ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION OF CROSSLINKED QUARTERNARY AMIDE-SULFONAMIDE RESIN AND USING FOR REMOVAL OF MERCURY IONS FROM AQUEOUS SOLUTIONS

M.Sc. THESIS

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Thesis Advisor: Prof. Dr. B. Filiz ŞENKAL

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇAPRAZ BAĞLI KUARTERNER AMİD-SÜLFONAMİD İÇEREN REÇİNE HAZIRLANMASI VE SULU ÇÖZELTİLERDEN CİVA İYONLARININ UZAKLAŞTIRILMASI İÇİN KULLANILMASI

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FOREWORD

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December 2012   Sena ALKAZAN
                                                                                          (Chemist)

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ABBREVIATIONS

CSPS	**:** Chlorosulfonated Polystyrene	
DMF	**:** Dimethyl formamide	
DVB	**:** Divinyl Benzene	
EDTA	**:** Ethylenediamine tetra acetic acid	
FT-IR	**:** Fourier Transform InfraRed	
NMP	**:** N-Methyl Pyrrolidone	
PS	**:** Polystyrene	

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k_1 : Pseudo-first-order rate constant
k_2 : Pseudo-second-order rate constant
R^2 : Correlation coefficient
q_e : Equlibrium concentration
q_t : Time dependence concentration
t : Time

PREPARATION OF CROSSLINKED QUARTERNARY AMIDE-SULFONAMIDE RESIN AND USING FOR REMOVAL OF MERCURY IONS FROM WATER

SUMMARY

In this thesis, crosslinked sulfonamide based resins were prepared starting from crosslinked chlorosulfonated polystyrene resin (CSPS).

The Resin 1 was prepared reaction with chlorosulfonated polystyrene (CSPS) and excess of N,N-dimethylethylenediamine. The Resin 2 was obtained from quaternization of the Resin 1 with 2-chloroacetamide in dimethyl formamide (DMF) solution.

Resin 1 and Resin 2 were characterized by using analytical methods and Fourier Transform InfraRed (FT-IR).

Mercury and heavy metal uptake of the resins

$HgCl_2$ was used in mercury adsorption experiments. The mercury sorption capacities of the sorbent were determined by mixing weighed amount of polymer sample (0.1 g) with 20 mL aqueous Hg (II) solutions (0.074M, 0.050 M and 0.025M). The mercury loading capacities were calculated from the initial and final Hg (II) contents of the solutions.

Sorption experiments were repeated with other heavy metal ions. Resin 1 was used to remove other metal ions as well as Hg(II).

Since, in ordinary conditions the amide and sulfonamide groups are 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(II) is expected to be highly selective. Other metal ions sorption capacities of the Resin 2 between 0.20-0.30 mmol.g-1 were observed . Therefore, overall the results clearly indicate that Hg(II) sorption is extremely selective.

Batch kinetic sorption experiments for Resin 2

Batch kinetic sorption experiment was performed by using $HgCl_2$ solution $(3.74 \times 10^{-4}$ M).

The rate constant of adsorption was studied with the help of the pseudo-first-order rate expression of Lagergren model and the pseudo-second-order kinetic rate expression of Ho and McKay.

The pseudo-first-order equation assumes that the adsorption rate decreases linearly as the adsorption capacity increases, which is suitable especially for low concentrations. A linear form of this model is:

$$\ln(q_e - q_t) = \ln q_e - \left(\frac{k_1}{2.303}\right)t \tag{1}$$

The pseudo-second-order kinetic model assumes that the rate limiting step is the interaction between two reagent particles. This model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where k_2 is the constant of pseudo-second-order rate (g/mg min), and q_t is the adsorption amount at time t. Plotting t/q_t vs t, straight lines were obtained. And the constant k_2 and q_e values for Hg (II) was calculated. Accordance with the pseudo-second-order reaction mechanism, the overall rate of Hg (II) adsorption processes appears to be controlled by the chemical processes, through sharing of electrons between adsorbent and adsorbate, or covalent forces, through the exchange of electrons between the particles involved.

The pseudo-first-order kinetic model having a low value for R^2, does not present a good fit with experimental data. In contrast, in the case of pseudo-second-order kinetic model, the high values of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic model.

Regeneration of Resin 2

Mercury loaded Resin 2 was regenerated by using glacial acetic acid. Regeneration capacity was found as about 3.0 mmol/g resin. According to these results, Resin 2 was regenerated efficiently.

ÇAPRAZ BAĞLI KUARTERNER AMİD-SÜLFONAMİD İÇEREN REÇİNE HAZIRLANMASI VE SULU ÇÖZELTİLERDEN CİVA İYONLARININ UZAKLAŞTIRILMASI İÇİN KULLANILMASI

ÖZET

Ağır metal kirliliği günümüzün en önemli çevre problemlerinden biridir. Bunun en önemli sebebi çeşitli endüstirilerin ürün ve atıklarında bulunan ağır metal içerikleridir.

Metal iyonları doğada yok olmamakla birlikte, zamanla birikerek toksisite seviyesi de artmaktadır. Çok düşük konsantrasyonlarda bile, zararlı ağır metal iyonları, gelişim bozukluklarına, kansere, organ ve sinir sistemi tahribatına, daha ileri safhalarda ise ölüme neden olabilmektedir.

Ağır metal kontaminasyonu en çok hava ve su yoluyla gerçekleşmektedir. Ağır metaller doğal sularda ve atık sularda bulunabilir. Endüstriyel atık suların deşarj edildiği veya yatağından dolayı yüzeysel sularda ve yeraltı sularında ağır metallerin varlığı, bulunduğu ortama ve bu tip suları kullanan canlılara zehir etkisi yapabilir. Bunun yanı sıra ağır metaller, su canlılarının bünyelerinde birikirler. Bu birikim ağır metal konsantrasyonlarının önemini bir kat daha fazla artırmaktadır. Bu yüzden ağır metal içeren endüstriyel atık suların, alıcı ortamlara deşarjlarından önce arıtılması, ekolojik dengenin ve insan sağlığının korunması açısından önemlidir.

İnsanların ihtiyaçlarının artması ile bağlantılı olarak sanayilesmedeki gelişmeler, atık su miktarını ve ağır metal yükünü art,tırmıstır. Madencilik, metal sanayi, petrol rafinerileri, deri sanayi ve fotoğraf stüdyoları ağır metal kirliliğine katkıda bulunan başlıca kaynaklardan bazılarıdır .

Bunların yanı sıra evsel atık sular, çöp depolama alanları sızıntı suları, tarım arazilerinin yağış ile yıkanması ve asit yağmurları da atık sulardaki ağır metal konsantrasyonlarında artışa neden olmaktadır. Kurşun, kadmiyum, nikel, civa ve çinko, atık sularda karşılaşılan yaygın ağır metallerdir. Ağır metallerin konsantrasyonları, atık suyun kaynağına göre farklılık gösterir.

Faz ayırma metotlarındaki gelişmelere paralel olarak ağır metallerin giderim teknolojilerinde önemli gelişmeler olmuştur. Çökeltim, iyon değistirme, elektrokimyasal süreçler ve membran prosesleri, endüstriyel atık suların arıtımında yaygın olarak kullanılmaya başlanmıştır. Ancak bu proseslerin uygulamasında teknik ve ekonomik yönden zorluklar olabilmektedir. Bu nedenle, atık sulardan özellikle toksik metalleri giderilmesi amacıyla teknolojik yönden yeni araştırmalar yapılmış ve bunun sonucunda adsorpsiyon ve biyosorpsiyon prosesleri uygulama alanına girmeye başlamıştır.

Civa, endüstiride yaygın kullanım alanı bulan ve çevre kirliliğine neden olan en önemli ağır metaldir. Bütün civa komponentlerinin, yüksek toksisitesi nedeniyle sıvı atıklardan ve içme sularından uzaklaştırılması, çevre için özel bir öneme sahiptir.

Civa gibi inorganik maddelerin atık sulardan uzaklaştırılması organik maddelere nazaran daha zor bir prosestir. Çünkü inorganik maddelerin giderilmesi için, bu

maddelerle kimyasal bağ oluşturabilecek ligand grupları taşıyan adsorbanlara ihtiyaç vardır.

Civanın seçici olarak giderilmesinde ligand bağlı polimerlerin kullanımı bir çok bilimsel makale ve derlemenin konusunu oluşturmaktadır.

Üzerinde heteroatom ya da doymamış bağlar bulunan polimerler ağır metalleri bağlama yeteneğine sahiptirler. Doğada hemen her maddenin baska bir maddeyi tutma eğilimi vardır. Burada önemli olan tutmanın miktarı ve seçimliliğidir.

Civa seçiciliği ve civayı bağlama kapasitesi yüksek olan sülfür ve amid ligandları, en yaygın olarak kullanılan ligand çeşitleridir.

Atom yada molekül halindeki civa, yapısında sülfür veya sülfür hidrojen kombinasyonu olan moleküller ile bağlanmaya isteklidir. Bu büyük birleşme isteği nedeniyle sülfür içeren ligandlar çok yakın ilgiye maruz kalırlar.

Nitrojen civa ile bağ yapma eğilimi olan, önemli diğer bir atomdur. Özellikle amid ligandları civa iyonu ile kompleks oluşturmaya meyillidirler. Amid bileşikleri, mono yada diamido civa bileşikleri oluşturmak için civa iyonlarıyla rahatlıkla reaksiyona girer.

Bu çalışmada, çapraz bağlı klorosülfonlanmış polistiren reçineden başlanarak, çapraz bağlı sülfonamid reçine hazırlanmış ve civa seçiciliği araştırılmıştır.

Reçine 1, klorosülfonlanmış polistiren (CSPS) ve N,N-dimetiletilendiamin'in fazlasının reaksiyona sokulmasıyla hazırlanmıştır. Reçine 2 ise, Reçine 1'in dimetil formamid (DMF) çözücüsünde 2-klor asetamid ile kuarternizasyonu yoluyla elde edilmiştir.

Reçine 1 ve Reçine 2'nin karakterizasyonları, analitik metotlar ve Infrared Spektrofotometresi (FT-IR) kullanılarak yapılmıştır.

Reçinelerin Civa ve Ağır Metalleri Tutması

Civa adsorpsiyon deneylerinde $HgCl_2$ kullanılmıştır. Hazırlanan reçinelerin civa tutma kapasiteleri, Hg(II)'nin çeşitli konsantrasyonlarda hazırlanan (0.074 M, 0.050 M and 0.025 M) sulu çözeltilerinin, belirli bir miktar reçine ile etkileştirilmesi sonucu belirlenmiştir. Civa yükleme kapasiteleri, çözeltilerin başlangıç ve sonuç Hg(II) içeriklerinden hesaplanmıştır. Deneyler Cd(II), Mg (II), Zn (II) ve Fe(III) ağır metalleri ile de tekrarlanarak reçinelerin bu metal iyonlarını tutma kapasiteleri incelenmiştir.

Reçine 1, hem Civa (II) iyonlarını hem de diğer metal iyonlarını adsorplamıştır.

Normal şartlarda amid ve sülfonamid grupları, amid grubundaki azotun elektron verme eğiliminin düşük olması dolayısıyla, geçiş metallerinin iyonlarıyla koordinatif bağ yapamaz. Bu nedenle Reçine 2'nin Civa (II) tutmasının oldukça seçici olması beklenmektedir.

Reçine 2'nin Civa (II)'yi tutma kapasitesi yaklaşık 3 mmol / g, diğer metal iyonlarını tutma kapasiteleri ise 0.20-0.30 mmol / g reçine olarak tespit edilmiştir.Elde edilen sonuçlar da reçinenin Hg(II)'ye karşı oldukça seçici olduğunu göstermektedir

Reçine 2 için kinetik adsorpsiyon deneyleri

Kinetik deneyleri $HgCl_2$'nin sulu çözeltisi (3.74×10^{-4} M). kullanılarak yapılmıştır.

Reçine 2'nin adsorpsiyon kinetiği, zamana karşı reçinenin civa tutma kapasitesi (q_t -mg adsorbe edilmiş civa iyonu/g reçine) grafiği ile incelenmiştir..

Adsorpsiyon hız sabitleri, yalancı birinci mertebe kinetiği için Lagergren modeli ile, yalancı ikinci mertebe kinetiği için ise Ho ve McKay'ın modeli ile çalışılmıştır.

Özellikle düşük konsantrasyonlar için uygun olan Lagergren modelinde, adsorpsiyon kapasitesi arttıkça adsorpsiyon hızının doğrusal olarak azaldığı kabul edilir. Bu modelin lineer biçimi Eşitlik 1'de verilmiştir.

$$\ln(q_e - q_t) = \ln q_e - \left(\frac{k_1}{2.303}\right)t \tag{1}$$

Yalancı ikinci mertebe kinetik modelinde ise hız belirleyici basamağın, iki reaktan arasındaki etkileşimin olduğu kabul edilerek yapılır. Bu model Eşitlik 2'deki gibi ifade edilir:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \tag{2}$$

Eşitlik 2'de k_2 ; yalancı birinci mertebe hız sabitini (g / mg dakika) , q_t ise zamana bağlı (t) adsorplanan madde miktarını belirtmektedir. Elimizdeki veriler doğrultusunda " t / q_t "ye karşı "t" grafiği çizildiğinde doğrusal bir ilişki elde edilir.

Hg(II)'ye ait yalancı birinci mertebe hız sabiti (k_2) ve denge konsantrasyonu (q_e) değerleri hesaplanmıştır.

Yalancı ikinci mertebe reaksiyon mekanizmasına göre, kimyasal proseslerde Hg (II) adsorpsiyonunun toplam hızını adsorplanan ve adsorplayıcı gruplar arasındaki elektronların paylaşılmasıyla, kovalent bağlarla ve partiküller arasındaki elektron alış verişi ile belirlenmektedir.

Yalancı birinci mertebe kinetik modeli düşük korelasyon katsayısı (R^2) değerleri nedeniyle, verilerimizle uygunluk göstermemektedir. Buna karşılık, yalancı ikinci mertebe kinetik modeli uygulandığında, elde edilen yüksek korelasyon katsayıları göstermiştir ki, verilerimiz yalancı ikinci mertebe kinetik modeliyle oldukça uyumludur.

Reçine 2'nin Geri Kazanımı

Reçinelerin etkin olarak kullanılabilmesi için reçinenin geri kazanımı büyük önem taşımaktadır.

Bu çalışmada civa yüklü Reçine 2'nin, glasiyel asedik asit kullanılarak geri kazanımı sağlanmaya çalışılmıştır. Reçine 2'nin geri kazanım kapasitesi 3.0 mmol / g reçine olarak bulunmuştur. Bulunan sonuca göre reçinenin geri kazanımından verim alındığı görülmüştür.

1. INTRODUCTION

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy metals into the environment, such as mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc.

Mercury is used in a wide variety of industries such as electrical paints, fungicides, chlor-alkali, paper and pulp, pharmaceutical, etc.. Because of the high toxicity of all mercury compounds, the extraction of mercuric ions from aqueous wastes and drinking water are special environmental importance. One estimate of the total annual global input of mercury to the atmosphere from all sources including natural, anthropogenic, and oceanic emissions is 5500 tons.

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies. These technologies include chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption.

Ion exchange resins have been widely used in the removal of inorganics. On the other hand, the selective and quantitative separation of metal ions related to water pollution problems has received increasing importance in recent years. Two common ligand types, sulfur and amide are being used currently in the design of polymer sorbents for binding mercuric ions selectively. Amide containing polymers include an iminodiacetamide, a dipridylamide and polythiourea on charcoal are another important for binding highly selective Hg(II). Amide groups form covalent mercury–amide linkages under ordinary conditions.

In this study, new polymeric resin with quaternary amide containing sulfonamide based sorbent has been prepared for removal of mercuric ions. Mercury sorption

characteristics and regeneration conditions of the resulting resins have been studied. Affinity of the resins for other metal ions such as Cd(II), Mg(II), Zn(II) and Fe(III) have been also be investigated.

2. THEORY

2.1 Toxic Metal Ions and Their Harms

Many metals are of concern because of their toxic properties and some metals are also essential for survival and health of animals and humans. Thus metals have been classified as essential, beneficial, or toxic.

Trace elements recognized as essential for human health include iron, zinc, copper, chromium, iodine, cobalt, molybdenum, and selenium. On the other hand it is increasingly recognized that higher intakes of some of the trace elements may have beneficial health effects in relation to risk reduction of degenerative diseases such as cardiovascular disease and cancer. There is increasing use of various standards worldwide that express the maximum acceptable limits for human exposures for various substances present in the environment including nutritionally essential trace elements.

The second group of elements thought to be beneficial to life such as silicon, manganese, nickel, boron, and vanadium. Some of these elements may be essential to vegetative life and perhaps beneficial to human health but, generally, they are not yet accepted as essential for human health.

Lastly toxic metals are regarded as purely toxic metals such as lead, cadmium, uranium and mercury, which are not known to provide any essential or potentially beneficial health effect at any level of exposure [1]. Environmental contamination with metal ions is of growing public concern because of health risks posed by human and animal exposure. Even at a very low level, detrimental heavy metal ions can cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death [2].

2.2 Mercury

Mercury is the most mobile metal of all the metals. In its ground or zero-oxidation state (Hg^0), mercury is the only metal that is liquid at room temperature. Liquid

metallic mercury can form stable amalgams with a number of other metals. Mercury has two oxidation states each capable of forming a variety of chemical compounds. In the mercurous state, two atoms of mercury, each having lost one electron, form the mercurous ion ($Hg-Hg^{++}$). Mercuric mercury (Hg^{++}), where two electrons have been lost from one atom of the metal, forms most of the compounds of mercury. Mercuric mercury can also form a number of ''organic mercury'' compounds by bonding to a carbon atom, for example, the phenyl ($C_6H_5-Hg^+$) and methyl (CH_3-Hg^+) mercuric cations [3].

The average content of the earth's crust is approximately 50 ppb mercury, mainly as sulfide. Mercury is used in catalysts, paints, dental fillings, electrical equipment and for several laboratory purposes. Mercury is widely applied in industry and agriculture. The main industrial uses of Hg are chlor-alkali industry (electrolysis), electrical and control instruments industry, laboratory products, dentistry (dental amalgams), and pulp and paper industry. In agriculture, Hg is used as a seed dressing in grain, potatoes, flower bulbs, sugar cane, etc., and as a foliar spray against plant diseases [4].

Most human exposure to mercury vapor is in the occupational setting sand from dental amalgam, and to methyl mercury in diets containing fish and seafood [5]. Owing to the introduction, in recent years, of controls over the uses of mercury, occupational exposures have diminished. In fact, gold mining has become a major source of human exposure in many developing countries in recent years [6-8].

Mercury is present in many health care products, not just the old-fashioned thermometers, but in sphygmomanometers, dilation and feeding tubes, batteries, fluorescent lamps, laboratory chemicals [2], as a solvent for the silver-tin amalgams used in dental fillings [1].

There are substantial differences in toxicity of elemental mercury metal, inorganic mercury salts,and organometallic mercury compounds.

Metallic mercury (liquid mercury, quicksilver, hydrargyrum (hence Hg), elemental mercury), is a silver white metal which melts at -38.7°C. Mercury is best known as a liquid metal, having a vapour pressure (a measure of the amount of vapour 'given off') of 0.002 mm Hg at 25°C. This approximately doubles for every 10°C increase in temperature, so that heating metallic mercury greatly increases the associated

risks, as inhalation is the usual route of toxicity. Inhaled mercury vapour accumulates in the body, and in particular the central nervous system, which is the site of its major toxic actions [1]. Elemental mercury is found in ore, fossil fuels, mining, volcanoes, medical waste incinerators (vapor); thermometers, barometers, dental amalgam (liquid); and fluorescent light bulbs, disk button batteries, thermostats, switches, home remedies [3].

Inorganic mercury salts are present in nature in various colours ranging from the white oxides to the browns and blacks of the sulphide compounds. They are also commonly used in industry. They have been used in medicine in teething powders, skin-lightening creams and as preservatives in certain medicines particularly as eyedrops. Mercury (I) chloride (calomel) was widely used as a purgative in the form of the 'blue pill'. The toxicity of mercury salts varies with their solubility. Usually mercury (I) compounds are of low solubility and significantly less toxic than mercury (II) compounds. Inorganic mercury salts present a far greater hazard than elemental mercury if ingested orally, owing to their greater water solubility.Mercury salts are usually non-volatile solids, so poisoning by inhalation is rare, though toxicity may arise if aerosols are deposited in the lungs[1]. Inorganic mercury is found in mercury salts (combined with either chlorine, sulfur, or oxygen). Currently banned in the United States, inorganic mercury had been used in products such as calomel teething powders and skin lighteners, and fungicidal diaper rinse [3].

Organic mercury compounds are an important cause of poisoning. Mass outbreaks have occurred throughout the world, either inadvertently secondary to pollution, or via direct ingestion of organic mercury compounds. In the developed world, exposure is most commonly via the aquatic food chain, where micro-organisms convert elemental mercury to organic mercury before being eaten by larger invertebrates and so on up the chain, ending with man [1]. Organic mercury is found in three compounds: methyl-, ethyl- and phenyl mercury. Methyl mercury is the most toxic, formed by microorganisms from elemental mercury found in the environment via human or natural sources . Incineration of mercury containing products is a key human source. Consuming fish is the primary route of exposure in children. Others sources include fungicides, industrial waste, and breast milk. Ethylmercury, found in thimerosal, was used as an antiseptic and preservative as in childhood vaccinations as well as contact lens solution [3]

2.2.1 Clinical effects of mercury

Elementel mercury; at high concentrations, vapor causes acute necrotizing bronchitis and pneumonitis. insomnia, forgetfulness, and mild tremor, to progressive tremor, erethism seen as red palms, salivation, excessive sweating. It accumulates in the kidneys producing protenuria or nephrotic syndrome.

Inorganıc mercury; ingestion, generally inadvertent or a suicidal gesture, results in hemorrhage, gastrointestinal ulceration, and circulatory collapse. Infants exposed to teething powder, diaper rinse, or latex paint often developed acrodynia— childhood mercury poisoning—or pink disease, which is characterized by painful extremities, maculopapular rash, hypertension, peripheral neuropathy, and renal tubular dysfunction.

Organic mercury; route of exposure, dose, age, and compound all cause varying toxicity. Acute toxicity signs include paesthesias to generalized weakness, visual and hearing impairment, tremor, muscle spasticity, coma, and death . Long-term exposure is much the same. Chronic fetal exposure leads to symptoms showing afterbirth such as psychomotor retardation, blindness, deafness, seizure disorders, and cerebral palsy . The fetus and infant are known to be more at risk due rapid brain development and mercury's neurotoxicant properties. Ethyl mercury has caused hypersensitivity as well as generating concerns about triggering autism in infants after routine immunizations [3].

2.3 Functional Polymers

Since the first generation of ion-exchange resins and membranes, the development of functional polymer chemistry and technology has made remarkable progress in recent years. For example, studies related to the preparation and design of several enzymes and nucleic acid models have advanced dramatically, and the development of the technology necessary to use these polymers is of current interest.

Functional polymers, in a broad sense, include a variety of polymeric materials and a number of engineering plastics. These polymer systems often exhibit more specific and better properties if processed as polymer aggregates. For example, organic polymers with polyconjugated double bonds consisting of special structures are known as synthetic metals, which show substantially high electron conductivity in a

fiber or film form. On the other hand, ceramic materials with new properties, such as elasticity, have only recently prepared by organic synthetic techniques.

Recently, microporous polymeric materials as well as microcapsules have become of interest in a variety of industrial fields, not only in the general chemical industry, but also in the pharmaceutical, biomedical and electronics industries. For example, fluorine-containing resins are important, particularly, as a safe and durable anti-thrombogenic biomaterial. Microporous membranes made of vinyl polymers are being applied as separators or filters to concentrate oxygen from air and to manufacture ultrahigh grades of water for the semiconductor industry. Other types of microporous vinyl polymers are being used as highly hydrophilic materials in the fields of cosmetics and environmental hygiene.

The science and technology required for the preparation of microcapsules from different natural and synthetic polymeric materials has made rapid progress. They are being used in various fields for their ability to solidify liquids; to isolate reactive compounds; to remove color, odor, and toxicity; as well as to regulate and control the release of included compounds. The immobilization of enzymes and the development of polymeric drugs are also playing an important role.

In addition, highly water-absorbing and oil-absorbing resins are of interest. These have developed rapidly in recent years by unique grafting and crosslinking of hydrophilic polymers. Transparent polymeric materials with optical functions are also noteworthy. Some are biocompatible, such as poly(2-hydroxethyl methacrylate), which serves as a material for soft contact lenses. Plastic optical fibers are also widely used as substitutes for glass and quartz devices in various fields of technology, especially the biomedical and communication sciences.

The chemistry of so-called electronic functional polymers, in a narrow sense, has developed into a very exciting subject, particularly in the last 10 years. Some of the most attractive materials in this field are the photosensitive and photoresponsive polymers. By using these phenomena, specifically designed polymers undergo reversible crosslinking reactions to become insoluble or soluble. A variety of both negative and positive types of photoresists are being produced. They are initially used in printing, paint, and color industries. The technology to exploit deep ultraviolet (UV) radiation resist with reversible functionality will be one of the most

important developments in this industry in the near future. Other subjects of interest in this field, which are under development, are the electronic or X-Ray sensitive resists, as well as the design of more functional photomemory materials.

In connection with biomedical polymers, the chemistry of the polymeric drugs is under continuous advancement. The most effective anti-carcinogenic reagent is now targeted by the design of specifically functionalized polymers. The functional polymeric composites are also particularly attractive as implant materials [9].

2.3.1 Properties of functional polymers

There are a number of considerations in the choice of the functional polymers to be used in a specific application functionalized polymer must possess 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.

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 contamned 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 porous 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 gel-type resins

This type of resins are generally prepared by suspension polymerization using a mixture of vinyl monomer and small amounts (less than 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 cannot 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 [10].

2.4 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

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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 [11].

Among the many ligands [12] introduced 8-acryloyloxyquinoline is one of the recent origin.

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 [13].

2.5 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 Figure 2.1.
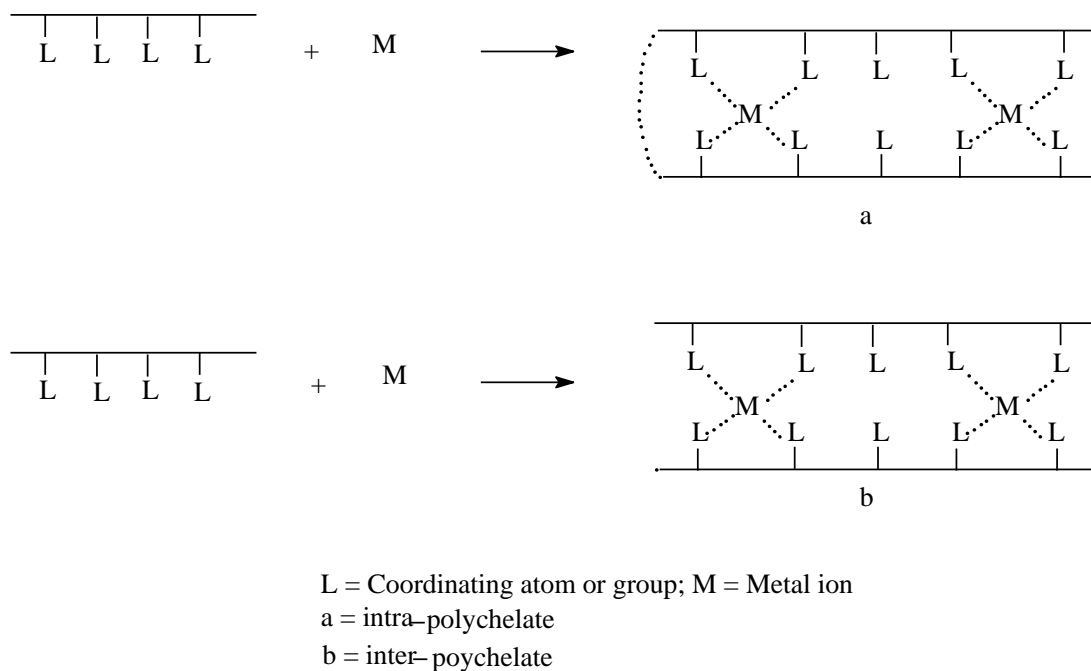

L = Coordinating atom or group; M = Metal ion
a = intra‒polychelate
b = inter‒poychelate

Figure 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 [14].

2.6 Mercury Sorbents Depending on Their Functional Group

Sulfur and amide are the two common ligand types, which are being used currently in the design of polymer sorbents for binding mercuric ions selectively. Mercury, in its various forms, has a great affinity for certain atoms. Sulfur is one of the most important atoms that mercurial have a great attraction to. The mercury atom or molecule will tend to bind with any molecule present that has sulfur or a sulfurhydrogen combination in its structure. Thus sulfur containing ligands has received much recent attention, in part due to this great affinity. Nitrogen is the other important atom that has a great affinity for mercury ion. Especially amide ligands tend to complex with mercury ion. Amide compounds readily react with mercuric ions under ordinary conditions to give mono- or diamidomercury compounds. The mercury–amide linkage is believed to be covalent rather coordinative [15]. In the past decade, there are several studies were conducted on removal of Hg(II) ions from aqueous media by polymers carrying pendant sulfur and nitrogen containing ligands. Senkal et al. synthesized poly(acrylamide) grafted poly(styrene) (Figure 2.2) and removed mercury ions with 5.75 mmol/g sorbent removing capacity [16].
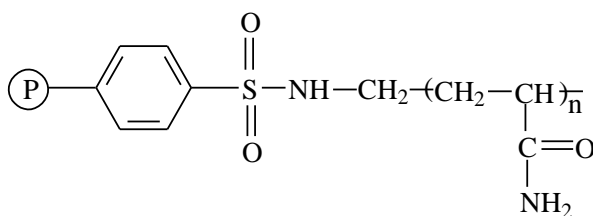

Figure 2.2 : Poly(acrylamide) grafted poly(styrene) [16].

Crosslinked Poly(glycidyl methacrylate) (PGMA) based resin with acetamide functional group (Figure 2.3) were demonstrated to be efficient in the removal of mercury by Senkal et al. in 2006. The mercury sorption capacity of the resin was found as 2.2 mmol/g resin in this study [17].
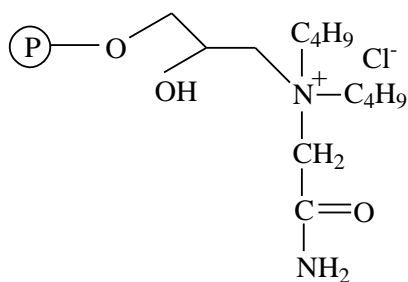
Figure 2.3 : Crosslinked PGMA based resin with acetamide functional group [17].

Cellulose based sorbents have been studied by several research groups all around the world because of the excellent properties that cellulose serves. Poly(acrylamide) grafted onto cellulose was synthezied by Bicak et al. (Figure 2.4) has been demonstrated to be a very efficient selective sorbent for removal of Hg(II) from aqueous solutions [18].
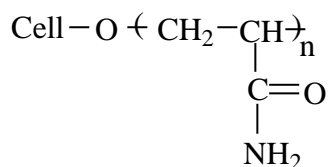

Figure 2.4 : Poly(acrylamide) grafted cellulose [18].

A new polymeric resin with thiol pendant functions has been prepared for the extraction of mercuric ions. The thiol containing sulfonamide based resin with 3.5 mmol/g total nitrogen content is able to selectively sorb mercury from aqueous solutions. The mercury sorption capacity of the resin is around 1.70 mmol/g under non-buffered conditions [19].

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3. EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

Styrene (Fluka), Divinylbenzene (55 % grade)(DVB) , Dibenzoyl peroxide (Fluka), Gum Arabic, Chlorosulfonic acid (Fluka), Triethyl amine (Fluka), Diphenylcarbazide (E-Merck), Mercury(II) chloride (E-Merck), Iron(III) chloride (E-Merck), Magnesium sulphate (E-Merck), Zinc sulphate (E-Merck), Cadmium nitrate (E-Merck), Hydrochloric acid (HCl) (E-Merck), Ethylenediamine tetra acetic acid (E-Merck), Eriochrome black-T (E-Merck), N,N-dimethyl ethylenediamine (Aldrich), Chloroacetamide (Aldrich), Dimethyl formamide (DMF), 2-methyl pyrrolidone (NMP), Ethanol, Acetic acid.

3.1.2 Instruments

UV-vis spectrophotometer (Perkin Elmer, Lamda 25) and Thermo FT-IR (with ATR).

3.2 Preparation of Polymeric Sorbents

Crosslinked poly (styrene-divinyl benzene) beads was synthesized and chlorosulfonated with chloro sulfonic acid. The obtained resin was reacted with N,N-dimethyl ethylenediamine and chloroacetamide to prepare sulfonamide based quaternary acetamide sorbent.

3.2.1 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 [20]. The beads were sieved and the 420-590 μm size fractions were used for further reactions.

3.2.2 Chlorosulfonation of the beaded polymer

The beaded polymer was chlorosulfonated using chlorosulfonic acid as described in the literature [20] as follows: 10 g of crosslinked PS-DVB resin was interacted with 45 mL of chlorosulfonic acid at 0 ^{0}C for 2 h and at room temperature for 18 h. The reaction mixture was added slowly to ice-water mixture and was stirred at 0 ^{0}C for 20 min. Chlorosulfonated resin was filtered under vacuum and was washed with excess of cold water, acetone and ether respectively. 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 (5M), the chlorine content was determined by the mercuric-thiocyanate method [21] and was found to be about 3.50 mmol. g^{-1} which corresponds to ~61 % chlorosulfonation.

3.2.3 Sulfonamidation reaction with chlorosulfonated polystyrene resin (CSPS) and *N,N*-Dimethylethylenediamine (Resin 1)

Chlorosulfonated resin (10 g.) was added portion wise to a stirred of N-N Dimethylethylenediamine (12 mL) (0.05 mol) in 2-methyl pyrrolidone 30 ml at 0^{0}C. 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 9.86 g.

3.2.3.1 Determination of sulfonamide content of the Resin 1

Sulfonamide content of the sorbent was determined titrimetrically. For this purpose, the sulfonaminated polymer sample (0.1057 g) was added to 10 mL of 0.5 M NaOH and continuously shaken for 24 h. After filtration, 5 mL of the filtrate was titrated with 0.5 M HCl solution. By comparison with the result for the unreacted solution, the sulphonamide content was found as 2.84 mmol.g^{-1}.

3.2.4 Reaction of crosslinked tertiary amine containing beads with chloroacetamide (Resin 2)

4 g of tertiary amine containing beads were soaked into a solution of 3 g (0.0321 mol) 2-chloroacetamide in 30 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 4.7 g.

3.2.4.1 Chloride analysis

The quaternization yield was followed by analysis of the chloride ions in the final product. Thus, 0.1 g of the quaternized beads was boiled in 9 mL of 10% NaOH solution for 3 h. Analysis of the chloride ion solution was performed by the mercuric thiocyanate method as described in the literature.[20] Chloride content of the sorbent was found as 2.5 mmol/g.

3.3 Mercury and Heavy Metal Uptake Measurements of The Resins

The mercury and heavy metal sorption capacities of the resins were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous $HgCl_2$ solution (0.074 M).

Similar experiments were repeated under the same conditions with different initial mercury concentrations (0.025 and 0.05M). No buffer was used in these experiments. The sorbed amounts were calculated according to the residual mercury contents, as previously described. The relevant data are listed in Table 1. The mixtures was stirred for 24 hours at room temperature and then separated by 0.45 μm filter membrane. The Hg(II) concentration was determined colorimetrically using diphenylcarbazide [22]. The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solutions. The pH of mercury solutions remained almost constant, in the 3.1–3.9 range, throughout the extraction process. To inspect mercury efficiency of the resin, metal extraction experiments were repeated with Cd(II), Zn (II), Mg(II), and Fe(III) solutions (Table 1).

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 ethylenediamine tetra acetic acid (EDTA) solution (0.1 M).

3.4 Mercury Sorption Kinetics of the Sorbent

In order to estimate efficiency of the Resin 2 for trace mercury batch kinetic experiment was performed using high diluted $HgCl_2$ (3.70×10^{-4} M) solutions. For this purpose 0.2 g of sorbent was wetted with 1 mL of distilled water and added to a solution of Hg (II). The mixture was stirred magnetic stirring bar and aliquots of the solution (5 ml) were taken at appropriate time intervals for analysis of the residual Hg (II) contents by the method as mentioned above. Batch kinetic experiments were also performed at pH=6.

3.5 Regeneration of the Adsorbent

For desorption studies, Hg-loaded adsorbent was collected, gently washed with distilled water to remove any unabsorbed metal ions, and then every 0.1 g Hg-loaded adsorbent was left in contact with 10 mL of glacial acetic acid and stirred at 80 $^{\circ}$C for 2 hours. After cooling, the mixture was filtered and 2 mL of the filtrate was taken out for colorimetric analysis of the mercury ion.

4. RESULTS AND DISCUSSION

4.1 Preparation of Crosslinked Polymeric Sorbents

In this study, crosslinked polystyrene–DVB copolymer was prepared and the beads were modified with chlorosulfonic acid , N,N-dimethyl ethylenediamine and chloroacetamide respectively.

4.1.1 Preparation of chlorosulfonated polystyrene resin (CSPS)

Crosslinked polystyrene–DVB copolymer was prepared by using suspension polymerization method according to the literature [20]. The polymer was chlorosulfonated by using excess of chlorosulfonic acid at room temperature for 24 h.
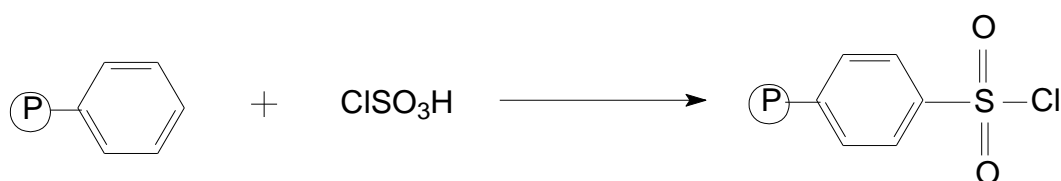

Figure 4.1 : Chlorosulphonation of crosslinked polystyrene.

Chloride analysis of the product in the fist step (3.50 mmol.g^{-1}) revealed a degree of chlorosulfonation of ~ 63 %.

4.1.2 Reaction with CSPS resin and N,N-dimethyl ethylenediamine (Resin 1)

Excess of N,N-dimethyl ethylenediamine was dissolved in NMP (N-Methyl pyrrolidone). Chlorosulfonated polystyrene resin was added portion wise at 0^0C. The reaction was continued at 0 ^{0}C for 2h and at room temperature for 24h. The sulfonamide based tertiary amine containing resin was filtered and washed with excess of water and methanol respectively. The resin was characterized by detection of sulfonamide content according to the literature [20]. Sulfonamide content was found as about 2.84 mmol.g^{-1}.
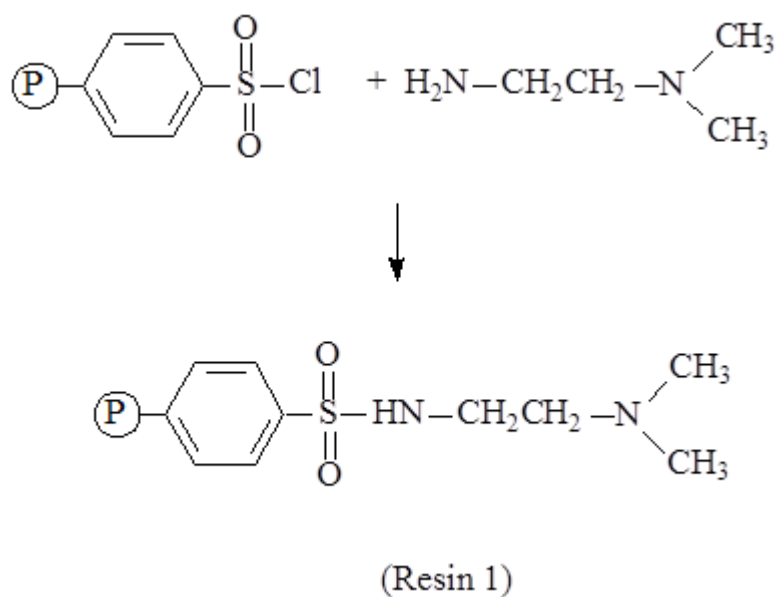
Figure 4.2 : Preparation of Resin 1.

4.1.3 Reaction of crosslinked amine-containing beads with chloroacetamide (Resin 2)

Reaction of crosslinked tertiary amine function resin1 in dimethylformamide with excess 2-chloroacetamide yielded a product with a chloride content of 2.5 mmol/g, corresponding to about 73.5% quaternization.
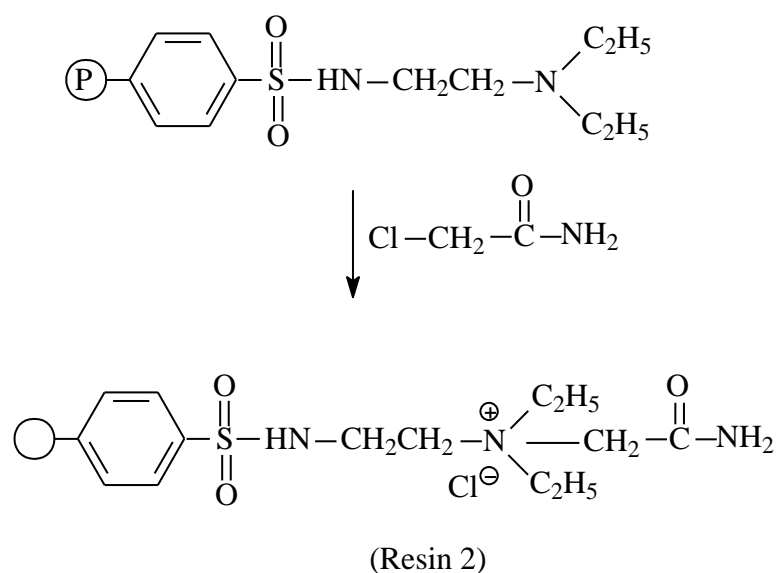

(Resin 2)

Figure 4.3 : Preparation of Resin 2.

Spectroscopic characterization of the resins were performed by FT-IR. In the sulfomidation products for Resin 1 and Resin 2, S=O stretching vibrations of sulfonamide group appear at about 1311 and 1149 cm^{-1}. In addition, the sharp peak at

about 1685 cm^{-1} corresponds to C=O stretching vibration of the amide group in the Resin 2.
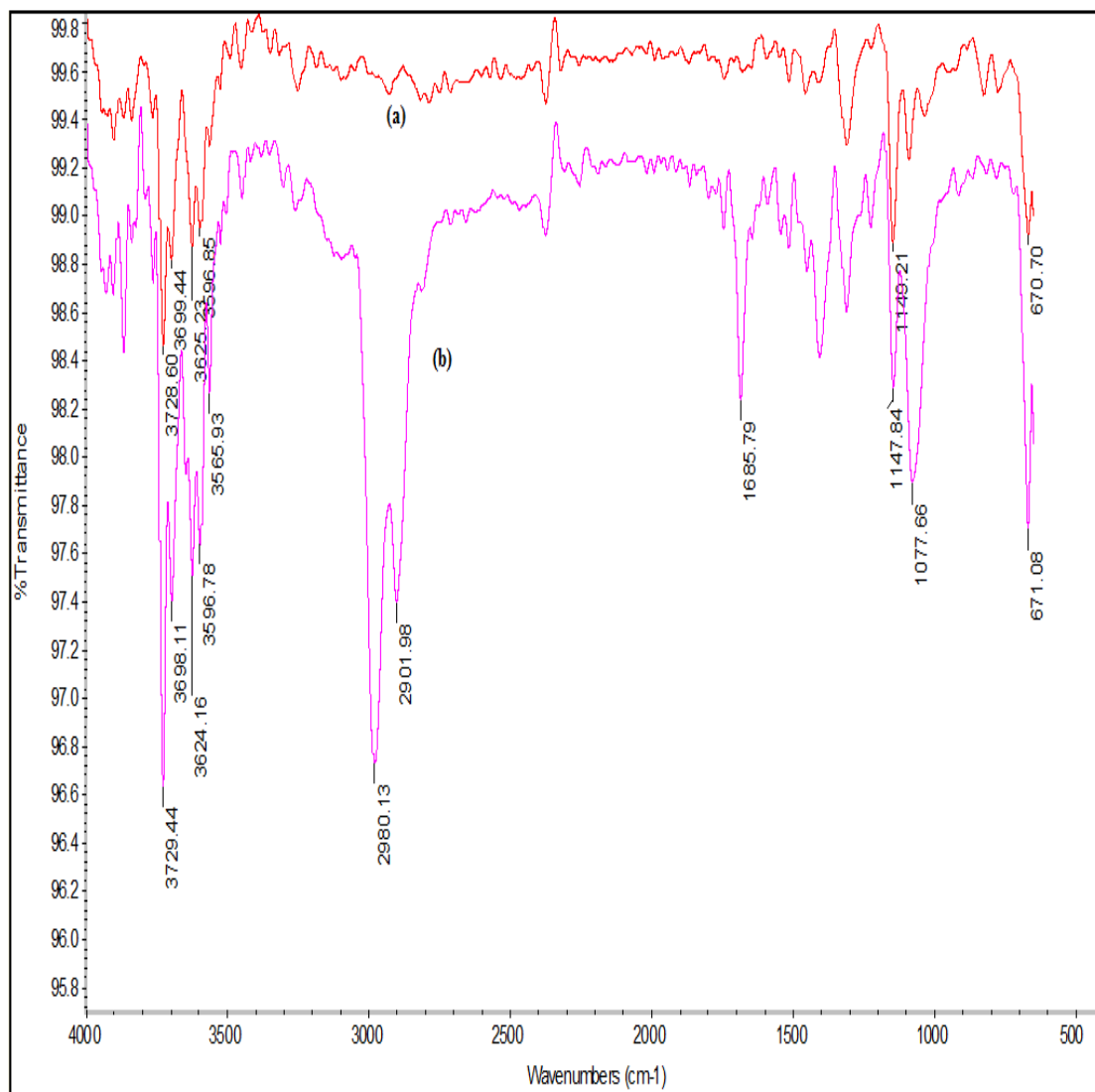

Figure 4.4 : FT-IR spectra of the Resin1 (a) and Resin 2 (b).

4.2 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) solutions with different concentrations (0.074 M,0.05 M and 0.025 M).

The mixture was stirred for 24 h and the filtered. The Hg (II) concentrations were determined colorimetrically using diphenyl carbazide [22].

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

4.2.1 Metal uptake of Resin 1

The sulfonamide containing polymeric sorbent was an efficient sorbent to remove mercury. On the basis of the basic reaction of the mercuric ions with sulfonamide groups, this yielded covalent mercury–sulfonamide linkages [23]. The mercury binding of the polymer can be depicted as shown in Figure 4.5.
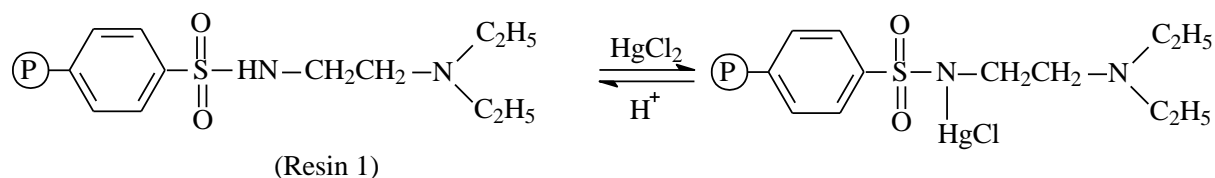

(Resin 1)

Figure 4.5 : Mercury uptake of Resin 1.

The pH of mercury solutions remained almost constant, in the 3.1–3.9 range, throughout the extraction process. Buffer solutions were not used in the experiments because their use is not practical in real application conditions.

Resin 1 has sulfonamide and tertiary amine functions . Especially, amine function group remove heavy metal ions such as Cd (II), Mg(II), Zn (II) and Fe (III) as well as Hg(II) ion 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 [M]	Resin capacity (mmol / g.resin)
Hg(II)	0.074	2.00
Hg(II)	0.050	1.95
Hg(II)	0.025	1.83
Cd(II)	0.150	1.60
Mg(II)	0.15	2.20
Zn(II)	0.15	2.00
Fe(III)	0.15	2.20

4.2.2 Mercury uptake of the Resin 2

Resin 2 has sulfonamide and quaternary amine-amide functions. Based on the basic reaction of mercuric ions with amide and sulfonamide groups, yielding covalent

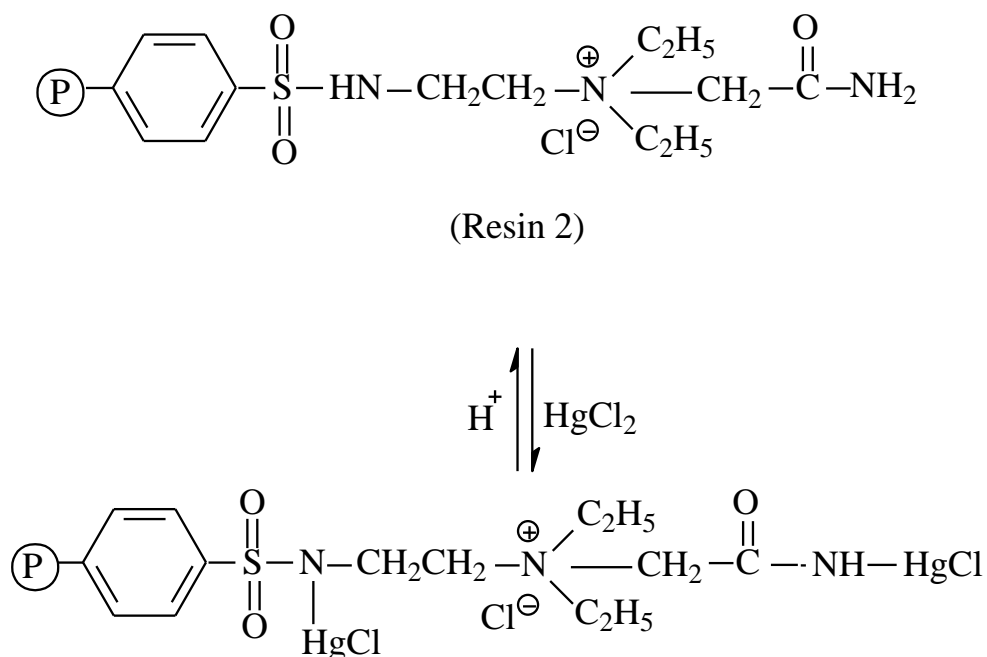mercury-amide and mercury-sulfonamide linkages, mercury binding of the resin can be shown in Figure 4.6.

(Resin 2)

Figure 4.6 : Mercury uptake of Resin 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 0.074 M $HgCl_2$ solution was 3.30 mmol.g^{-1}.

In the 0.025-0.074 M initial mercury concentration range loading capacity of the polymer did not change . To inspect selectivity of the quaternary resin, metal extraction experiments have been reported with Cd (II), Mg(II), Zn(II) and Fe(III).

Since, in ordinary conditions the amide and sulfonamide groups are 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. Other metal ions sorption capacities of the Resin 2

between 0.20-0.30 mmol.g-1 were observed (Table 4.2). Therefore, overall the results clearly indicate that Hg^{2+} sorption is extremely selective.

Table 4.2 : Metal uptake characteristics of the Resin 2.

Metal ion	İnitial concentration (M)	Resin capacity (mmol.g^{-1})	Recovered metal (mmol.g^{-1})
Hg(II)	0.074	3.45	3.20
Hg(II)	0.050	3.30	3.01
Hg(II)	0.025	3.15	-
Cd(II)	0.150	0.32	-
Mg(II)	0.150	0.25	-
Zn(II)	0.150	0.30	-
Fe(II)	0.150	0.24	-

4.3 Kinetics of the mercury sorption

To examine the efficiency of the Resin 2 for trace quantities, kinetic experiments were investigated with extremely diluted $HgCl_2$ solutions (3.70×10^{-4} M).

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 plot in

Figure 4.7. shows that within about 1 hour of contact time, the Hg(II) concentration falls to zero.

The rate constant of adsorption was studied with the help of the pseudo-first-order rate expression of Lagergren model and the pseudo-second-order kinetic rate expression of Ho and McKay [24–26].

The pseudo-first-order equation assumes that the adsorption rate decreases linearly as the adsorption capacity increases, which is suitable especially for low concentrations [27]. A linear form of this model is:

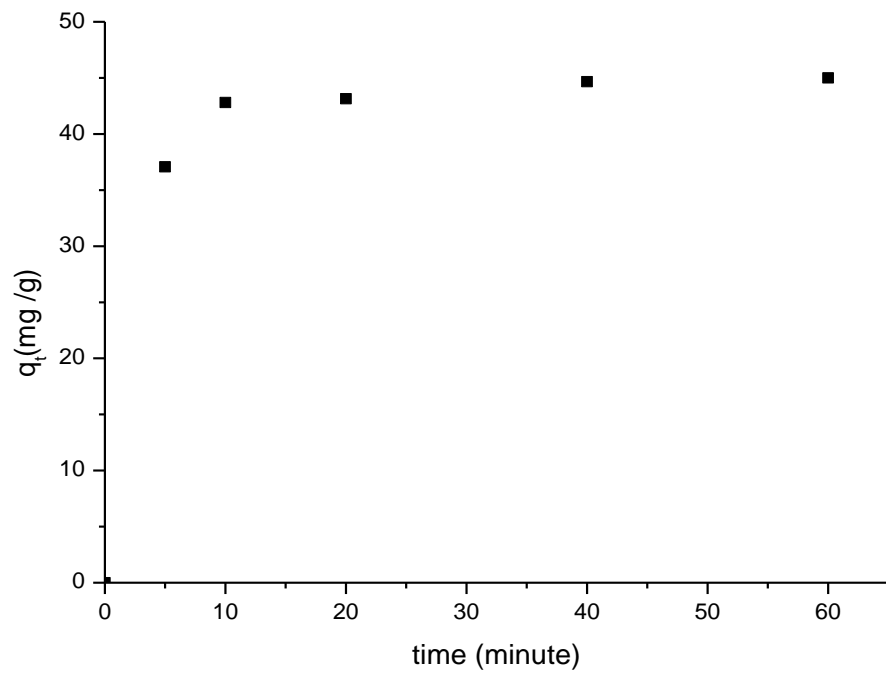$$\ln(q_e - q_t) = \ln q_e - \left(\frac{k_1}{2.303}\right)t \tag{4.1}$$
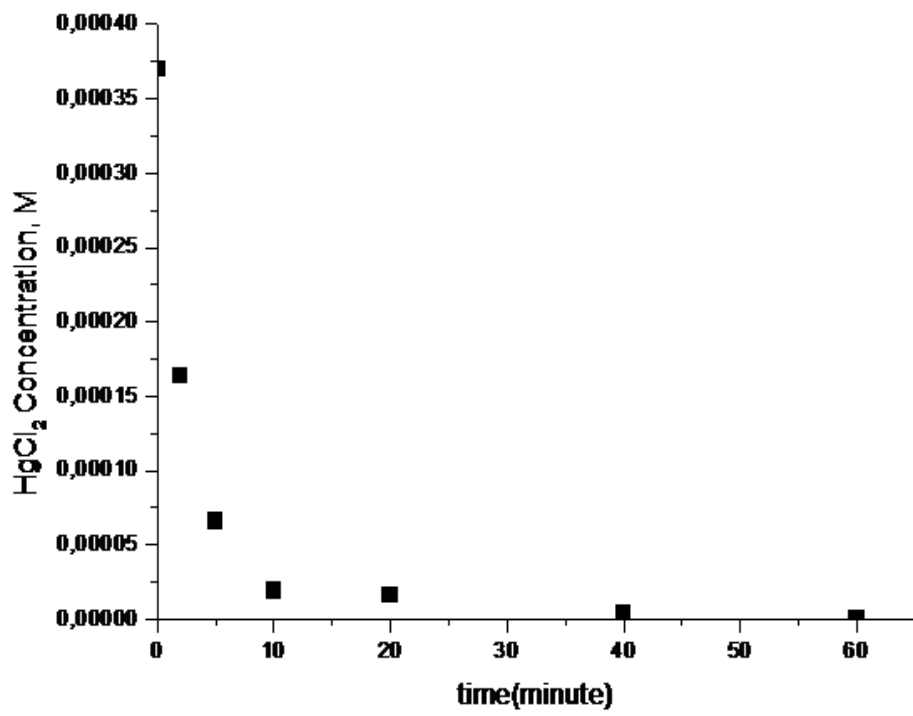
Figure 4.7 : Hg (II) adsorption kinetics of the Resin 2.

where q_t and k_1 are the amount of mercury adsorbed at time t (mmol/g) and the equilibrium rate constant of pseudo-first-order kinetics (1/ min), respectively. The linear fitting of $\log(q_e-q_t)$ with the contact time (t) can be approximated as pseudo-first-order kinetics (Figure 4.8). The low correlation coefficient values obtained for the pseudo-first-order model indicated that adsorption was not occurred exclusively onto one site per ion.
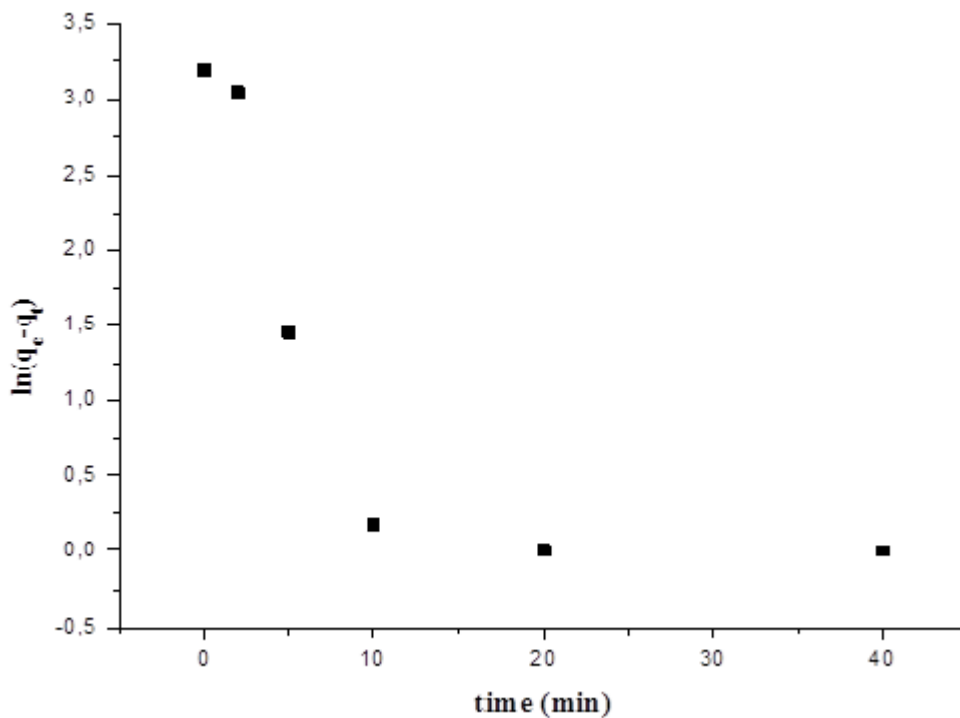

Figure 4.8 : The pseudo 1st order model plots of Hg(II) adsorbed by the Resin 2.

The pseudo-second-order kinetic model assumes that the rate limiting step is the interaction between two reagent particles [27].

This model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e}$$

(4.2)

where k_2 is the constant of pseudo-second-order rate (g/mg min), and q_t is the adsorption amount at time t. Plotting t/q_t vs t, straight lines were obtained (Figure 4.9). And the constant k_2 and q_e values for Hg (II) was calculated and shown in Table 4.3. Accordance with the pseudo-second-order reaction mechanism, the overall

rate of Hg (II) adsorption processes appears to be controlled by the chemical processes, through sharing of electrons between adsorbent and adsorbate, or covalent forces, through the exchange of electrons between the particles involved [28].
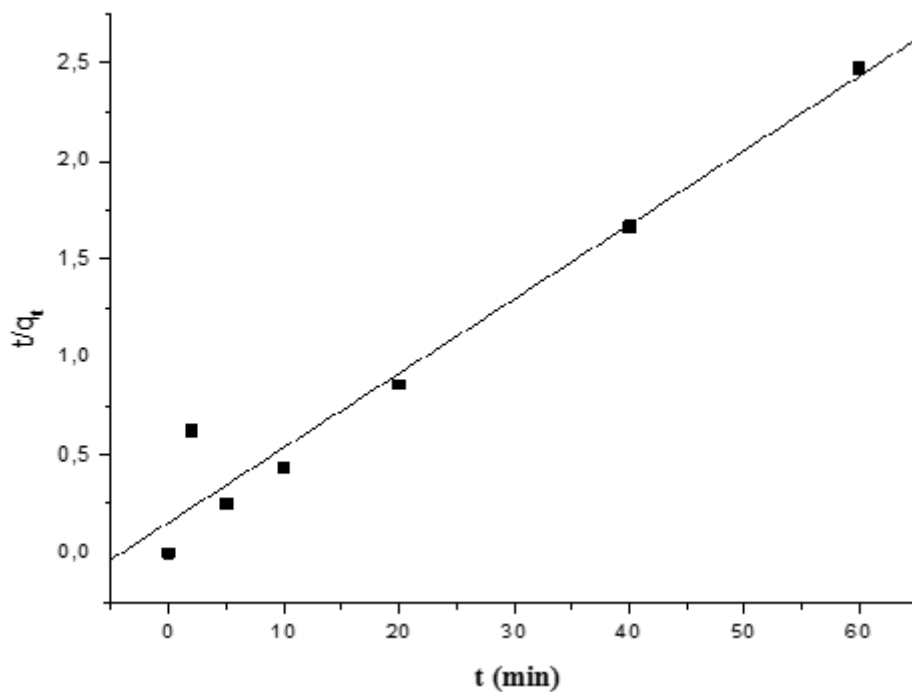

Figure 4.9 : The pseudo 2nd order model plots of Hg(II) adsorbed by the Resin2.

Parameters of the kinetic models of Hg(II) adsorption onto Resin 2 is given in Table 4.3.

Table 4.3. Parameters of the kinetic models of Hg(II) adsorption onto Resin 2.

Kinetic models	Parameters	Hg (II)
Pseudo-first-order	k_1 (1 / min)	0.075
	q_e (mg/g)	9.80
	R^2	0.570
Pseudo-second-order	k_2 (g/ mg min)	43
	q_e (mg/g)	45.0
	R^2	0.9999

According to the data of Table 4.3, the pseudo-first-order kinetic model having a low value for R^2, does not present a good fit with experimental data. In contrast, in the

case of pseudo-second-order kinetic model, the high values of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic model.

4.4 Regeneration of Resin 2

Mercury loaded Resin 2 was regenerated by using glacial acetic acid. Regeneration capacity was found as about 3.0 mmol/g resin. According to these results, resin was regenerated efficiently.

5. CONCLUSION

The new sulfonamide based resins were prepared starting from crosslinked chlorosulfonated polystyrene (CSPS). Resin 1 has sulfonamide and tertiary amine groups. In order to determine possible interference from foreign ions on the mercury uptake, we first treated the polymeric sorbent with each of metal ions; Fe(III), Cd(II), Mg(II) and Zn(II) separately. Hence, these experiments show that the mercury uptake by the polymeric sorbent is not selective. Under non-buffered conditions, the mercury uptake capacity is around 2.00 mmol/g.

Resin 2 was prepared by quternization of Resin 1 with chloroacetamide. The mercury sorption capacity was calculated as about 3.30 mmol/g and the resin, having carbon amide and sulfonamide groups, shows a reasonable mercury selectivity over Zn(II), Cd(II), Mg(II), and Fe(III) ions.

Since, in ordinary conditions the amide and sulfonamide groups are 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.

The mercury sorption of the Resin 2 obeys pseudo-second-order kinetics.

The recovery of mercury can be achieved by elution with acetic acid at 80°C without hydrolysis of the amide groups. Regenerebility of these materials with acetic acid makes them attractive for large scale applications.

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