikli, Soylak & Elci, 2009; Yang, Li, Shi & Wang, 2005; Yang, Yan & Lin, 2004). Only, for Zn-PCV comlex the sorption was controlled at pH 2, 4 and 6 (Table 3.1). Its sorption was very low, but within the studied pH, pH 6 was preferred for further study. The studied pH was 8 for Cd(II)-PCV, Ni(II)-PCV and Pb(II)-PCV and 7 for Cu(II)-PCV (Narin, Soylak, Elci & Dogan, 2000; Buke, Divrikli, Soylak & Elci, 2009). In the studies for THPP, the applied pH for metal complexation was preferred as 10 (Yang, Li, Shi & Wang, 2005; Yang, Yan & Lin, 2004). As shown in Table 3.2, the tendencies of sorbents towards metal ions with THPP were much higher than for PCV ones except lead. The sorption capacities of studied sorbents prepared using PCV were very low as given in literature. Much less concentrations of metals have been sorbed by polymeric resins loaded with PCV. The results obtained with this ligand was in unison with studies done before. The sorption degree of all metals except cadmium was around 100 % with polymeric resins loaded with chelating agent, THPP.

To control precision of sorption studies, 2 µg mL^{-1} of metal ion was loaded onto prepared resins for five paralel run. The obtanied results were given in Table 3.3. The presicion as relative standard deviation (RSD%) was in range of 0.02 to 5.12 %. It could be concluded that the precision was good.

To determine sorption capacities of sulphonated Str/DVB-THPP for Cu, Cd, Ni, Zn and Pb, 10 mL of 15 µg mL^{-1} solution of metal ion was mixed with 0.025 g of sorbent applying batch technique given in Section 2.6. The sorption capacities of sulphonated Str/DVB-THPP for Cu(II), Ni(II), Zn(II) and Pb(II) were found as 4965, 4865, 4370, 4990 µg g^{-1} sorbent, respectively.

The sorption abilities of poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP resins for low concentrations of studied metal ions such as 0.05, 0.2 and 0.5 µg mL^{-1} were also studied. The sorption and recovery of all metal ions with these two loaded polymeric resin was accompolished successfully.

Only for Cu(II)-poly(Str/DVB)-THPP complex, linear working range was studied and the linearity was obtained from 0.02 and 5 µg Cu(II) mL^{-1}.

Table 3.1 Sorption percentage of Zn-PCV complex at different pH

Resins	Sorption (%)		
	pH		
	2	4	6
Str/DVB-PCV	7.9	9.45	14.0
Sulphonated Str/DVB-PCV	10.4	16.18	23.46

Table 3.2 Sorption percentage of polymeric resins loaded with chelating agents for studied metal ions

Resins	Sorption (%)				
	Cu(II)	Cd(II)	Ni(II)	Zn(II)	Pb(II)
For PCV					
Str/DVB	36.5	34.1	5.8	14.5	69.4
Sulphonated Str/DVB	40.5	12.9	6.8	25.3	72.42
For THPP					
Str/DVB	96.3	66.7	91.7	97.6	98.4
Sulphonated Str/DVB	95.3	85.9	97.3	97.6	99.3

Table 3.3 Repeatability of sorption studies for 2 μg mL^{-1} of metal ion (n=5)

Resins	RSD(%)				
	Cu(II)	Cd(II)	Ni(II)	Zn(II)	Pb(II)
For PCV					
Str/DVB	0.92	0.25	0.97	4.38	0.02
Sulphonated Str/DVB	0.84	0.87	2.77	5.12	0.02
For THPP					
Str/DVB	1.33	3.61	1.67	0.48	0.02
Sulphonated Str/DVB	1.39	2.17	1.55	0.52	0.02

3.4 Desorption Studies

In order to determine the stripping conditions of metal ions from the loaded polymers, a 10 mL sample solution containing 20 μg of metal ion at predicted pH was passed through the column at 1 mL min^{-1} flow rate. In order to recover quantitatively sorbed metal ion from loaded sorbents, nitric acid concentration was varied from approximately 0.1 mol L^{-1} to 4 mol L^{-1}. Elution studies were only done for THPP loaded polymeric resins for all studied metal ions except lead. The

elements could be recovered quantitatively by passing 2 mL of HNO_3 solution through the loaded column as seen from Figures 3.10-3.14. Desorption percentage of lead with all loaded polymeric resin was 80 % using 1 – 4 mol L^{-1} nitric acid. Cadmium was eluted using 2 mol L^{-1} HNO_3 as 80 % and 50 % from sulphonated Str/DVB-THPP and poly(Str/DVB)-THPP, respectively. For desorption of copper, 2 mol L^{-1} HNO_3 was suitable, recovery percentages were 75 % and 95 % for poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP, respectively. Nickel was desorbed by 2 mol L^{-1} HNO_3 as 82 % for poly(Str/DVB)-THPP and 42 % for sulphonated Str/DVB-THPP. Finally, elution of zinc was found as 99 % or sulphonated Str/DVB-THPP and 85 % for poly(Str/DVB)-THPP with 4 mol L^{-1} HNO_3.
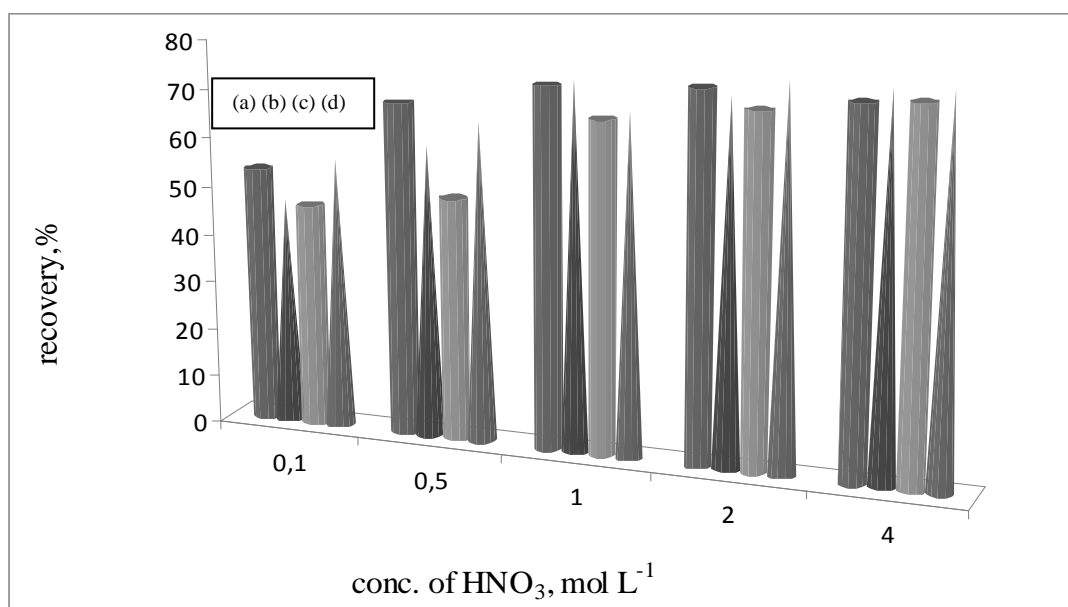

Figure 3.10 Effect of concentration of eluent for desorption of Pb from poly(Str/DVB)-PCV (a), sulphonated Str/DVB-PCV (b), poly(Str/DVB)-THPP (c), sulphonated Str/DVB-THPP (d)
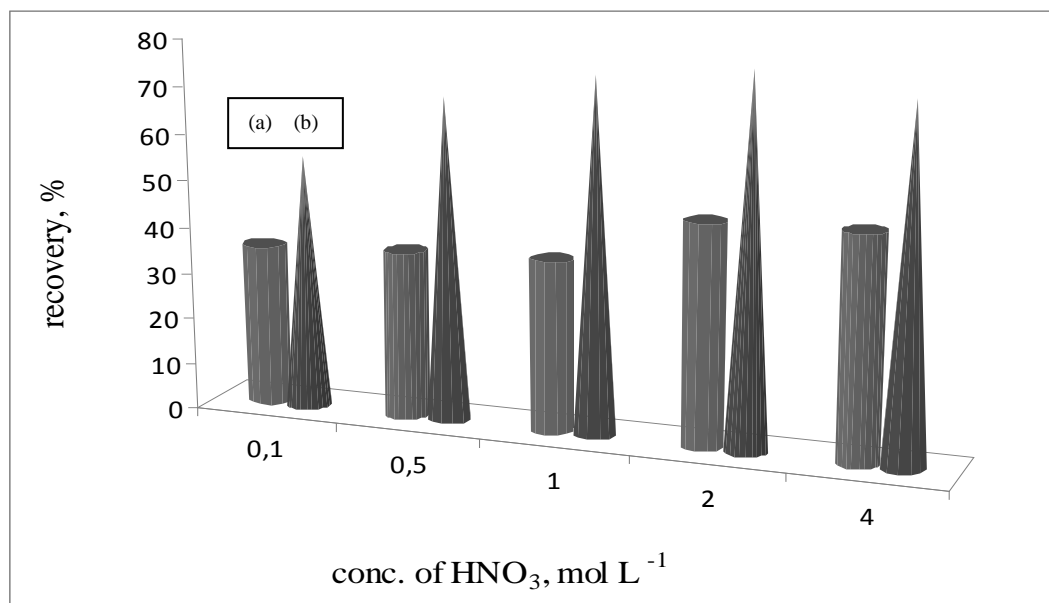
Figure 3.11 Effect of concentration of eluent for desorption of Cd from poly(Str/DVB)-THPP (a), sulphonated Str/DVB-THPP (b)
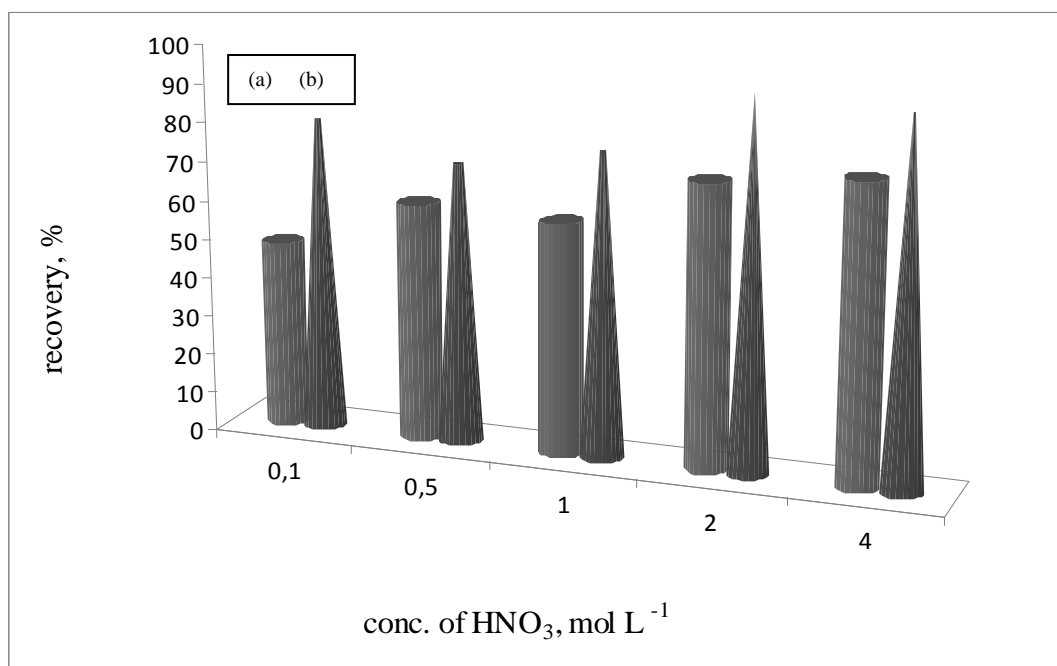

Figure 3.12 Effect of concentration of eluent for desorption of Cu from poly(Str/DVB)-THPP (a), sulphonated Str/DVB-THPP (b)
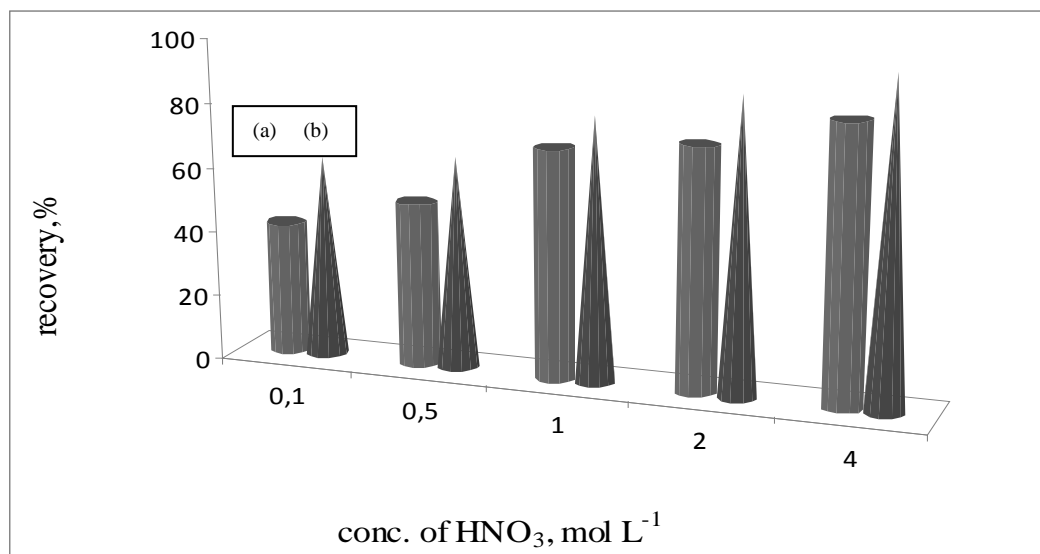
Figure 3.13 Effect of concentration of eluent for desorption of Zn from poly(Str/DVB)-THPP (a), sulphonated Str/DVB-THPP (b)
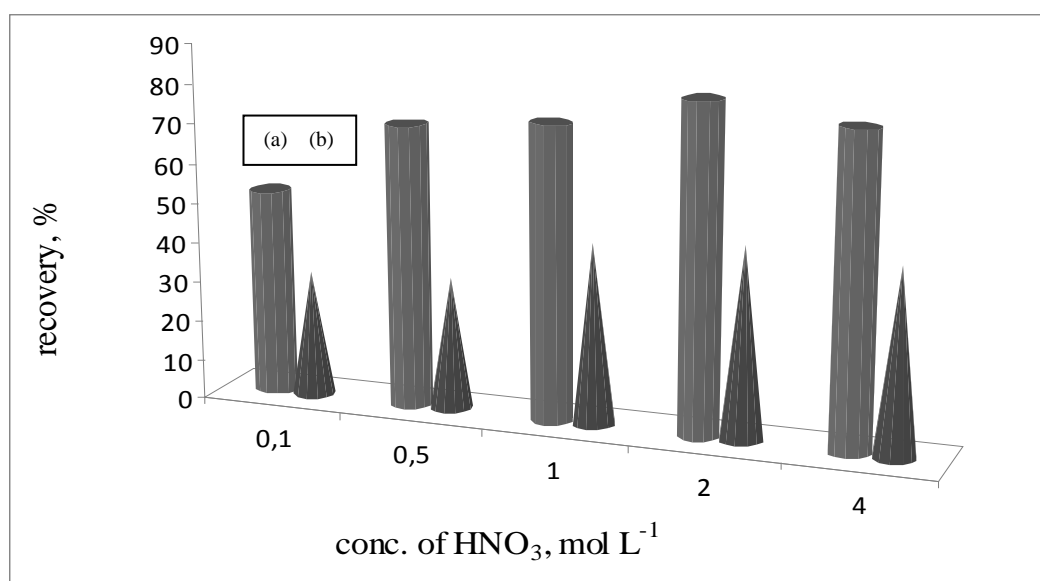

Figure 3.14 Effect of concentration of eluent for desorption of Ni from poly(Str/DVB)-THPP (a), sulphonated Str/DVB-THPP (b)

CHAPTER FOUR

CONCLUSIONS

One of the aim of this work was to develop polymer based sorbents and their characterization by FT-IR and SEM analysis. Then the tendencies of sorbents towards metal ion were checked to evaluate the progressed sorbents for sorption of metal ions.

For this; poly(styrene-divinylbenzene), sulphonated styrene-divinylbenzene copolymer and polyester-styrene polymers were synthesized by high internal phase emulsion method. Chelating agents as tetra hydroxy phenyl porphyrin and pyrocatechol violet were impregnated onto these polymers. By FTIR, and SEM analysis, the resulting polymers were characterized. The amounts of attached THPP onto poly(Str/DVB) and sulphonated Str/DVB were calculated as 0.2840 and 0.2993 mmol g^{-1} polymer, respectively. The amount of PCV onto poly(Str/DVB) and sulphonated Str/DVB were calculated as 0.5716 and 0.4384 mmol g^{-1} polymer, respectively.

The loaded and unloaded polymers were used for detecting their sorption abilities towards metal ions. Polyester-styrene had no tendency to metal ions. The other unloaded polymers sorbed Pb(II), Cu(II), Cd(II), Ni(II) and Zn(II) ion at pH 4 - 7 moderately. When the sorption capacities of loaded polymers were compared, polymers loaded with THPP have much tendency towards metal ions. Besides sorption process, desorption of metal ios were studied. Using nitric acid, successful desorption was achieved by increasing its concentration. Using 2 or 4 mol L^{-1} HNO_3, quantitative recovery of Cu, Pb, Cd, Ni and Zn from poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP was accompolished. The repeatabilities of sorption and desorption process were assigned as good. The sorption capacities of poly(Str/DVB)-THPP and sulphonated Str/DVB-THPP for Cu(II), Ni(II), Zn(II) and Pb(II) were found as around 5000 µg g^{-1} sorbent. The linear range of THPP-poly(Str/DVB) for

Cu(II) ion was between 0.02 and 5 µg mL^{-1}. At low concentrations, THPP loaded polymers had capabilities for sorption of all studied metal ions.

The THPP loaded poly(Str/DVB) and sulphonated Str/DVB resins was successfully used for selective extraction of copper, cadmium, zinc, nickel and lead from aqueous solutions. These sorbents provide sufficient sorption capabilities of >8 µg metal ion g^{-1} sorbent at given pH. The sorbents loaded with THPP can be used for separation and preconcentration of the studied metal ions in aqueous solutions.

For further studies, linear ranges of other ions with THPP loaded polymers can be studied. The progressed polymers loaded with THPP can be used to show their applicability to real samples for studied metal ions.

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