İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPERATION OF NEW POLYMERIC SORBENTS FOR REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

M.Sc. Thesis by

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Programme: Polymer Science and Technology

JANUARY 2005

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Date of submission : 27 December 2004

Date of defence examination: 26 January 2005

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JANUARY 2005

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SULU ÇÖZELTİLERDEN AĞIR METAL İYONLARININ AYRILMASI İÇİN YENİ POLİMERİK SORBENTLERİN HAZIRLANMASI

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Tezin Enstitüye Verildiği Tarih : 27 Aralık 2004
Tezin Savunulduğu Tarih : 26 Ocak 2005

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OCAK 2005

ACKNOWLEDGEMENT

This master study has been carried out at Istanbul Technical University, Chemistry Departmentof Science & Letter Faculty.

First of all, I would like to express my gratitude my supervisor Assos.Prof.Dr. B.Filiz Şenkal and Prof.Dr. Niyazi Bıçak for sharing their deep knowledge, experience and continuous encouragement throughout my research.

I also would like to thank to my colleagues Bünyamin Karagöz and Mustfa Gazi for their helpfull attitude during my labaratory works.

Finally, I would like to dedicate this thesis to my parents Reşit and Nermin Yavuz, my wife Gülşen Altay. I owe much to my family for all their self-sacrifice, patience and support during all my education.

Ocak 2005 Erdem Yavuz

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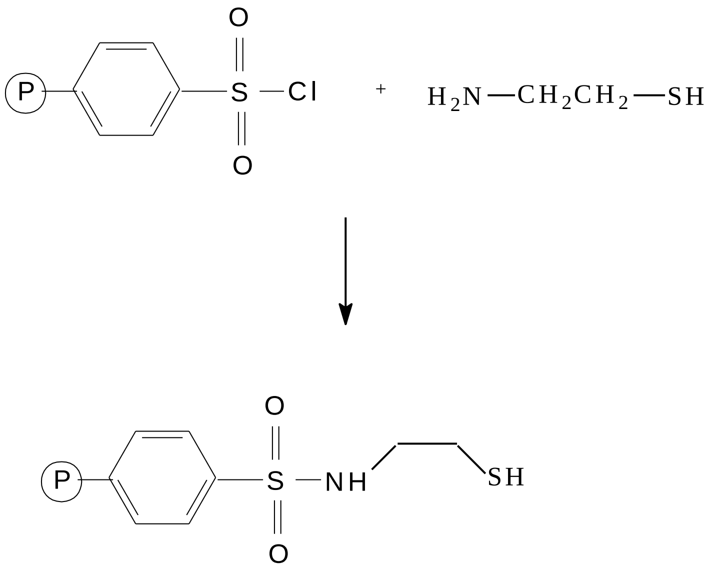
PREPERATION OF NEW POLYMERIC SORBENTS FOR REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

SUMMARY

In this thesis, four types' polymeric sorbents were prepared for removal of heavy metal ions from aqueous solutions.
These resins were called resin 1, resin 2, resin 3 and resin 4 respectively. Resin 1 and Resin 2 were prepared starting from chlorosulfonated polystyrene resin.

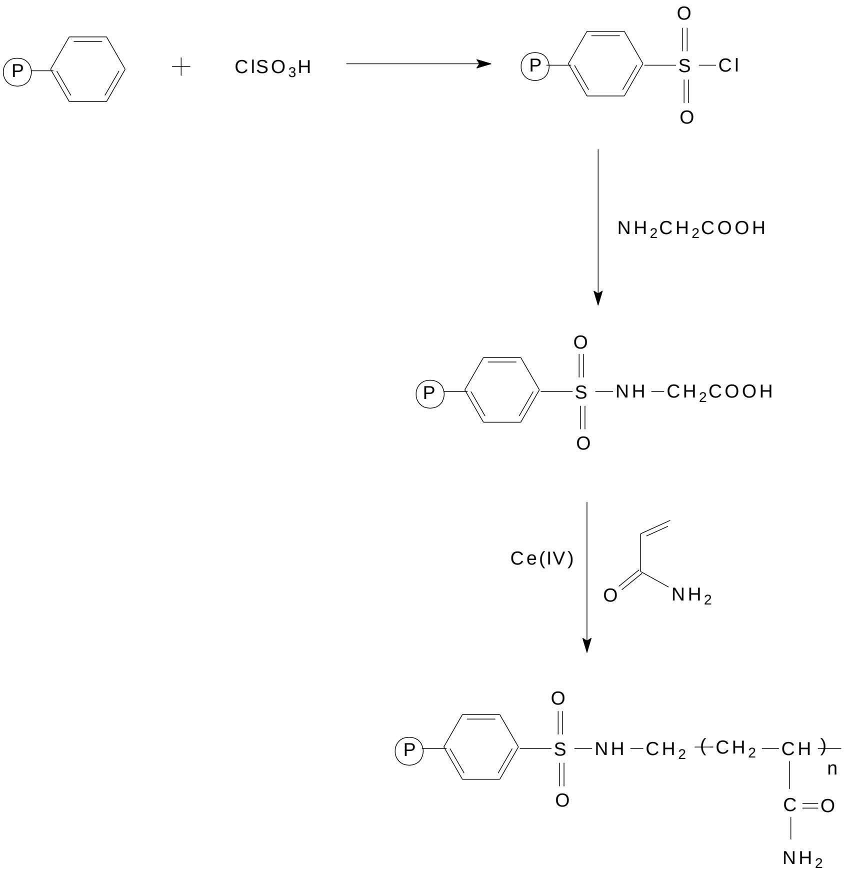
Resin 1: Chlorosulfonated polystyrene resin was reacted with excess of cystamin in NMP (N-methyl pyrrolidone).



(1)

At the end of the reaction, thiol containing resin was obtained and this resin was used to remove Heavy metal ions such as Hg (II), Cd (II), Zn(II) and Fe (III) successfully from aqueous solutions. The heavy metal loading capacities of the resin was found as Hg (II): 2.9 $mmol.g^{-1}$, Cd (II): 1.85 $mmol.g^{-1}$, Pb (II):1.30 $mmol.g^{-1}$, Zn (II): 0.30 $mmol.g^{-1}$, Fe (III): 2.00 $mmol.g^{-1}$.

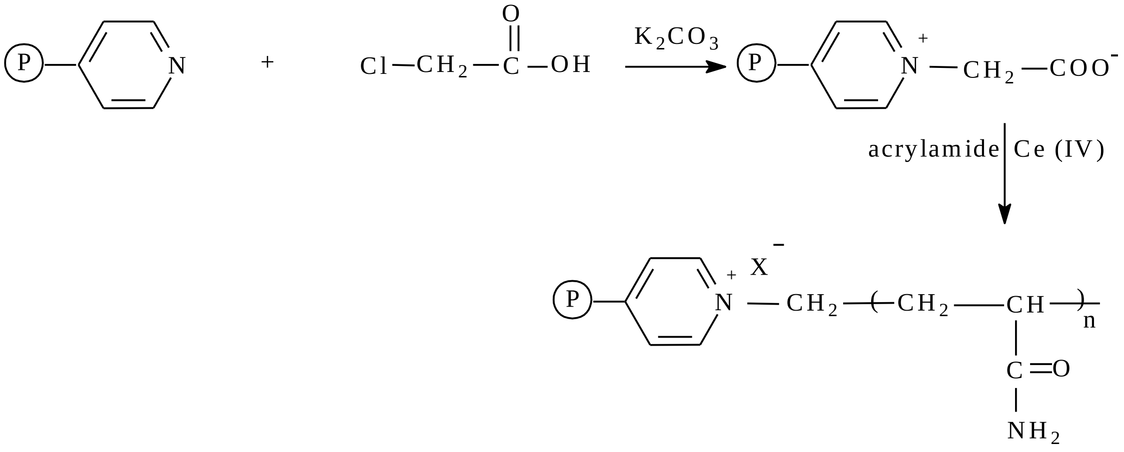
Resin 2 : Poly (acrylamide) was grafted from carboxylic acid groups onto cross linked poly (styrene) beads using a redox polymerization methodology. A beaded polymer with a poly(acrylamide) surface shell was prepared in three steps, starting from poly (styrene- divinyl benzene) (PS-DVB) (10% crosslinking) based beads with a particle size of 420-590µm, according to the synthetic protocol; chlorosulfonation, sulfamidation with glycine and grafting using a concentrated aqueous acrylamide solution with cerium ammonium nitrate.



(2)

The resulting polymer resin with 220 wt % of grafted poly (acrylamide) has been demonstrated to be an efficient mercury-specific sorbent, able to remove Hg (II) from solutions at ppm levels.The mobility of the graft chains provides nearly homogenous reactions conditions and rapid mercury binding ability. The mercury sorption capacity under non-buffered conditions is around 5,75 mmol/g. No interference arises from common metal ions such as Cd(II), Fe(II), Zn(II), and Pb(II).

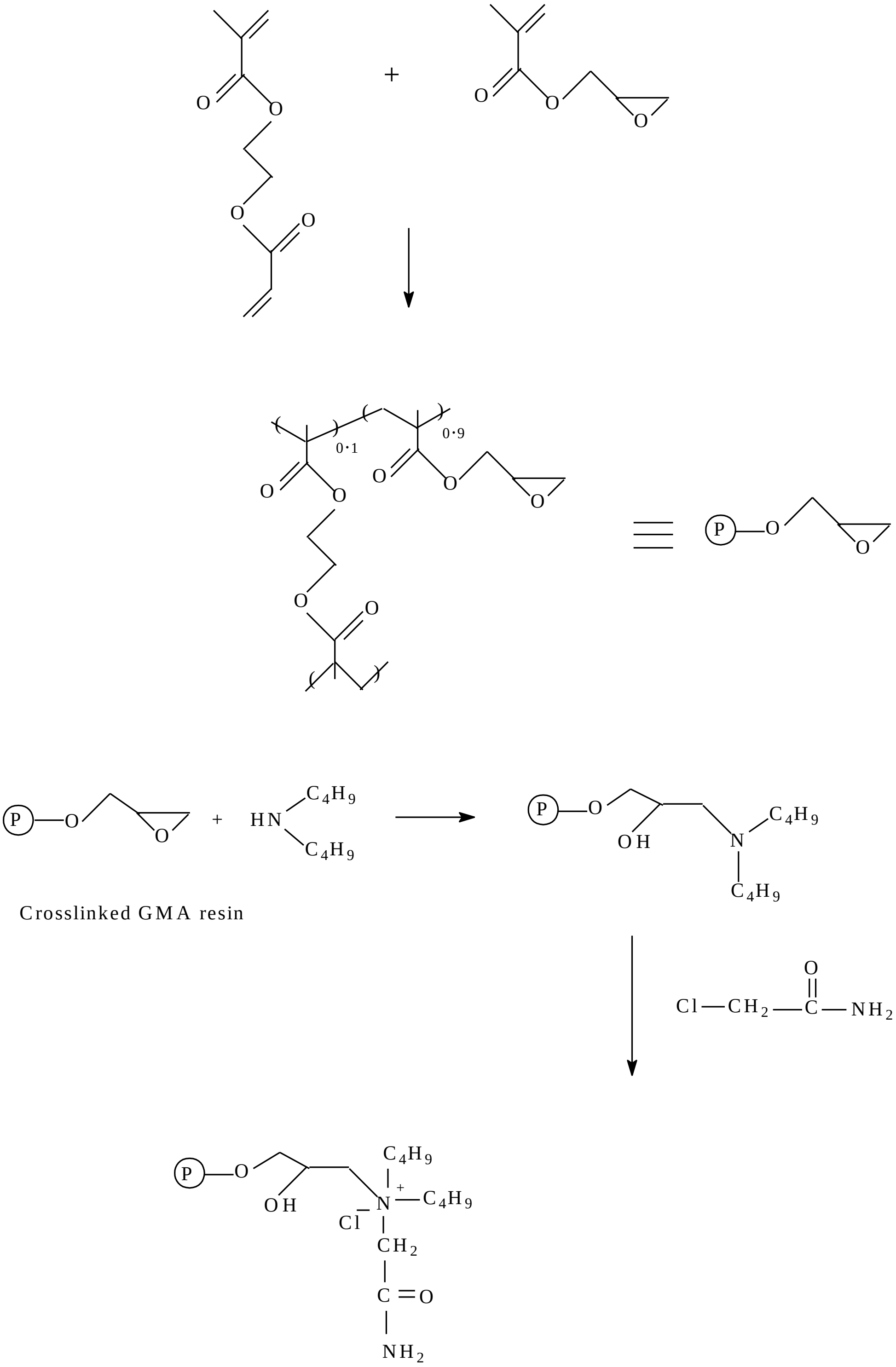
Resin 3 : Poly(acrylamide) is grafted onto crosslinked poly (4-vinyl pyridine)(P4-VP) resin “Reillex 425”. Quaternization of (P4-VP) with potassium chloroacetate gave crosslinked poly (4-vinyl pyridine) having carboxymethyl pyridinium groups.
Acrylamide was grafted by redox initiation through the carboxyl groups with cerium ammonium nitrate.
The resulting polymer resin with 111.7 wt % of Poly (acrylamide) grafts is a high capacity (3.36 mmol g^{-1}) mercury specific sorbent.
Experiments showed that some foreign ions such as Zn (II), Pb (II), Fe (III) and Cd (II) are not sorbed by the resin in the same reaction conditions.



X : Cl^- or OH^-

(3)

Resin 4: A mercury specific polymer sorbent was prepared from crosslinked copolymer of glycidyl methacrylate (GMA) (0.9 mol) with ethylene glycol dimethacrylate (EGDMA) (0.1 mol). Its two steps modification through epoxy functions by treating with dibutylamine and subsequent reaction with chloroacetamide. The resulting polymer resin with 2.5 $mmol.g^{-1}$ chloroacetamide density is effective in selective mercury extraction from aqueous solutions. The mercury sorption capacity under non-buffered conditions is around 2.4 $mmol.g^{-1}$. Presence of Cd(II), Pb(II), Zn(II) and Fe(III) does not affect the mercury uptake.



Crosslinked GMA resin
0·1
0·9
P
HN
C_4H_9
OH
N
$Cl-CH_2-C(=O)-NH_2$
Cl^-
N^+
CH_2
C=O
NH_2

(4)

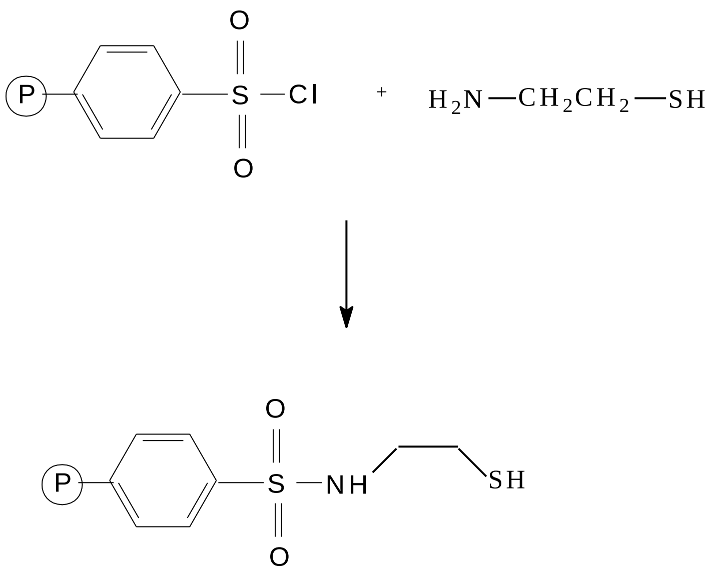
Regeneration of the resins:

Resin 2, Resin 3 and Resin 4 have amide groups. The sorbed mercury in these resins can be eluted by repeated treatment with hot acetic acid without hydrolysis of the amide groups. Resin 1 can be regenerated by using mineral acids such as HCl and HNO_3 , because thiol groups and sulfonamide groups are not hydrolysis easily. Also, mercury uptake kinetic measurement studies for these resins were performed.

SULU ÇÖZELTİLERDEN AĞIR METAL İYONLARININ AYRILMASI İÇİN YENİ POLİMERİK SORBENTLERİN HAZIRLANMASI

ÖZET :

Bu tezde ağır metal iyonlarını sulu çözeltilerden giderilmesi için dört çeşit poimerik sorbent hazırlandı.
Bu reçinelar sırasıyla reçine 1, reçine 2, reçine 3 ve reçine 4 olarak isimlendirilmiştir. Reçine 1 ve reçine 2 klorosulfolanmış polistirenden hareketle hazırlanmıştır. Reçinelerin hazırlanma metodu aşağıda verilmiştir:**Reçin 1 :** Klorosulfolanmış polistiren reçine sisteamin'in fazlasıyla NMP varlığında reaksiyona sokulmuştur.

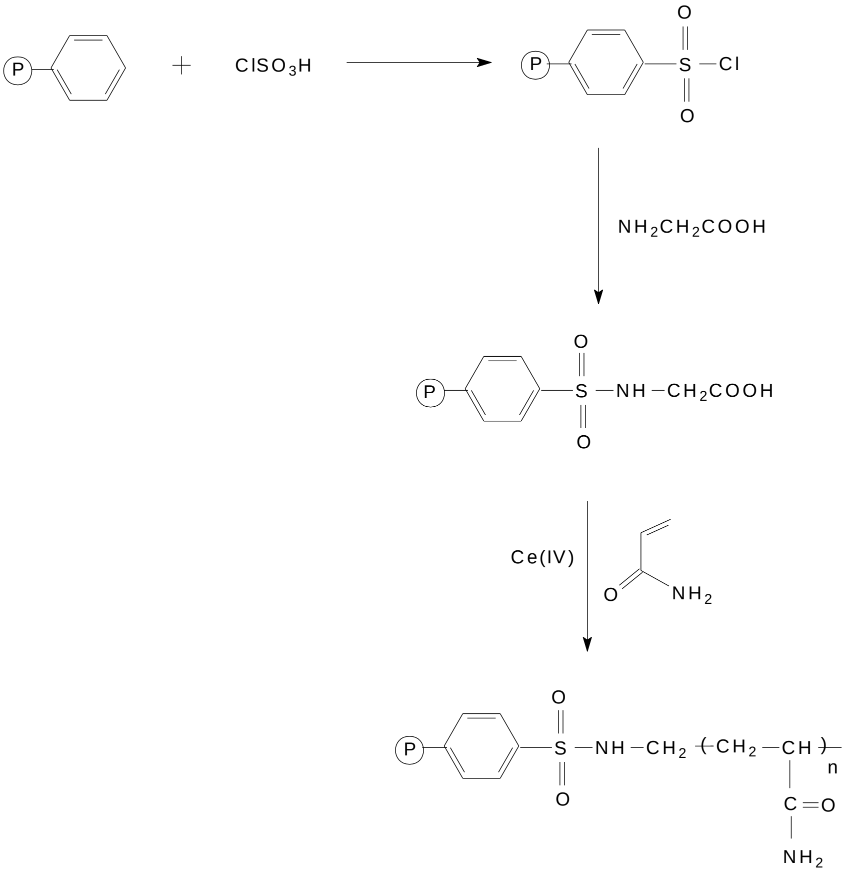


(1)

Reaksiyon sonunda tiol içeren reçine elde edilmiştir ve bu reçine Hg (II), Cd (II), Pb (II), Zn (II) ve Fe (III) gibi ağır metal iyonlarının sulu çözeltilerden giderilmesinde başarıyla kullanılmıştır. Reçinelerin ağır metal yükleme kapasiteleri Hg (II): 2.9 mmol.g^{-1}, Cd (II): 1.85 mmol.g^{-1}, Pb (II):1.30 mmol.g^{-1}, Zn (II): 0.30 mmol.g^{-1}, Fe (III): 2.00 mmol.g^{-1} olarak bulunmuştur.

Reçine 2 : Poli (akrilamid) Çapraz bağlı poli (stiren) kürecikler üzerine karboksilik asit gruplarından bir redoks polimerizasyon yöntemi kullanılarak graft edilmiştir. Poliakrilamid bağlı kürecik şekilli polimer 420-590μm partikül boyutlu poli (stiren-divinil benzen) (PS-DVB) (10% crosslinking) reçinelerden başlanarak aşağıdaki protokole göre üç basamakta hazırlanmıştır; klorosulfonlama, glisin ile sulfoamidleşme ve seryum amonyum nitrat içeren konsantre sulu akrilamid çözeltisi ile graft.

Elde edilen, ağırlıkça 220 % graft derecesindeki, poli (akrilamid)'in civayı çözeltilerden ppm derecesinde uzaklaştırmak için efektif bir civa-selektif sorbent olduğu gösterilmiştir. Graft zincirlerin hareketliliği homojen reaksiyon koşulları ve hızlı civa yükleme kabiliyeti kazandırmıştır. Tamponsuz koşullarda civa yükleme kapasitesi yaklaşık 5.75 mmol / g.reçine'dir.



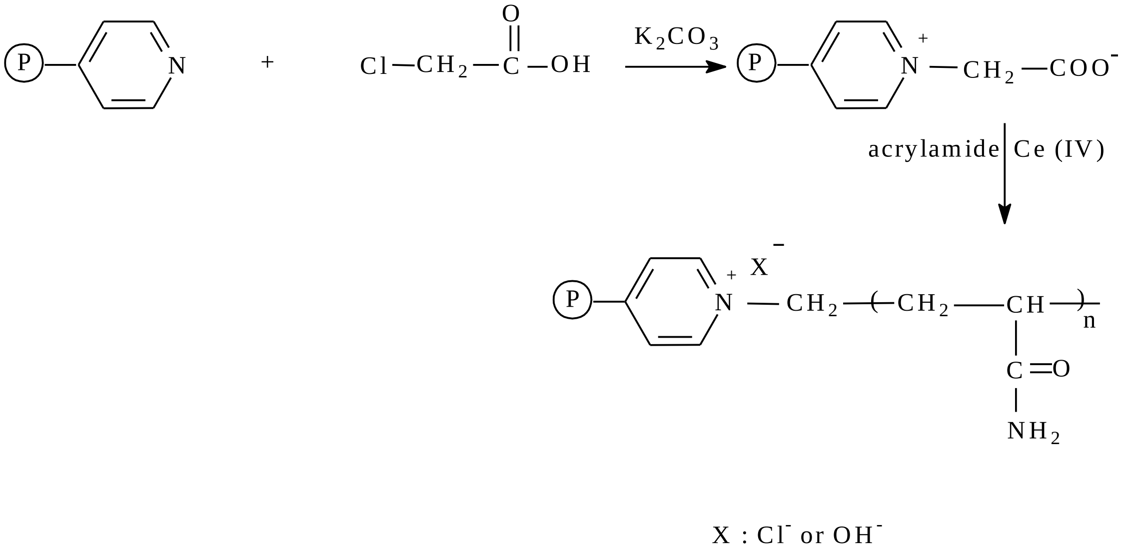
(2)

Reçine 3 : Poli (akrilamid) çapraz bağlı poli (4-vinil piridin)(P4-VP) reçine 'Reillex 425' üzerine graft edilmiştir. Potasyum kloroasetat ile quaternerleşme karboksimetil piridinyum içeren poli (4-vinil piridin) vermiştir.

Akrilamid, redoks ile karboksil gruplarından seryum amonyum nitrat kullanılarak graft edilmiştir.

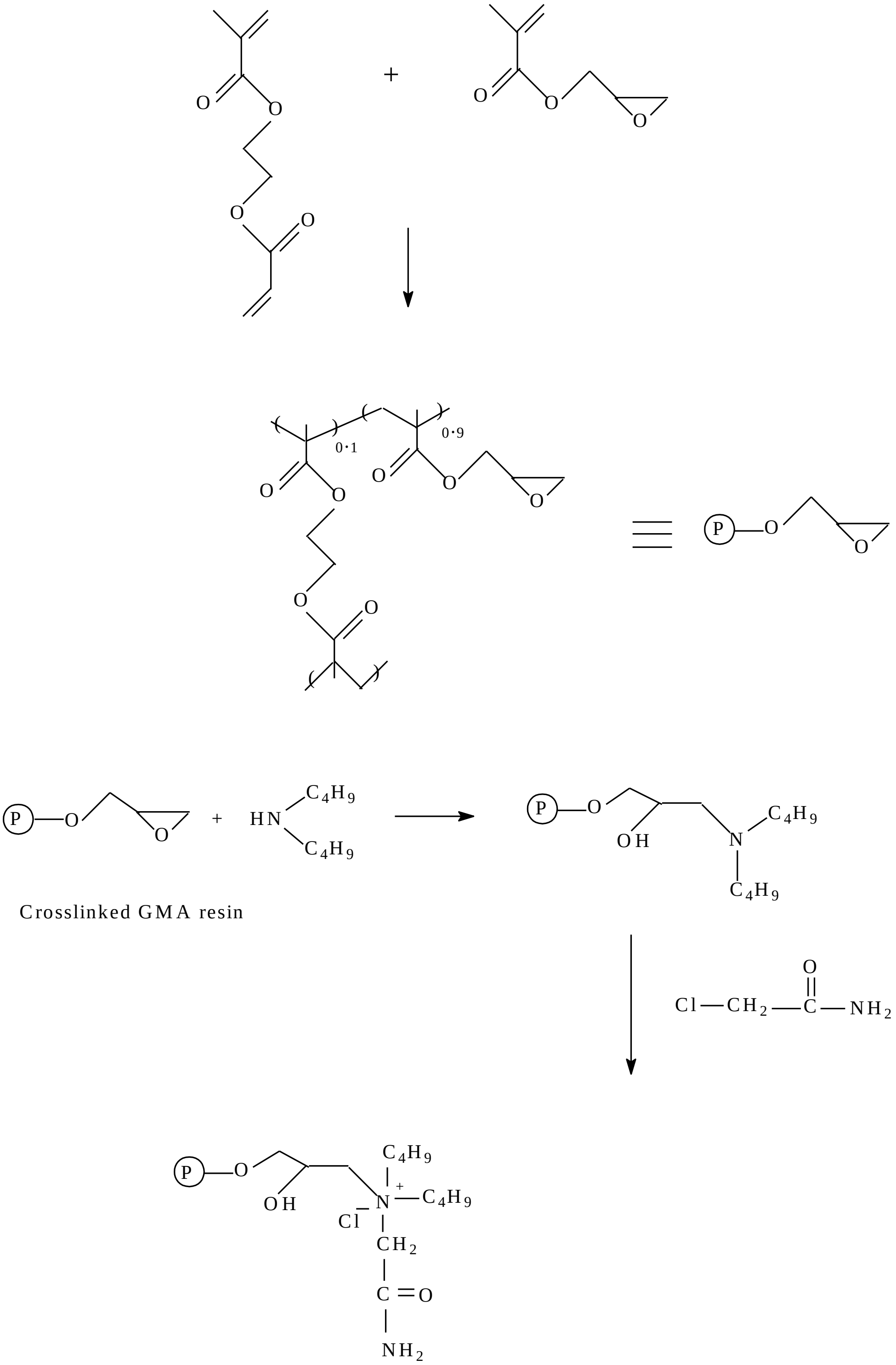
Elde edilen, ağırlıkça 117 % graft derecesindeki, polimer yüksek kapasiteli (3.36 mmol / g.) bir civa spesifik sorbentir.

Zn (II), Pb (II), Fe (III) ve Cd (II) gibi bazı yabancı iyonların aynı koşullarda reçine tarafından tercih edilmediği deneylerle gösterilmiştir.



(3)

Reçine 4 : Civa spesifik sorbent çapraz bağlı glisidil metakrilat (GMA) (0.9 mol) ile etilen glikol dimetakrilat (EGDMA) (0.1 mol) kopolimerinden hazırlanmıştır. Epoksi fonksiyonuna yönelik iki modifikasyon basamağı dibutiamin ve takiben klorasetamidle reaksiyondur. Ele geçen 2.5 mmol / g. klorasetamid yoğunluğuna sahip reçine sulu çözeltilerden civa ekstraksiyonu için efektiftir. Tamponsuz koşullarda civa civa yükleme kapasitesi 2.4 mmol.g^{-1}. Cd (II), Pb (II), Zn (II) ve Fe (III)'ün varlığı civa yüklemeyi etkilemez.


+
0·1
0·9
P
O
HN
C4H9
OH
N
Crosslinked GMA resin
Cl—CH2—C—NH2
Cl−
N+
CH2
C=O
NH2

(4)

Reçinelerin Rejenerasyonu :

Reçine 2, reçine 3 ve reçine 4 amid grubuna sahiptirler. Bu reçinelerdeki yüklü civa amid grubu hidroliz olmaksızın tekrarlanan sıcak asetik asit etkileşimleriyle geri kazanılmıştır. Tiol ve sulfonamid grupları kolay hidroliz olmadığından Resin 1 HCl ve HNO_3 gibi mineral asitlerle rejenere edilmiştir. Ayrıca bu reçineler için civa yükleme kinetik ölçümleri gerçekleştirilmiştir.

1. INTRODUCTION

It is increasingly recognized that, when polymers are used as supports for catalysts or organic reagents, the reactivity and selectivity of supported catalysts or reagents may be seriously changed by so-called ‘polymer effects’, the origins of which may be physical (viscous diffusion effects, steric effects, site separation effects, local concentration effects, etc) or chemical (microenvironmental interactions, coordination unsaturation,etc). Some examples of these effects have been published [1-4].

It is then no longer possible to depict the polymer support as a simple letter P surrounded by a circle, as has so often been done before. It is also no longer possible to consider the rigid and inert material like a stone cast into the liquid reaction medium. The support interacts with the surrounding medium. It may or may not swell, depending on its thermodynamic affinity with the medium and its method of synthesis. It may selectively absorb one of the reactants or products, as a result of preferential solvation. This may arise for thermodynamic reasons or because steric restriction is experienced in the micropores.

Styrene-based polymers remain by far the most widely used supports, possibly because they are commercially available, as the basis of ion exchange resins, and because they have been used by the pioneers in the field of Merrifield polypeptise synthesis.

2. THEORITICAL PART

2.1 Properties and characterization of functionalized polymers

There are a number of considerations in the choice of the functional polymers to be used in a specific application functionalized polymer must posses a structure which permits adequate of reagent in the reactive sites. This depends on the extent of swelling compatibility the effective pore size, pore volume (porosity) and the chemical, thermal and mechanical stability of the resins under the conditions of a particular chemical reaction on reaction sequence. This in turn depends on the degree of the crosslinking of the resin and the conditions employed during its preparation.

We studied crosslinking polymers in this thesis. The use of crosslinked polymers in chemical applications is associated with some advantages, such as the following.

1-) Since they are in soluble in our solvents, they offer the greatest is of processing.
2-) They can be prepared in the form of spherical beads and can be separated from low molecular weight contamined by simple filtration and washing with very use solvents.
3-) Polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents.
4-) More highly crosslinked resins may be prepared with very porose structures which allow solvents and reagents to penetrate inside of the beads to contact reactive groups.
The following is a classification of the types of crosslinked polymers which are most frequently encouraged with enhanced properties.

a) microporose pore gel-type resins are generally prepared by suspension polymerization using a mixture of vinyl monomer and small amounts(less tan %10 ; in most cases less than % 0.5 - % 2) of a crosslinking agent containing no additional solvent.

Swellable polymers are found to offer advantage over non-swellable polymers of particular interest is their lower fragility, lower sensitivity

b) Macropores and macroreticular resins

The mechanical requirements in industrial applications force the use of higher crosslinking densities for preparing density with enhanced properties. Macropores and macroreticular resins are also prepared by suspension polymerization using higher amounts of crosslinking agents but with the inclusion of an inert solvent as diluents for the monomer phase.

Macroreticular resin is non-swelling and a macro pores a rigid material with a high crosslinking it retains its overall shapes and volume when the precipitate is removed.

To sudden shock and their potential to achieve a higher leading capacity during functionalization however, a degree in crosslinking density will increase swelling but will also result in soft gels which generally have low mechanical stability and readily in fragment even under careful handling. Gels with lower density of crosslinking are difficult to filter and under sever conditions can degrade to produce soluble linear fragments in addition gel type resins that are likely crosslinked may suffer considerable mechanical damage as a result of rubit and extreme change in the nature of the solvating media and can not be subjected to study and high pressures. Macropores resins with less than % 1 crosslinking generally have low mechanical stability while macropores resins with more than % 8 crosslinking are mechanically stable but unfortunately give rise to acute.

2.2 Harms of Heavy Metal ions

Metal ions are non-biodegradable in nature, and their intake at a certain level are toxic [5]. Environmental contamination with metal ions is of growing public concern because of health risks posed by human and animal exposure. The separation of metal ion, present as contaminants in water, is complicated because of the number of variables that must be considered, including the solution composition, salinity, pH, temperature, and the presence of organic substances. It is well known, for example, that heavy metal ions such as Pb(II) and Hg(II), which are toxic to most organisms, have found their way into the water system from different processes [6].

Therefore, there is great interest in recovering metal ions for both environmental and economic reasons [7-8].
A serious problem encountered in the removal of the metal ions is that the target species are usually in low concentration and in complex mixtures. The innocuous ions, such as sodium and potassium, can saturate the extractants before they can effectively remove the toxic metal ions. Attempts to solve problems of removal of heavy metal ions have led to development and application of several techniques such as precipitation, adsorption, extraction and sorption or ion exchange [9-11].

With respect to the low concentrations and handling of large volumes of aqueous solution, extraction procedures are not economical, and precipitation procedures require the addition of relatively large amounts of chemicals, whereas applications of sorption or exchange on solids are preferable [12].

This makes the use of exchangers for selective separation of heavy metal ions very attractive. The ion exchange resins contain functional groups capable of complexing or ion exchanging with metal ions. Because interacting function group with the metal ions is covalently bound to an insoluble polymer, there is no loss of extractant into the aqueous phase. The chelating resins are ion-exchange-containing groups that are also able to complex metal ions.

The high metal ion selectivity of chelating exchangers is attributed not only to electrostatic forces but also to coordination bonds in metal chelating groups. The commercial resin Chelanine (Fluka), Bio-Rex-70, and Chelex 100 correspond to examples of ion-exchange resins that contain groups with a strong ability to bind heavy metal ions.

Their sorption mechanism is through chelation instead of simple ion exchange and, as a consequence, they should be much more selective than ion exchange resins. It has been also claimed that their selectivity is at least qualitatively in agreement with the complexation constants of similar chelating monomers with metal ions in aqueous solution, although this is true only very roughly.

Such adsorbents have a larger specific surface and very small diameter, thus ensuring high kinetic parameters. As a result, adsorption and concentration procedures become more convenient and easier.

2.3 Complexation of polymeric ligand and metal ion

The analytical applications of chelating polymer depend on many factors. Normally a metal ion exists in water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration must be replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and and/or donor atom capable of forming complexes with metal ions in solution and it is logical to classify chelating polymers on that basis.

This method of classification is not meant to imply that these systems are mutually exclusive. Indeed some polymers can belong to more than one class, depending on experimental conditions [13].

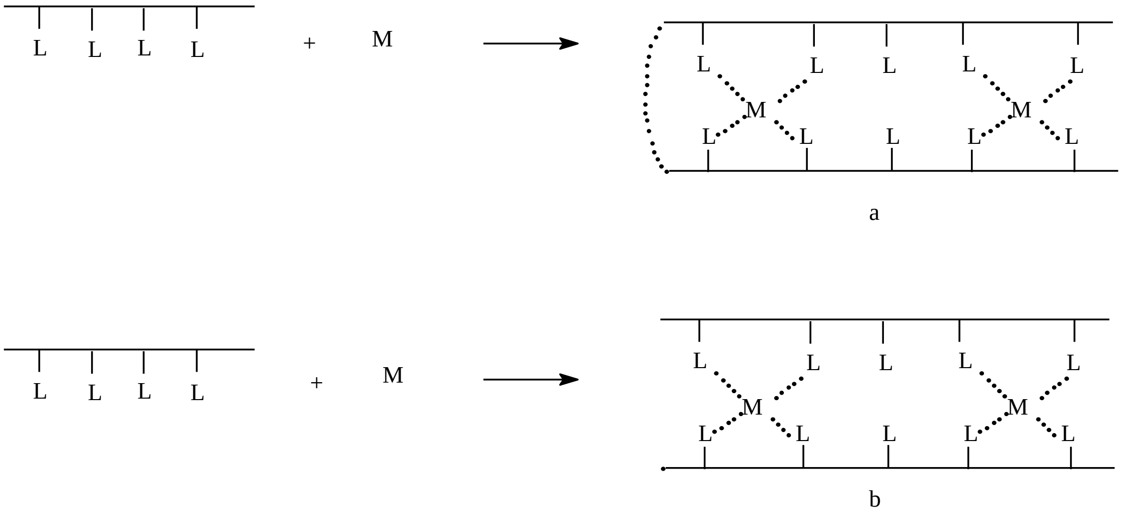
Among the many ligands [14] introduced 8-acryloyloxyquinoline is one of the recent origin.

This kind of polymer-metal complexes are prepared by the chemical reaction of a polymer, containing ligands with metal ions. Typical examples are listed table 2.

Generally, the reaction of a polymeric ligand with a metal ion or a stable metal complex, in which one coordination site remains vacant, results in different structures that can be grouped into pendant and inter/intra-molecular bridge polymer-metal complexes [15].

2.4 Inter/intra-molecular bridged polymer-metal complexes

When a polymer ligand is mixed directly with metal ion, which generally has four six coordinate bonding sites, the polymer-metal complex formed may be of the intra-polymer chelate type or inter polymer chelate type as shown in Scheme 2.1



L = Coordinating atom or group; M = Metal ion
a = intra−polychelate
b = inter−poychelate

Scheme 2.1 Inter/intra molecular bridged polymer-metal complexes

The coordination structure in this type of polymer-metal complex is not clear and it is often difficult to distinguish between inter/intra-molecular binding. Thus it is not easy to elucidate the polymer effect in studying the characteristics of the polymer-metal complexes. Intra-polymer metal complex is sometimes soluble, while inter-polymer metal complex results precipitation of the linear polymer-metal complexes as exemplified by poly (acrylic acid)-Cu(II) complex [16].

2.5 Some novel chelating Polymers

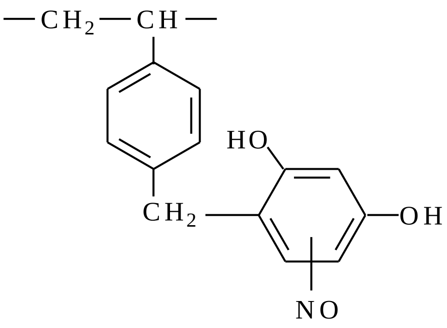
Among the earliest chelating resins to be studied were analogues of EDTA, Viz., Dowex A-1 Chelex-100 and Chelex-20,. These resins continue to be useful in a wide variety of systems. Some of the metals extracted from sea water and other systems with Chele-100 and Dowex A-1.

Kaczvinsky et al. [17] have described the synthesis of porous phenol-formaldehyde polymers containing iminodiacetic acid. The porosity was introduced by addition of a finely divided solid material (Template) that was insoluble under the reaction conditions and was removed by dissolution after the polymerization was complete. Silica gel, carbonates and various other salts were used as a templates. Resins containing different phenols were synthesized and their effectiveness for the removal of radioactive cesium and strontium from alkaline concentrated sodium salt solutions was examined.

A water-soluble poly(β-diketone)chelating resin has been prepared by the controlled oxidation of poly(vinyl alcohol) (PVA) with chromic acid. This polymer forms stable complexes with divalent and trivalent cations such as Co(II), Cu(II), Mn (II), Ni(II), Fe(I), Au(III) and UO_2 (II) and removes them completely from dilute aqueous solution. The ions may be recovered quantitatively from the resin complex by elution with dilute aqueous acid and it is claimed that the resin was reusable [18].

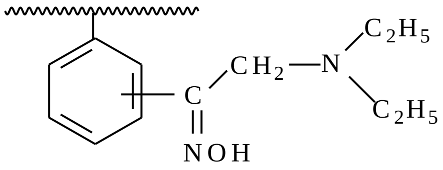
Nine poly(hydroxy anthraquinones and two poly(hydroxy napthaquinone)s have been screened to determine the greatest ability to accumulate uranium. 1,2-Dihydroxy anthroquinone(I) and 3-amino-1,2-dihydroxyathraquinone(II) have extremely high accumulation abilities, and to improve their adsorption characteristics have been immobilized by coupling with diazotized aminopolystyrene [19].

The immobilized 1,2-dihydroxyanthraquinone, had the most favorable features, such as high selectivity, rapid sorption rate, and applicability in both column and batch methods. A macroreticular polystyrene-base chelating resin nitrosoresorcinol(2.1) as a functional group was synthesized by Sugii and Ogawa [20]. The resin shows selectivity for Cu(II), Fe(II) and Co(II).



(2.1)

Sugii and Ogawa [20] synthesized a macroreticular polystyrene-based chelating resin with oxime and dietylamine functional groups (2.2). The resin was stable in acid and alkaline solutions.



(2.2)

Complex forming ability of divalent metal ions with kaliyappan et al. [21].
Studied a somewhat similar type of phenol-formaldehyde resin derived from 2-hydroxy-4-(meth)acryloylxy acetophenone.

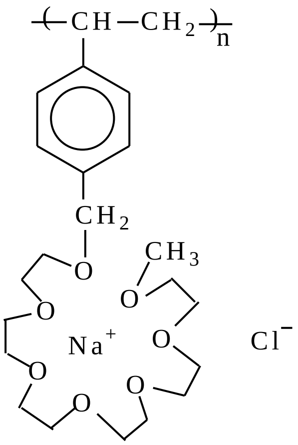
2.6 Polymers Carrying Pendant Complexing Ligands

The literature reveals a large number of polymers which fall under this broad definition. The division between monedentate ligands and polydentate ligands is omitted since the last class is usually defined under chelating polymers. Furthermore, polymeric monodentate ligands can, by cooperative complexation with single polymer chains, show a chelation effect. It is more advantageous therefore to present a division of different ligand groups.

2.6.1 Polymers Carrying Pendant Oxygen Ligands

Phenolic ion exchangers, usually as phenol-formaldehyde condensates, have appeared in the first generation of cation exchange resins, then abandoned in favor of the superior polyacrylates or polystyrene sulfonates. A phenol-formaldehyde copolymer which was shown to have higher selectivity towards Rb^+ and Cs^+ than the polystyrene sulfonate [22]. Formaldehyde condensates with phenol and aminocarboxilic acid [23] pyrocatechol or phyrogallol [24] are subject of two patents. The pyrocatechol polymer has a high (11.5 meg / g) exchange capacity, and shows good selective sorption of As, Sb, Bi and Mo. Styrene –DVB copolymers incorporating a azo-p-cresol and a azo salicylic acid [25], catechol, hydroquinone, naphtaquinone and benzoquinone [26] were also described. The quinone type polymers adsorbed Hg (II) selectively, where catechol resins absorbed Cr(VI).

Styrene-DVB copolymers carrying pendant a cyclic polyoxyethylene groups (2.3) for three-phase catalysis were reported by Yanagida, Takahashi and Okahara [27]. A special paragraph is devoted to macrocylic ethers. β-diketone polymeric ligands were mentioned by Bhaduri et al [28] who alkylated pentane-2,4-dione with chloromethyl-styrene-DVB copolymer with sodium ethoxide as base. The 3-methylene pentane-2,4-dionated polystyrene (2.4) was found to bind Cu(II), Ni(II), Ti(IV) which eluted only difficulty, even with strong complexing ligands as EDTA. A chelating poly(β-diketone) with good complexing and elution proporties for Au(III) and U(IV) was made by oxidation of polyvinylalcohol [29]. Others polymers carrying β-keto groups in the main chain, are the poly(bis- β-ketoesters) (2.5) reported by Davydova and Barabanov [30]., poly(sodium 3-o-vinyl benzyl) gluconate-co-acrylonitrile (2.6), made from the chloromethyl intermediate by nucleophilic displacement with sodium gluconate, was reported by Kobayashi and Semitomo [31].



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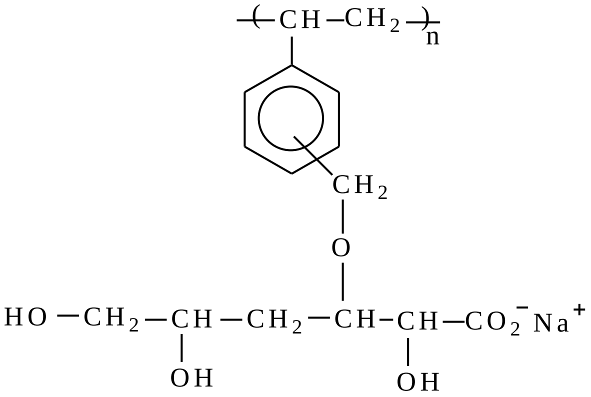

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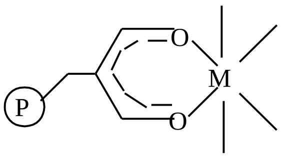

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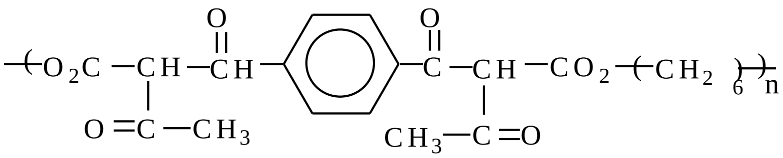

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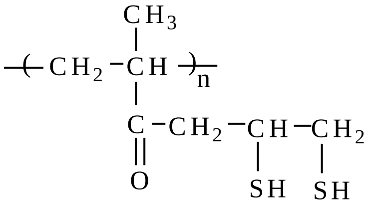
2.6.2 Polymers Carrying Pendant Sulfur Ligands

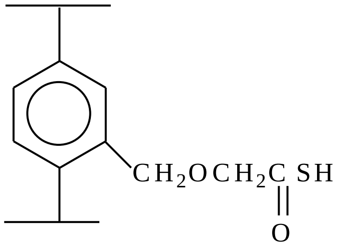
Sulfur ligands are known to complex or precipitate most of the heavy transition metals. The interest in polymers of this type is mainly in pollution abatement and in analytical applications. 4-thio methyl-polystyrene was described already by Parrish, [32] , and Egawa, Jogo and Maeda [33] reported macro reticular polyglycidyl methacrylate beads carrying pendant mercapto groups (2.7) for the complexation of Ag(I), Hg(II), Au(III). The conversion of chloromethylated polystyrene or amino methyl polystyrene into thiolated derivatives for peptide synthesis, and critical evaluation of intra polymeric alkylation and redox reactions were published [34].

Thioglycolate resins (2.8),(2.9) prepared from polymeric adsorbent XAD-4, for the collection and separation of Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II), CD(II), Pb(II) and U(VI) were described by Fritz and coworkers [35]. Similar polymers for the collection of heavy metals are dithiocarbamates and their derivatives. Polydithiocarbamate was made from polyethyleneimine by condensation with CS_2 [36,37,38] or formaldehyde [39].



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle O}{\overset{\|}{C}}-CH_2-\underset{\displaystyle SH}{CH}-\underset{\displaystyle SH}{CH_2}}{C}}H\right)_n\!-$$

(2.7)



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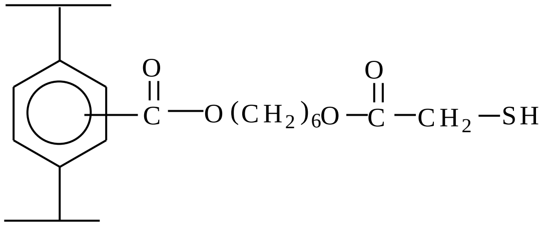


(2.9)

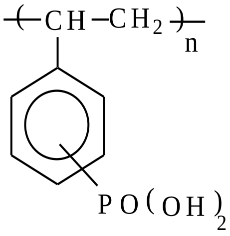
2.6.3 Polymers Carrying Pendant Phosphorous Ligands

Phosphoric acid esters and their thio derivatives as well as phosphine oxides are very effective extractants for uranium, gold and transition metals such as Zn(II), Co(II). Alternating copolymers containing phosphoric esters and thioesters were prepared by polymerization of the suitable monomers derivated from 4-Vinylphenolate and the corresponding phosphorylchloride derivative [40]. The polymers were tested mainly as flame retardants but were also found to bind heavy metals, notably Hg(II).

Bolster et al [41]. in a continuation of an earlier study by Kennedy and Small (46, ref. 2 therein) on metal complexes of poly(triallylphosphate), have concluded that the metal ion binding occurs via ion-solvation mechanism, in anaogy to the behaviors of the monomeric ligand. The polymer forms ML_2A_2 or ML_4A_2 complexes (m=metal ion, e.g. Co(II), Zn(II), Ni(II) and other transition cations, L= polymeric ligand, A= anion as Cl^-, Br^-, NO_3^-, ClO_4^-. The distribution coefficients are strongly dependent on the solvation power of the solvent. Another vinyl monomer used in addition polymerization is vinyl-ethyl phosphoric acid [42].

Several phosphorous polymers synthesized by functionalization of polystyrene: Marhol, Beranova and Cheng [43]., have prepared directly by phosphochlorination, or by acylation followed by phosphochlorination a series of polymers (2.10),(2.11),(2.12) containing phosphinic acids, which showed selectivity for trivalent cations against divalent cations. Chloromethyl polystyrene was converted by reaction with diphenylphosphine chloride to the diphenylbenzylphosphine polymer, and used to recover Co(II) and Rh(III) [44]. Polyampholitic sorbets were claimed phosphorylated crosslinked polystyrene, by the condensation of the hexametylenetetrammonium polystyrene with formaldehyde and H_3PO_2 [45] which presumably led to $\textcircled{P}-CH_2-NH-CH_2-PO(OH)_2$.

Another organophosphorous polyampholyte of the structure (2.13) was made by the direct condensation of polyethyleneimine, $(CH_2O)_n$ and H_3PO_2 as described by polykarpov et al [46]. Somewhat unusual polymers are the phosphorylated product of the polycondensation of the furfural and benzylbromide [47] and sulponated product of the condensation of diphenyl phosphonate with formaldehyde [48]. A general review on phosphorous containing polymers is given by Efendiev [49].



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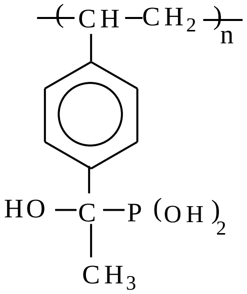

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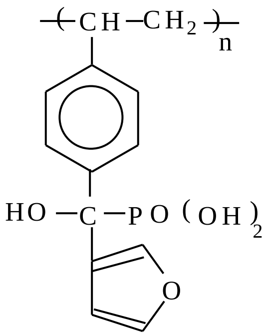

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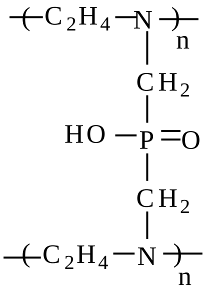
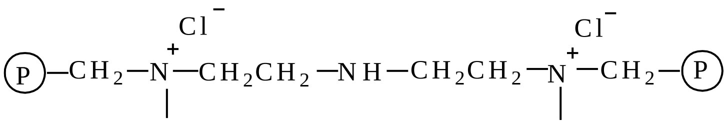


(2.13)

2.6.4 Polymers Carrying Pendant Nitrogen Ligands

Tertiary and quaternary polymeric amines are the most common anion exchangers, in contrast to primary and secondary amines which are ineffectual as anion exchangers, but form coordination complexes with most of the transition metal cations. Aminomethylated styrene –DVB copolymer has been described in several publications [50] and is commercial available [51]. Under the high pressure and temperature conditions, needed for direct aminolysis with ammonia, the primary amine polymer is further alkylated [52] has introduced a direct aminomethylation method via the reaction of polystyrene and chloromethylphthalimide followed by aminolysis. The laboratory Rossey [53] has introduced a direct conversion chloromethylpolystyrene to aminomethyl polystyrene under mild conditions, by quaternization with hexamethylenetetramine, followed by controlled hydrolysis. The polybenzylamine, thus conveniently produced, can complex metal cations [54]., or be further converted to other chelating polymers [55]. The incorporation of a chelating -[NH-CH_2-CH_2-NH]-$_n$ structure [56] (where n=

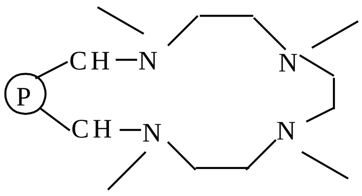
0,1,2,3) increases tremendously the stability constants of the polymeric ligand : metal ion complex. Egawa and Saeki [57] have prepared anion exchange resins by crosslinking chloromethylated styrene-DVB copolymers with di, tri or tetraethlene imine or by direct aminolysis at 170^{0}C of methylmethacrylate –DVB copolymer [58]. The corresponding polymers showed high affinity for Au (III), Hg (II) and Cu (I). Affinity for transition metal cations can be increased if the ethyleneimine structures are introduced under high swelling conditions [59] or in the presence of templating cations [60]. Polymer bound 1,2 and 1,3-diamines were reported by Ricard, Villemin and Richard [61], who reacted ethylenediamine directly with chloromethylpolystyrene, or with 1-hydroroxy-2-chloroethyl polystyrene (prepared by Friedel-Crafts alkylation followed by KBH_4 reduction). Again the true structure of the metal chelating entity is hard to predict, without metal binding data. The interesting variations in the predicted structure of the reaction productions between chloromethylpolystyrene and ethyleneimine derivatives is shown in polymers in (2.14), (2.15),(2.16),(2.17)



$$\text{(P)}-CH_2-\underset{|}{\overset{Cl^-}{\overset{+}{N}}}-CH_2CH_2-NH-CH_2CH_2-\underset{|}{\overset{Cl^-}{\overset{+}{N}}}-CH_2-\text{(P)}$$

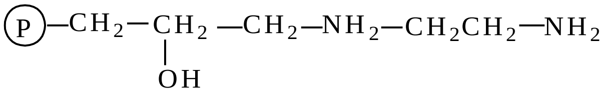
(2.14)

Mixed chelating anion exchange structure with affinity for anions. Egawa and Salki 1971



(2.15)

Pseudoazacrown-affinity for cations. Warshawsy, et al. 1976



$$\text{(P)}-CH_2-\underset{OH}{\underset{|}{CH_2}}-CH_2-NH_2-CH_2CH_2-NH_2$$

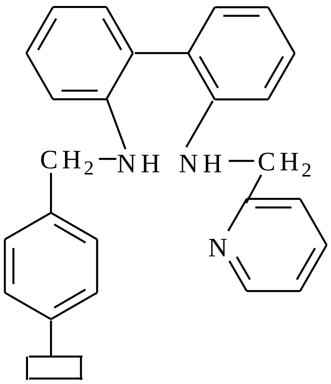
(2.16)

Linear non-crosslinked structure et al. 1980.

$$\textcircled{P}-CH_2-NHCH_2CH_2-NH_2 \qquad (2.17)$$

Another method to obtain ethyleneimine attached to polystyrene was by graft copolymerization of 2-methyl-2-oxazoline onto chlorometylated polystyrene. A heavy metal ion scavenger has been made condensing various ethyleneimineoligomers and polymers, thiourea and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) [62]. Amphoteric polymer, in the form of powder or flakes, absorbs heavy cations as Hg(II), Pb(II) even high acidities (1-10 M HCl), indicating the presence of strong anion exchange ligands. A similar condensate between polyethyleneimine and methylolthiourea was patented. Polyethyleneimine resin itself, obtained as a water insoluble by product during the synthesis of polyethylenepolyamine oligomers, was studied as a chelating anion exchanger for adsorption of crystal violet and neuococcin dyes and Cu (II), Fe (III) and CrO_4^{-2} ions [63].

Ethlenediamine chelates with mixed secondary-tertiary, aromatic amine 16, 17, 18 have been studied by Melby, Jones and Grinstead [64-65-66], N-(2-pridylmethyl)-2,2'-diaminobiphenyl polymer contain (2.18), or N,N'-bis (2- pridylmethyl)-2,2'diamino biphenyl polymer (2.19), contain a rigid tridentate or tetradentate chelating structure. Polymers XFS-4196 (2.20) and XFS-43084 (2.21) as well as polymer 16 have a flexible ligand structure.



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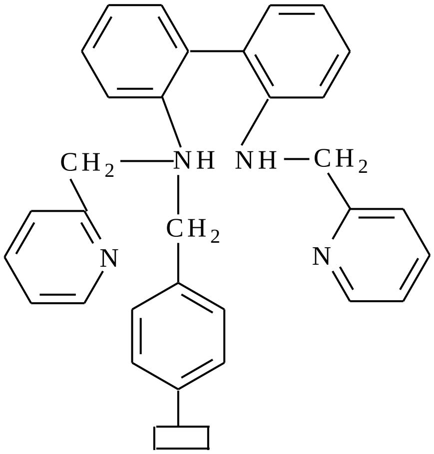

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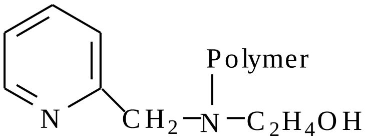
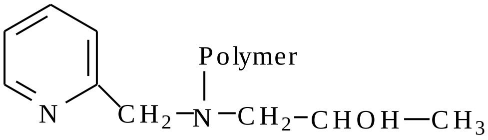


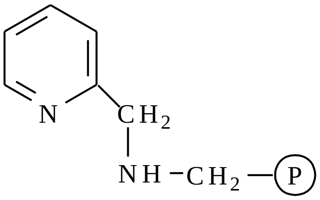
XFS 4196

(2.20)



XFS 43084

(2.21)



(2.22)

A triazine chelating resin incorporating vicinal amine groups absorbs several cations, but particularly Mo(VI) as reported by wang [67]. Polymers carrying amido groups [68] or mixed amido and hydrazido [69] groups were also published. The N-acetyl-N-methylpolybenzylamine was prepared by chloromethylation of XAD-4 followed by careful amination at liquid nitrogen temperature, than acylated. The interesting feature of this polymer is metal binding by a simple anion exchange mechanism.

3. EXPERIMENTAL

3.1 Materials and Instruments

Poly (4-vinyl pyridine) (P4-VP) beads (Reillex 425) (210-420 µm) (cross linked with 25% (w/w) commercial divinyl benzene (DVB), 55% of which is a mixture of meta and para isomers) was supplied from Reilly industry Inc.Indiana.USA. Chloroacetic acid (E.Merck), acrylamide (E.Merck), chlrosulfonic acid (Fluka), styrene (Fluka), and all the other chemicals used were analytical grade commercial products. Schmadzu UV/VIS 160A S

3.2 Preparation of polymeric sorbents

Four types of polymeric sorbents were prepared according following procedures.

3.3 Crosslinked Poly (styrene-divinyl benzene) beads

Beads were prepared by the suspension polymerization of a mixtured styrene (54 ml, 0.48 mol) and DVB (55 % grade, 10 ml, 0.038 mol) in toluene (60 ml), using gum-Arabic as stabilizer, according to a previously described procedure [70]. The beads were sieved and the 420-590 µm size fractions were used for further reactions.

3.4 Chlorosulfonation of the beaded polymer

The beaded polymer was chlorosulfonated using chlorosulfonic acid as described in the literature [70]. The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a polymer (0.2 g.) sample was added to 10

% NaOH (20 ml) and boiled for 4h. After filtration and neutralization with HNO_3 (5 M), the chlorine content was determined by the mercuric-thiocyanate method [71].This gave a final chlorosulfonation degree of 4 mmol. g^{-1}.

3.5 Preparation of sulfonamide based polymeric sorbents

Two types of the sulfonamide based polymeric resins were prepared starting from crosslinked polystyrene resin.

3.5.1 Preparation of cysteamin sulfonamide resin (Resin1)

Chlorosulfonated resin (10 g.) was added portion wise to a stirred of cysteamine 3.9 g. (0.05 mol) in 2-methyl pyrrolidone 30 ml at 0^0C. The mixture was shaken with a continuous shaker for at room temperature. The reaction content was poured into water (1L), filtered and washed with excess water and methanol respectively. The resin dried under vacuum at room temperature for 24 h. The yield was 14.8 g. The thiol content was determined according to the literature [72] and found to be 2.5 mmol.g^{-1}

3.5.2 Preparation of glycine sulfonamide resin (Resin 2)

The chlorosulfonated polymer (10 g.) was added portion wise to a stirred solution of glycine (4 g, 0.053 mol) in 2-methyl pyrrolidone (25 ml) at 0 ^{0}C. The mixture was shaken with a continuous shaker for 12 h at room temperature. The reaction content was poured into water (500 ml), filtered and washed with excess water. The product was dried under vacuum at 40^{o}C for 24 h. The yield was 12 g. The sulfonamide content was determined according to the literature [73] and found to be 3.98 mmol.g^{-1} .

3.5.2.1 Graft copolymerization of acrylamide from carboxylic acid groups

The carboxylic acid containing polymer (3 g.) was wetted with 5 ml of distilled water and left stand for 3h. To this mixture, 0.1 g. (1.8 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 5 ml of distilled water was added and shaken for 5 minute at room temperature. A solution of 9 g (0.126 mol) of acrylamide in 30 ml of distilled water was added to the mixture and shaken for 24h at room temperature with continuous shaker. The reaction contents were poured into water (500 ml), the resin filtered off and washed with excess water. The yield of crude product was 6.6 g.

Meanwhile, in order to examine homopolymer formation, 15 mL of filtrate was added to 50 mL acetone. About 28 mg of dry sample implies a 20 % of homopolymer yield.

3.5.2.2 Determination of the degree of grafting

The degree of the grafting was determined by Kjeldahl nitrogen analysis of the graft polymer sample as follows: 0.5 g. of were placed in 10 ml of concentrated H_2SO_4 and boiled for 10 h. The mixture was filtered and diluted to 50 ml with distilled water. The total nitrogen content of the filtrate was assayed by the Kjeldahl method, as given in the literature. This analysis gave nitrogen content of a 9.5 $mmol.g^{-1}$.

3.5.2.3 Swelling of the graft polymer

Due to hydrophilic poly (acrylamide) brushes, the bead polymer was expected to show water absorbance. Swelling of the polymeric beads was determined by determining the mass increase of the polymeric sample (0.1 g) soaked in distilled water in a crucible. After contact for 24 h, the increase in mass of the filtered sample (0.123 g) indicated a 23 % (w/w) water sorption.

3.5.3 Modification of crosslinked poly (4-vinyl pyridine) (P4-VP) beads (Resin3)

Crosslinked poly (4-vinyl pyridine) (P4-VP) beads was supplied from Reillex Company.

3.5.3.1 Quaternization of crosslinked (P4-VP) beads

Quaternization of polymer beads was carried out by reacting potassium salt of monochloroacetic acid solution, while 18.9 g (0.2 mol) chloroacetic acid was dissolved in 20 ml H_2O. Then 13.8 g (0,1 mol) K_2CO_3 in 25 ml of distilled water was added dropwise to the ice cooled solution of the chloroacetic acid while stirring.

A sample containing 10 g of the P4-VP resin was placed in this solution and the mixture was shaken by means of a continuous shaker for 48 h at room temperature .The mixture was heated to 70 ^{0}C for 4 h , filtered and washed with water. The product was filtered washed with excess of water and acetone respectively. The vacuum-dried sample weighed 14.8.g.

3.5.3.2 Estimation of the Carboxyl content

To 40 ml of 0.1 M NaOH solution 0.5 g of the quaternized resin was added and left to stand overnight .The mixture was filtered.

The filtrate was titrated with 0.1 N H_2SO_4 solutions. Carboxylic acid content was found as about 2.2 mmol.g^{-1} resin, which corresponds to 38.9 % of quaternization of the pyridine units.

3.5.3.3 Graft Copolymerization of acrylamide from carboxylic acid groups

The polymer sample with carboxymethyl pyridinium groups (3 g.) was wetted with 5 ml of distilled water and left stand for 2 h. To this mixture, 0.1 g. (1.8 mmol) of $Ce(NH_4)_2(NO_3)_6$ in 5ml of water was added and shaken for 2 minute at room temperature. A solution of 9 g. (0.126 mol) of acrylamide in 30 ml of distilled water was added to this mixture and shaken for 24 h at room temperature with a continuous shaker. The reaction contents were poured into water (500 ml), the resin filtered off and washed with excess water. The yield of crude product was 6.35 g.

Meanwhile, in order to examine homopolymer formation, 10 ml of filtrate was added to 40 ml of acetone. Evaporation of the solvents in the filtrate gave 21 mg of homopolymer 23.9 %.

3.5.3.4. Determination of the grafting degree

The degree of grafting was determined by Kjeldahl nitrogen analysis of the graft copolymer sample as follows: 0.2 g. of the bead were placed in 20 ml of concentrated

H_2SO_4 and boiled for 10 h. The mixture was filtered and diluted to 70 ml with distilled water. The total nitrogen content of the filtrate was assayed by Kjeldahl method, as given in the literature [73]. This analysis gave nitrogen content 6.88 of a mmol.g^{-1}.

3.5.4 Preparation of GMA-EGDMA copolymer beads (Resin 4)

Polyvinyl pyrrolidone (1 g) was dissolved in 115 mL of water. Then, the solution was transferred into a 1 L, three necked flask equipped with a nitrogen inlet, a mechanical stirrer, and a reflux condenser. A mixture of 20 mL (0.147 mol) GMA, 3.1 mL (16.3 mmol) of EGDMA and 0.5 gr ($3.05.10^{-3}$ mol) of azobisisobutyrolinitrile in 23 mL of toluen was added to the flask under a nitrogen stream. The mixture was heated to 70 ^{0}C and stirred continuously (ca.400 rpm) under a nitrogen atmosphere for 5 h.

The bead product was filtered and washed with an excess of water, acetone and methanol respectively. Then, it was dried in vacuum at room temperature for 24 h, and the yield was 23.8 gr.

3.5.4.1 Determination of the epoxy content

The epoxy content of the polymer beads was determined by a pyridine-HCl method described in the literature [74].

Titration of the filtrated pyridine-HCl solution with NaOH (0.052 M) gave 6.15 mmol.g^{-1} epoxy content.

3.5.4.2 Modification with dibutylamine

GMA-EGDMA copolymer resin (10 g) was put in 10 ml of dibutylamine in a 100 ml of flask. The mixture was stirred for 10 h at room temperature. The reaction mixture was heated at 90^{0}C in a thermo stated oil bath for 5h.

The reaction content was poured into water, filtered and washed with an excess of water. The product was dried at room temperature in vacuum 24h. The yield was about 14 g.

3.5.4.3 Determination of the amine content

For the determination of the amine content, 0.105 g. of the polymer sample was left in contact with 5.2 ml of HCl (0.1 M) for 10h. After filtration, 2 ml of the filtrate was taken and the acid content of the solution was determined by titration with 0.052 M NaOH solution in the presence of phenol-phatalein color indicator. A total amine content of the polymer was calculated as 3.4 mmol.g^{-1} resin.

3.5.4.4 Reaction of crosslinked amine containing beads with chloroacetamide

Tertiary amine containing beads 6 g of 420-590 μm size were soaked into a solution of 10 g. (0.107 mol) 2-chloroacetamide in 50 ml dimethyl formamide. The mixture was shaken by a continuous shaker for 2 days at room temperature, and then heated to 80 ^{0}C in a constant temperature bath for 48h. Beads were filtered and washed with dimethyl formamide, excess of water and acetone respectively. The vacuum dried sample weighed 7.3 g. This corresponds to 98.1 % of conversion.

3.5.4.5 Chloride analysis of Resin 4

The quaternization yield was followed by analysis of the chloride ions of the final product. Thus 0.1 g of the quaternized beads was boiled in 9 ml of %10 NaOH solutions for 3 h. Analysis of the chloride ions solution was performed by the mercuric thiocynate method as described in the literature [71]. This method gives 2.5 mmol. g^{-1} chloride content.

3.5.5. Regeneration of the resins

The heavy-metal loaded samples (0.2g.) were interacted with 10 ml of glacial acetic acid and stirred at 80^{0}C for 1h. after cooling, the mixtures were filtered, and 2 ml of the filtrate was taken out for colorimetric analysis of the heavy metal ion.

3.5.6 Mercury and heavy metal uptake measurements of the resins

The mercury and heavy metal sorption capacities of the polymers were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous Hg (II) solution (0.1 M).

The mixture was stirred for 24 h and the filtered. The Hg (II) concentrations were determined colorimetrically using diphenyl carbazide [75].

The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solution. 1 ml volume of the filtrate was used for determination of the residual mercury. In order to examine the selectivity of Hg binding, sorption capacity measurements were also performed using Cd (II), Pb (II), Zn(II), and Fe(III) ion solutions (0.15 M initial concentrations). Analyses of the residual metal contents of the supernatant solutions were performed by a complexometric titration method using EDTA solution (0.1 M).

3.5.7 Kinetics of the sorption

In order to estimate efficiency of the sorbents for trace mercury batch kinetic experiments were performed using high diluted Hg (II) solutions ($3.683.10^{-3}$ M). For this purpose the polymeric resins (0.2 g.) were wetted with distilled water (1.5 ml) and added to a solution of Hg (100 ml of 0.1 g. $HgCl_2$ in 90ml water). The mixtures were stirred magnetic stirring bar and aliquots of the solution (10 ml) were taken at appropriate time intervals for analysis of the residual Hg (II) contents by the method as described above.

RESULT AND DISCUSSION

4.1 Preparation of Crosslinked Polymeric Sorbents

4.1.1 Preparation of Sulfonamide based resin

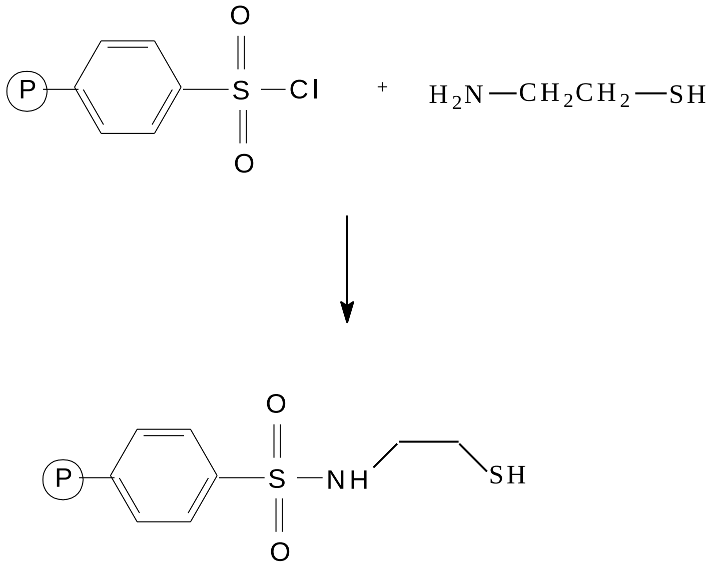
Crosslinked polystyrene–DVB copolymer was prepared by using suspension polymerization method according to the literature [70]. The polymer was chlorosulfonated by using excess of chlorosulfonic acid at room temperature for 24 h.

Scheme 4.1: Chlorosulphonation of crosslinked polystyrene

Chloride analysis of the product in the fist step (4 mmol.g^{-1}) revealed a degree of chlorosulfonation of ~ 70 %.

4.1.1.1 Preparation of Cysteamine Sulfonamide (Resin 1)

Excess of cysteamine was dissolved in NMP (N-Methyl pyrrolidone). Chlorosulfonated polystyrene resin was added portion wise at 0^{0}C. The reaction was continued at 0 ^{0}C for 2h and at room temperature for 24h. The Cysteamine resin was filtered and washed with excess of water and methanol respectively. The resin was characterized by detection of thiol content according to the literature [72]. Thiol content was found as about 5 mmol.g^{-1}.



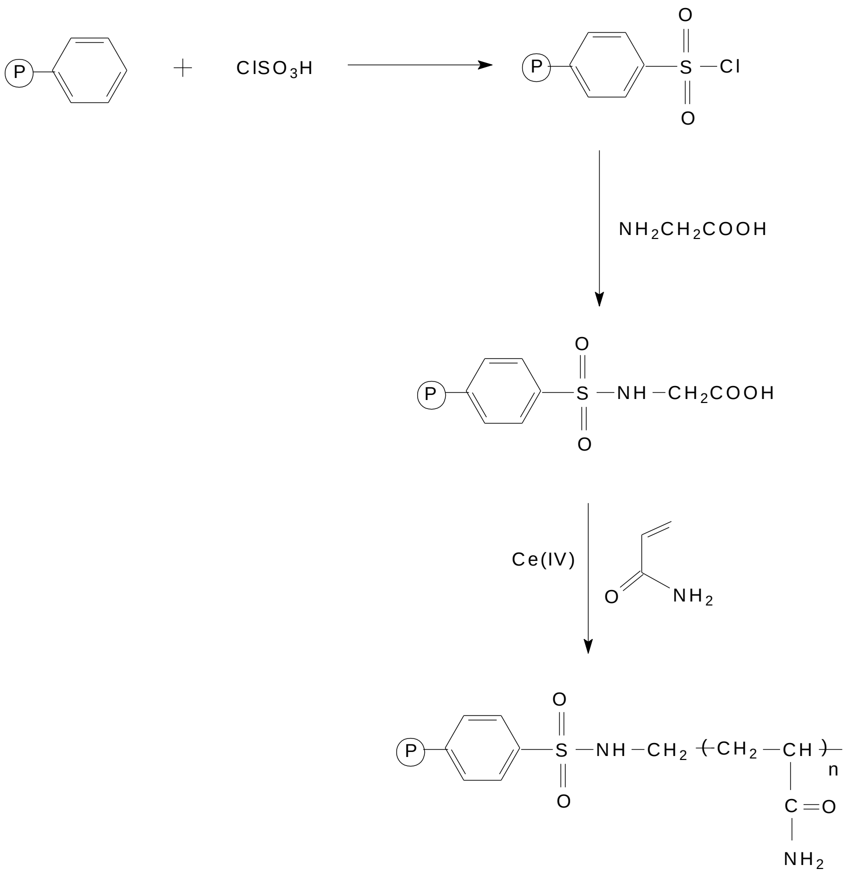
Scheme 4.2: Preparation of Cysteamine Sulfonamide

4.1.1.2 Preparation of glycine sulfonamide polymeric resin and acrylamide graft reaction (Resin 2)

Crosslinked poly (styrene-DVB-g-poly (acrylamide) was prepared successfully by grafting from glycine sulfonamidated styrene-divinylbenzene (420-590 µm), the latter being obtained via stepwise modifications shown in Scheme 4.2.

Chloride analysis of the product in the first step (4 mmol g^{-1}) revealed a degree of chlorosulfonation of ~ 70%. The second step was performed with essentially quantitative conversion of the chlorosulfonyl groups when excess glycine in NMP was used. The sulfonamide content was found to be 3.9 mmol g^{-1}; this amount is almost equal to the theoretical value of 4 mmol $g^{-1,}$ corresponding to 98 % conversion in the second step.

Finally, poly (acrylamide) brushes were anchored to the bead surface by graft polymerization of acrylamide from carboxylic acid groups on the crosslinked support.

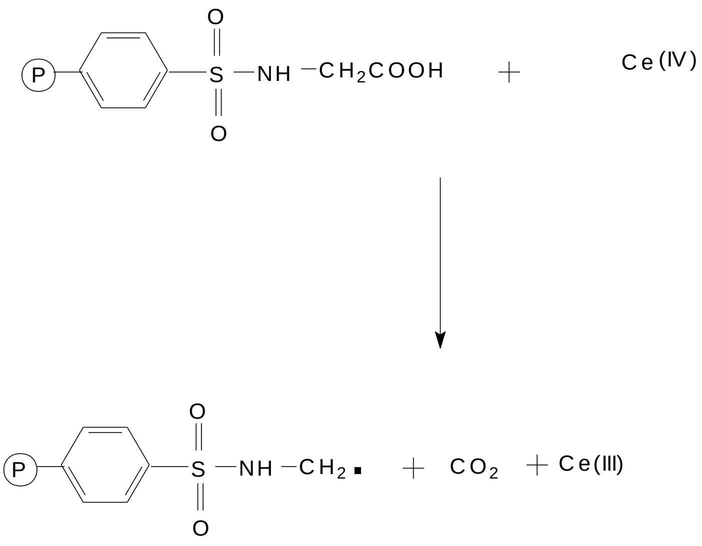


Scheme 4.3: Preparation of cystamine sulfonamide polymeric resin and acrylamide graft reaction

4.1.1.2.1 Grafting reaction mechanism

Grafting from carboxylic acid group by redox interaction with $Ce(NH_4)_2(NO_3)_6$ is a very complicated process because homopolymer formation is a side reaction .

For fast initiation, the reactivity of the reducing groups on the surfaces is of prime importance in grafting using the Ce (IV) method (Scheme 4.4).



Scheme 4.4: Grafting from carboxylic acid group

This requirement is fulfilled by the acid functionality, as described in the literature [76].The grafting degree depends on the reaction conditions and still possesses a high tendency to form homopolymers. Most likely, chain transfer to the solvent is responsible for the homopolymer formation·

Therefore, we have known that pretreatment of the bead polymer particles with a Ce(IV) solution for at least 3 min prior to the addition to the acrylamide is suitable to suppress homopolymer formation . This way, we obtained high mass increases (220%) in 24 h. at room temperature. Under this condition, homopolymer isolated by precipitation in acetone indicates a free polymer yield of 20% as by-product.

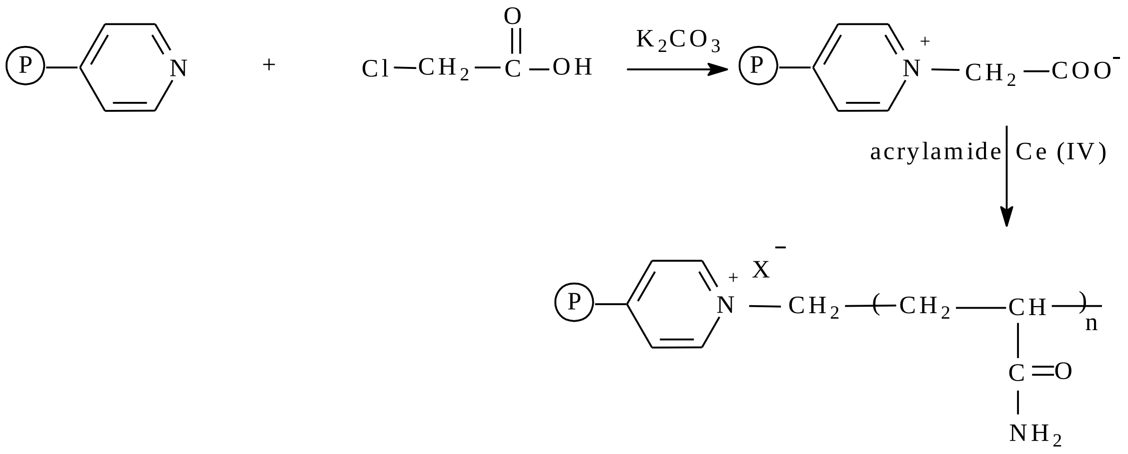
A longer interaction period with Ce (IV), prior to the addition of the monomer, causes the consumption of vast amounts of the initiator groups for direct oxidation and the degree of grafting falls sharply to low values. Initiation through carboxylic acid functions is believed to proceed via CO_2 elimination as described in the literature [77].

Kjeldehal nitrogen analysis of the graft polymer gave 9.5 mmol nitrogen /g of polymer. This indicates grafting, yields of 220 wt %, which is very close to the value found by mass increase.

4.1.2 Modification of crosslinked poly (4-vinyl pyridine) (P4-VP) beads

Crosslinked polyvinylpyridine-graft-polyacrylamide was prepared successfully by grafting from quaternized P4-VP- (210-420 μm). Quaternization was performed with chloroacetic acid. At the end of reaction carboxylic acid content of the product was found as 2.2 mmol.g^{-1} .

Finally, poly (acrylamide) brushes were anchored to the bead surface by graft polymerization of acrylamide from carboxylic acid groups on the crosslinked support.



X : Cl$^-$ or OH$^-$

Scheme 4.5 Modification of crosslinked poly (4-vinyl pyridine) (P4-VP) beads

4.1.3 Preparation of poly(glycidyl methacrylate) based resin

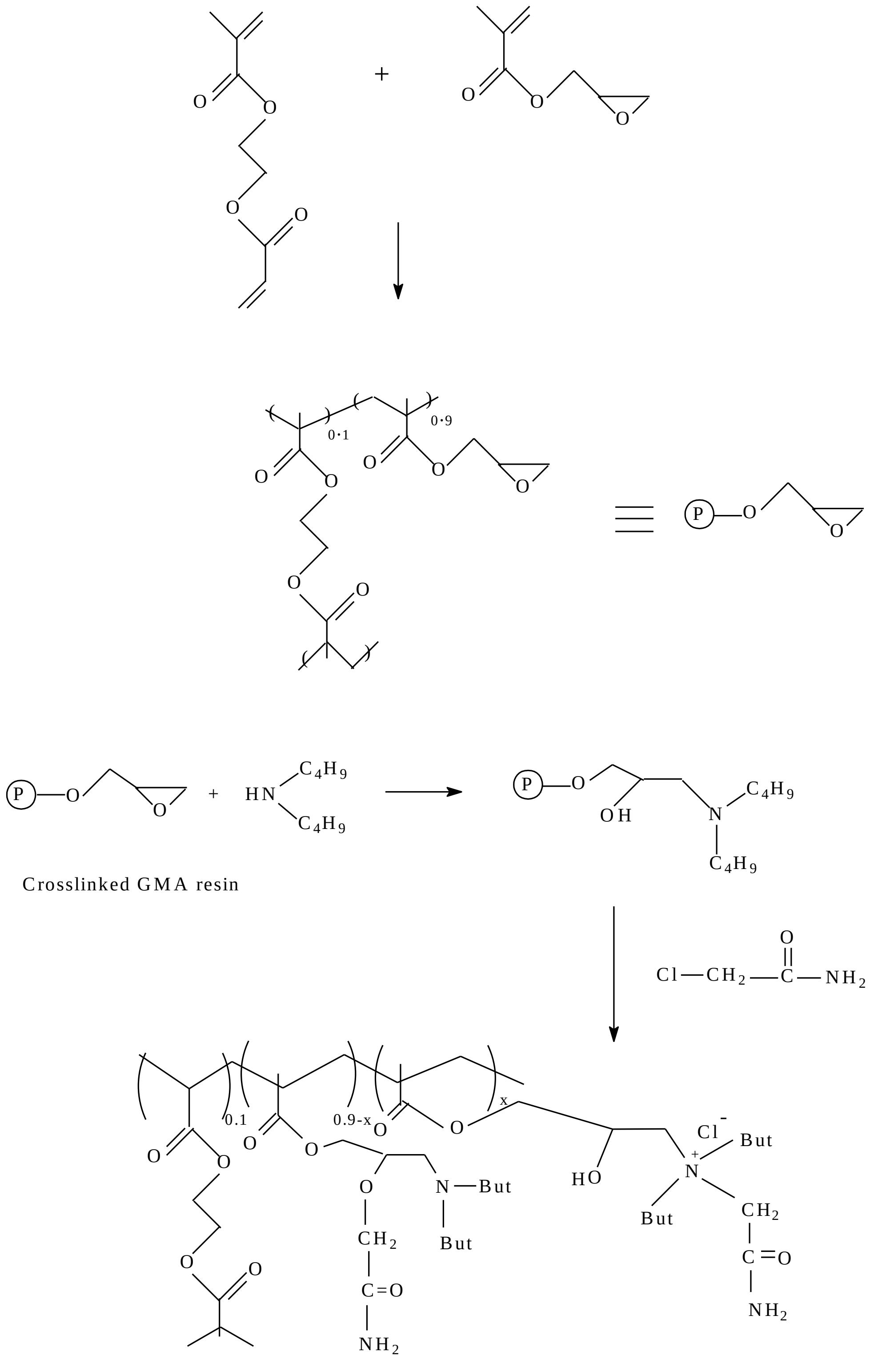
Glycidiyl methacrylate (GMA) based crosslinked polymers have advantages over other polymer supports due to ease of functionalization through the epoxide groups involved. Also remarkable resistance of its ester linkage to acid and base hydrolysis is an additional advantage to use as ligand carrying polymer.

In the present study, copolymer beads were prepared by suspension polymerization; a 210-420 μm size of the product is used in further elaborations. An analysis of the bead polymer sample by the pyridine-HCl method gives a 6.15 mmol of epoxy content per gram.

Reaction with dibutyl amine gives a tertiary amine containing with 3.4 $mmol.g^{-1}$ amine functions. Reaction of the crosslinked resin with tertiary amine function in dimethyl formamide with excess of 2-Chloro acetamide gives a product with 2.5 $mmol.g^{-1}$ chloride content (Scheme 5).

This corresponds to about 97% quaternization. However, quaternization of ethanol amines have been reported to rearrange to diethylamino ether moieties spontaneously [78].

In order to determine rearranged fragment we've searched an adequate analytical procedure. For this purpose the sample was iminursed into Eriochrome black T (M_w=461.39) solution. By colorimetrical analysis of residual dye (λ=523 nm) gave a 0.607 $mmol.g^{-1}$ quaternary amine content. This amount is about ¼ of the expected value. However, reliability of this analysis is doubtful. In the FT-IR spectra of the starting compound C-O stretching vibration band of CH-OH group becomes weak after the reaction. This can be ascribed to ether formation during quaternization. Based on this consideration structure of the resulting material can be depicted as in Scheme 4.6.



Scheme 4.6: Preparation of poly(glycidyl methacrylate) based resin

4.1.4. Mercury uptake measurements

The mercury sorption capacities of the resins were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous Hg (II) solution (0.1 M).
The mixture was stirred for 24 h and the filtered. The Hg (II) concentrations were determined colorimetrically using diphenyl carbazide [75].

The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solution.

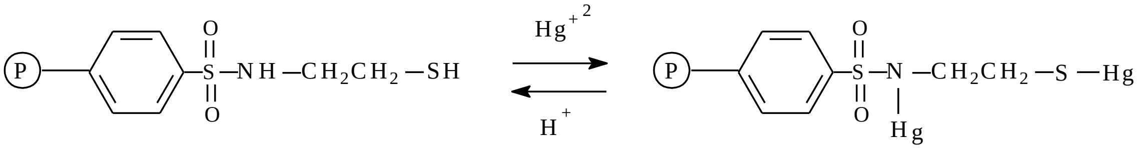
4.1.4.1 Heavy metal uptake of Resin 1

Resin 1 has thiol function group therefore it can be remove heavy metal ions such as Hg (II), Cd (II), Pb(II), Zn (II) and Fe (III) from aqueous solutions. All the metal uptake characteristics of resin 1 were given in Table 4.1.

Table 4.1 Metal uptake characteristics of the resin 1

Metal ion	initial concentration	Resin capacity (mmol / g.resin)	Recovered metal (mmol / g.resin)
Hg(II)	0,15	2,90	2,32
Hg(II)	0,50	2,85	2,30
Hg(II)	0,025	2,83	2,20
Cd(II)	0,15	1,85	-
Pb(II)	0,15	1,30	-
Zn(II)	0,15	0,30	-
Fe(III)	0,15	2,00	-

Resin 1 contains sulfonamide groups. Therefore sulfonamide groups can bind mercury. We can give removal of mercury in Scheme 4.6



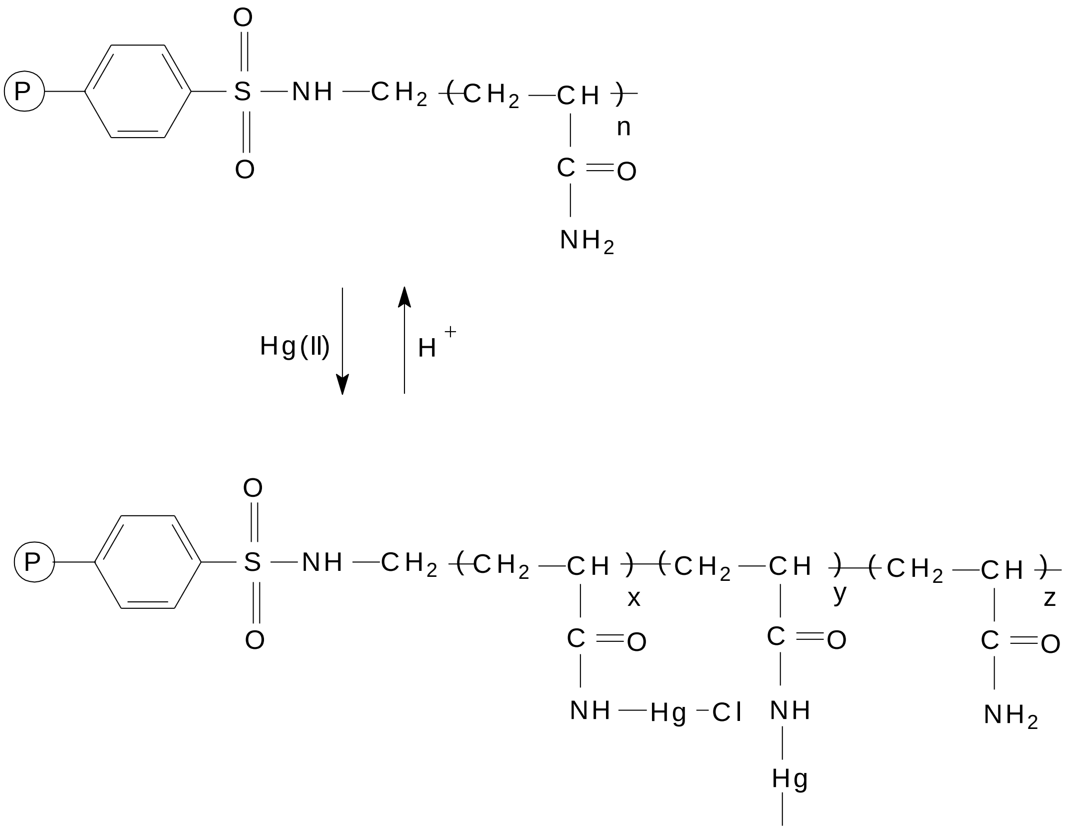
Scheme 4.7: Mercury uptake of resin 1

Theoretical capacity of the resin is about 5 $mmol.g^{-1}$. But, we found maximum loading capacity of mercury is 2.9 $mmol.g^{-1}$. According to this result, this quantity of mercury sorption is around a half of the theoretical capacity which implies sulfonamide nitrogen is less effective than thiol groups.

4.1.4.2 Mercury uptake characteristics of the Resin 2

The resulting beaded polymer with poly (acryl amide) grafts was expected to show the characteristics of semi homogenous reaction conditions. Flexible poly (acrylamide) graft chains should offer the opportunity for rapid interaction with aqueous Hg (II) solutions to form mercury-amide linkages. Although, in this work, we have not studied pH dependency of the mercury sorption, our previous experiences showed that mercury binding proceeds by simultaneous proton releasing as it was inferred by increase in pH of the mercury solutions while interacting.

There exist possible reaction sites, one sulfonamide group and carbon amide groups, available for the mercury binding. Mercury binding via carbonamide groups can occur in principle either by formation of monoamide or diamide Hg structures, which provide a means of capturing Hg^{2+} from aqueous solution (Scheme 4.8).



Scheme 4.8: Mercury uptake of resin 2

Aqueous solutions of $HgCl_2$ were used in Hg sorption experiments. The sorption capacity of the grafted beads was assessed by analysis of the excess Hg^{2+} in the supernatant solutions. The overall Hg^{2+} uptake capacity from 0.15 M $HgCl_2$ solution was high, (5.75 $mmol.g^{-1}$).

In 0.05- 0.15 M initial mercury concentration range loading capacity of the polymer did not change there is no limitation of diffusion inside the polymer particles, since the reactive sites are located on flexible poly (acrylamide) chains outside the particle surface. Also, the mercury binding takes place as if under homogenous conditions (Table 4.2).

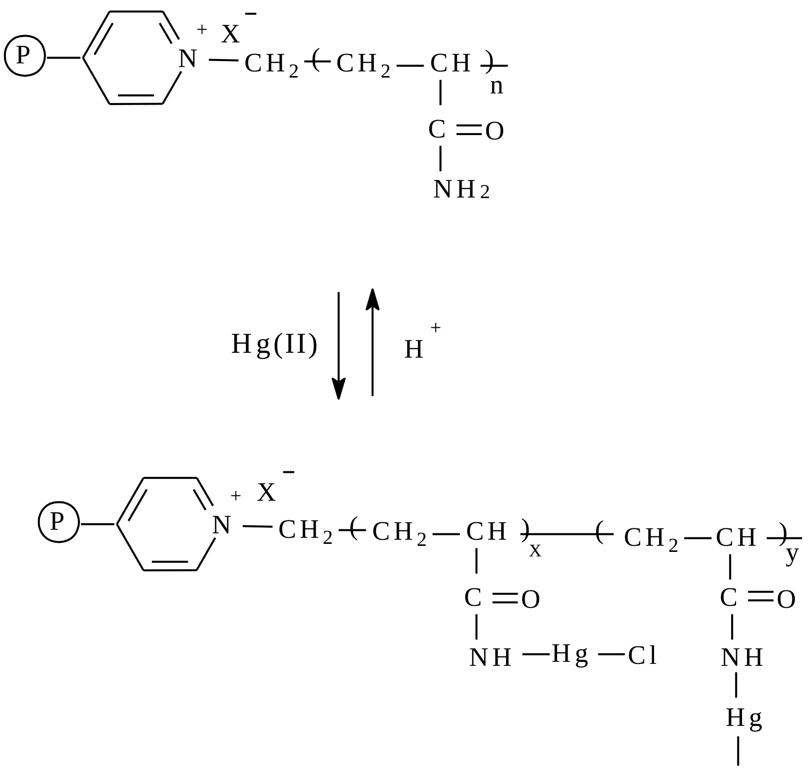
Table 4.2 Mercury sorption characteristic of the resin 2

initial concentration, M	sorbed Hg mmol.g^{-1}	mass increase, %	stripping Hg, mmol.g^{-1}
0.15	5.75	88	5.52
0.1	5.63	80	5.60
0.05	5.76	85	5.70

Since, in ordinary conditions the amide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen; the separation of Hg^{2+} is expected to be highly selective. To probe the degree of selectivity of the Hg^{2+}, the sorption experiments were repeated with other potentially contaminating ions. In particular, 0.15 M single metal ion solutions of Cd(II), Zn(II), Pb(II) were examined. Very small sorption capacities between 0.06-0.1 mmol.g^{-1}) were observed. Those small quantities are likely in experimental error limits. Therefore, overall the results clearly indicate that Hg sorption is extremely selective.

4.1.4.3 Heavy metal uptake characteristics of the Resin 3

Poly (acrylamide) graft chains and hydrophilicity of the quaternary groups offer opportunity for rapid interaction with aqueous Hg (II) solutions to form mercury-amide linkages. Mercury binding mechanism was depicted in Scheme 4.7



Scheme 4.9: Mercury uptake of resin 3

Aqueous solutions of $HgCl_2$ were used in mercury sorption experiments. The mercury sorption capacity of the grafted resin from 0.1 M $HgCl_2$ solution was found as 3.36 $mmol.g^{-1}$.

In 0.025-0.1 M of initial mercury concentration range loading capacity of the polymer did not change. Practically, there is no limitation of diffusion inside the polymer particles, because the reactive sites are located on flexible poly (acrylamide) chains. Also, the mercury binding takes place as if under homogenous conditions (Table 4.3).

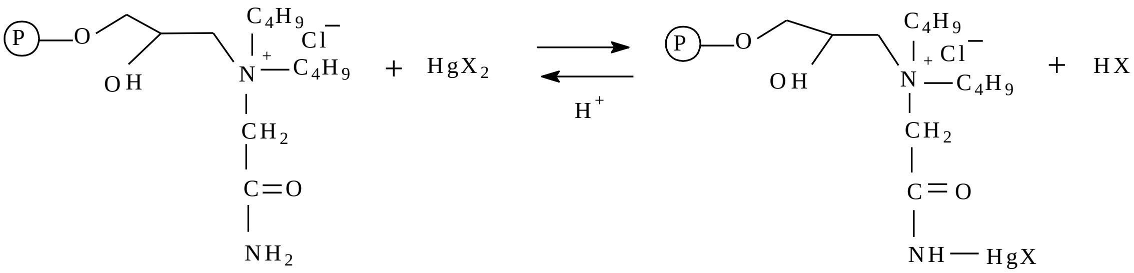
Table 4.3 Metal uptake characteristics of the resin 3

Metal ion	İnitial concentration (M)	Resin capacity (mmol.g^{-1})	Recovered metal (mmol.g^{-1})
Hg(II)	0.10	3.36	3.20
Hg(II)	0.05	3.12	3.01
Hg(II)	0.025	3.45	3.25
Cd(II)	0.15	0.19	-
Pb(II)	0.15	0.20	-
Zn(II)	0.15	0.18	-
Fe(II)	0.15	0.77	-

Since, in ordinary conditions the amide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen; the separation of mercury ions is expected to be highly selective. To prove the selectivity of the mercury sorption, experiments were repeated with other metal ions. In particular, 0.15 M single metal ion solutions of Cd (II), Zn (II), Pb (II) and Fe (III) were examined. Very small sorptions (0.18-0.77 mmol.g^{-1}) were detected. Overall the results clearly indicate that mercury sorption is very selective (Table 4.3).

4.1.4.4 Heavy metal uptake characteristics of the Resin 4

The quaternary amine-amide containing resin obtained is a mercury-selective sorbent which binds mercury through the amide groups (Scheme 4.10).



Scheme 4.10 : Mercury uptake of resin 4

Based on the basic reaction of mercuric ions with amide groups, yielding covalent mercury-amide linkages, mercury binding of the resin can be shown in Scheme 2.

Mercury sorption of the resin has been studied in non-buffered conditions. Because the use buffer is not practical in large scale mercury extractions and the buffer components might be competitive in the mercury uptake, pH of the Hg (II) solutions are slightly acidic and remain almost constant in the 3.1-4.0 range during the mercury extractions.

Aqueous solutions of the $HgCl_2$ were used in the mercury sorption experiments. The sorption capacity of the bead sample was estimated by the analysis of the excess Hg^{+2} in the supernatant solutions. The overall Hg^{+2} uptake capacity from 0.1 M $HgCl_2$ solution was 3.3 mmol.g^{-1}

In the 0.025-0.1 M initial mercury concentration range loading capacity of the polymer did not change (Table 1). To inspect selectivity of the quaternary resin, metal extraction experiments have been reported with Cd (II), Pb(II), Zn(II) and Fe(III). Very small capacities between 0.20-0.80 mmol.g^{-1} were observed (Table 4). Therefore, overall the results clearly indicate that Hg sorption is extremely selective.

Table 4.4 Metal uptake characteristics of the resin 4

Metal ion	İnitial concentration (M)	Resin capacity (mmol.g^{-1})	Recovered metal (mmol.g^{-1})
Hg(II)	0,10	3.30	2.00
Hg(II)	0,05	3.43	2.10
Hg(II)	0,025	3.22	2.02
Cd(II)	0.150	0.30	-
Pb(II)	0.150	0.20	-
Zn(II)	0.150	0.22	-
Fe(III)	0.150	0.80	-

4.2 Batch kinetic sorption experiments

Batch kinetic sorption experiments from highly dilute Hg (II) solutions (3.683.10-3 M) indicate relatively fast binding of mercury. The curves in Fig.1, Fig.2, Fig.3 and Fig.4 indicate a second order kinetics for resin 1, resin 2, resin 3 and resin 4 respectively.

The kinetics of the mercury sorption depends on many factors, such as stirring rate and pH of the solution. To obtain information about kinetic profiles of the mercury sorption, we performed experiments by the batch method with low mercury concentrations under non-buffered conditions. The concentration-time plots obey second order kinetics with respect to the Hg (II) concentration. As can be inferred from the figures the mercury binding is reasonable fast for resin 2 and resin 3. The fast reaction can only be ascribed to the flexibility of the dangling polyacrylamide chains in water.

Table 4.5 Second order rate constant of the resins

Resin	k, M^{-1}.s^{-1}	Correlation factor
Resin 1	0,63	0,998
Resin 2	65	0,989
Resin 3	1,17	0,983
Resin 4	0,323	0,980

CONCLUSION

Four types of new polymeric crosslinked sorbents were prepared successfully in this study.

Polymer characterizations were performed by using analytical determination methods according to the literature.

Resin 1 is a thiol containing polymer. Thiol groups are ascribed in many literatures as mercury selective. In our study, Resin 1 can also remove other metal ions such as Cd (II), Pb (II) and Fe (III) from water.

Graft copolymerization of acrylamide from carboxylic groups can be carried out using Ce(IV). Resin 2 and Resin 3 are high capacity mercury sorbents. Since, in ordinary conditions the amide group is not capable of forming coordinative bonds with other transition metal ions, as a result of the reduced electron-donating character of the amide nitrogen; the separation of mercury ions is very highly selective.

Also trace mercury sorption kinetic of the resins were performed. Rate constant of the graft copolymers are higher than others. Flexible acrylamide groups provide homogeneous reaction condition.

Regenerebility of these materials with acetic acid makes them attractive for large scale applications.

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APPENDIX 1

Fig 1. Concentration-time plot of $HgCl_2$ solution for resin 1

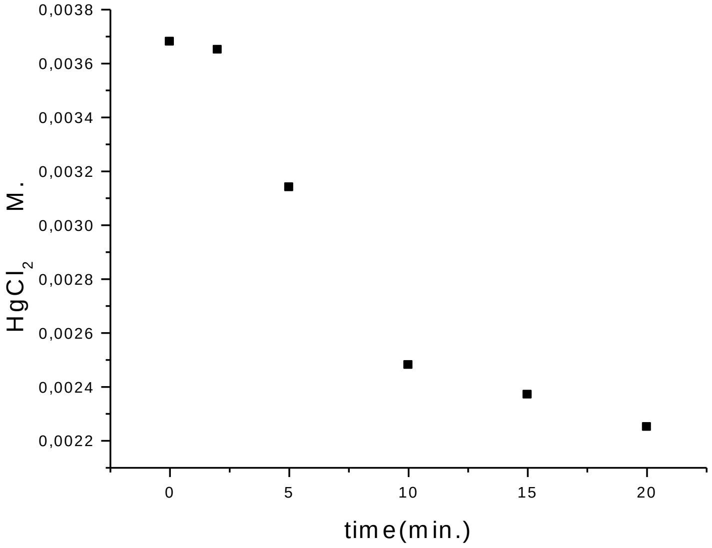
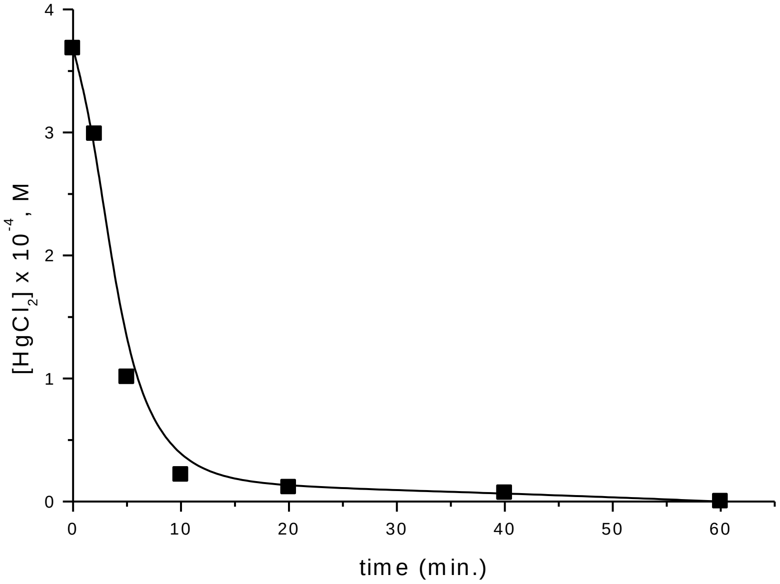


Fig 2. Concentration-time plot of $HgCl_2$ solution for resin 2



APPENDIX 2

Fig 3. Concentration-time plot of $HgCl_2$ solution for resin 3

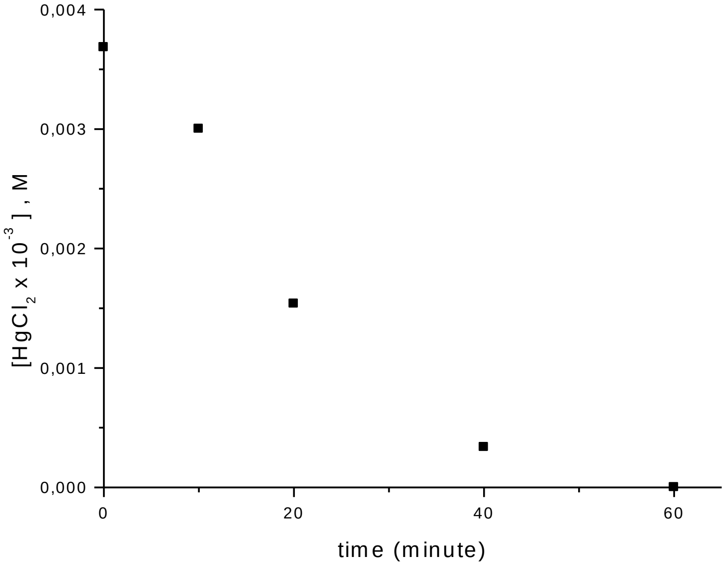
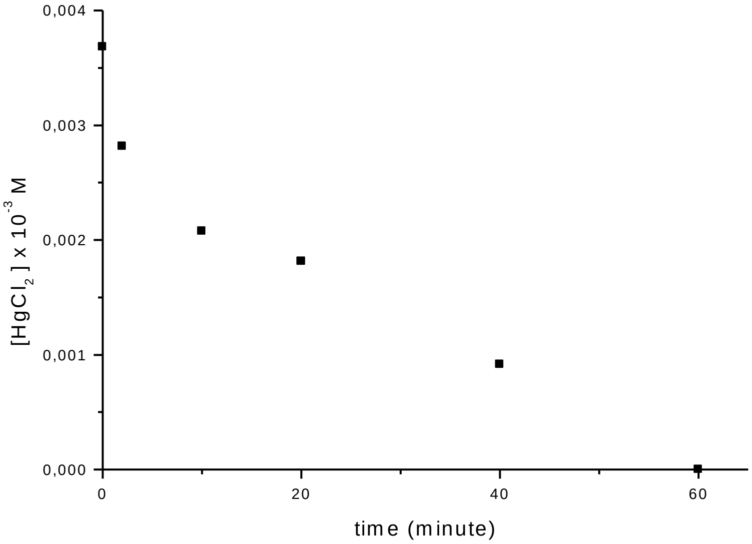


Fig 4. Concentration-time plot of $HgCl_2$ solution for resin 4



AUTOBIOGRAPHY

He was born in 1975 in İstanbul. He graduated Kemal Hasoğlu High School and attended to the İstanbul Technical University, Faculty of Chemistry-Metallurgy, Departmant of Chemical Engineering. In 2002, he began as a master student in İstanbul Technical University, Polymer Science and Technology. He is a research assistant in İstanbul Technical University, Department of Chemistry.