ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF SULFONAMIDE GROUP CONTAINING CELLULOSE AND POLY(HEMA-MMA-EGDMA) BASED SORBENTS FOR REMOVAL OF MERCURY IONS FROM AQUEOUS SOLUTIONS

M.Sc. Thesis by
Seda CEKLI

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JUNE 2011

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M.Sc. Thesis by
Seda CEKLI
(515081017)

Date of submission : 06 May 2011
Date of defence examination: 14 June 2011

Supervisor (Chairman) : Prof. Dr. Bahire Filiz SENKAL (ITU)
Members of the Examining Committee : Assoc. Dr. Yesim GURSEL (ITU)
Prof. Dr. Ulker Beker (YTU)

JUNE 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SULU ORTAMLARDAN CİVANIN UZAKLAŞTIRILMASI İÇİN SÜLFONAMİD GRUBU İÇEREN SELÜLOZ VE POLY(HEMA-MMA-EGDMA) ESASLI SORBENTLERİN HAZIRLANMASI

YÜKSEK LİSANS TEZİ
Seda ÇEKLİ
(515081017)

Tezin Enstitüye Verildiği Tarih : 06 Mayıs 2011
Tezin Savunulduğu Tarih : 14 Haziran 2011

Tez Danışmanı : Prof. Dr. Bahire Filiz ŞENKAL (İTÜ)
Diğer Jüri Üyeleri : Doç. Dr. Yeşim GÜRSEL (İTÜ)
Prof. Dr. Ülker BEKER (YTÜ)

HAZİRAN 2011

FOREWORD

To become a scientist is a hard way to walk and I am happy to introduce my first step. Like every firsts, it was tough but special.

At this point, my deepest thanks go to my advisor, Prof. Filiz SENKAL. We have been working together for four years and she was always so kind, helpful and supportive to me. She has a very deep knowledge. I have learned a lot from her and I appreciate it.

In addition, I would like to express my appreciation for Prof. Yesim GURSEL. She was also so supportive and kind. I always felt free to ask for her precious helps.

I especially like to thank Dr. Erdem YAVUZ because he answered patiently every single question I asked in the past four years and shared his time with me in the laboratory. I will not forget his helps, advices and friendship.

While working in laboratory, studying in class, teaching in lectures, sometimes I stressed. This is why; I like to thank people in my life from ITU for helping me relaxing. You were all good listeners. Thank you very much.

And my friends… May be you were not next to me in the laboratory, in the library or in the class, but you were always there whenever I needed. My biggest thanks go to Onur Cagsal. *We will always be there for each other*. Pinar Esin, spending time with you is priceless (like in that famous commercial). Ece Ismailoglu, like a sister, always there, always so close. You all have a big influence on me. Thank you!

Finally, I like to thank my family. This the last thank but the most special one. My dear mother, I am aware what are you doing for us. If you were not supporting me in all stages of my life, maybe I would not write these sentences. My brothers, you know I love you both and grateful for your support. And my dad, this thesis is dedicated in loving memory of you…

May 2011 Seda Cekli

Chemist

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ABBREVIATIONS

AGU	**:** Anhydroglucose Unit
AIBN	**:** Azobisisobutyronitrile
AN	**:** Acrylonitrile
CR	**:** Congo Red
DMF	**:** Dimethyl formamide
EDTA	**:** Ethylene Diamine Tetraacetic Acid
EGDMA	**:** Ethylene Glycol Diethacrylate
FT-IR	**:** Fourier Transform Infrared Spectroscopy
GMA	**:** Glycidyl Methacrylate
GP	**:** Grafting Percentage
HEMA	**:** Hydroxyethyl Methacrylate
MMA	**:** Methyl Methacrylate
NMP	**:** 2-methyl pyrrolidone
PAN	**:** Poly(acrylonitrile)
PGMA	**:** Poly(Glycidyl Methacrylate)
POM	**:** Polarized Optical Microscope
UV-vis	**:** Ultraviolet-Visible

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PREPARATION OF SULFONAMIDE GROUP CONTAINING CELLULOSE AND POLY(HEMA-MMA-EGDMA) BASED SORBENTS FOR REMOVAL OF MERCURY IONS FROM AQUEOUS SOLUTIONS

SUMMARY

In this thesis, two types of polymeric sorbents were prepared for removal of mercury ions from aqueous solutions. These sorbents were called as Sorbent 1 and Sorbent 2 respectively.

Sorbent 1 was prepared starting from poly(acrylonitrile) (PAN) grafted cellulose. PAN was grafted onto cellulose by redox polymerization method in the presence of Ce(IV). PAN grafted cellulose was modified with ethylenediamine to obtain aminated sorbent. Then, the sorbent was reacted with benzensulfonyl chloride to prepare sulfonamide containing cellulose based Sorbent 1.

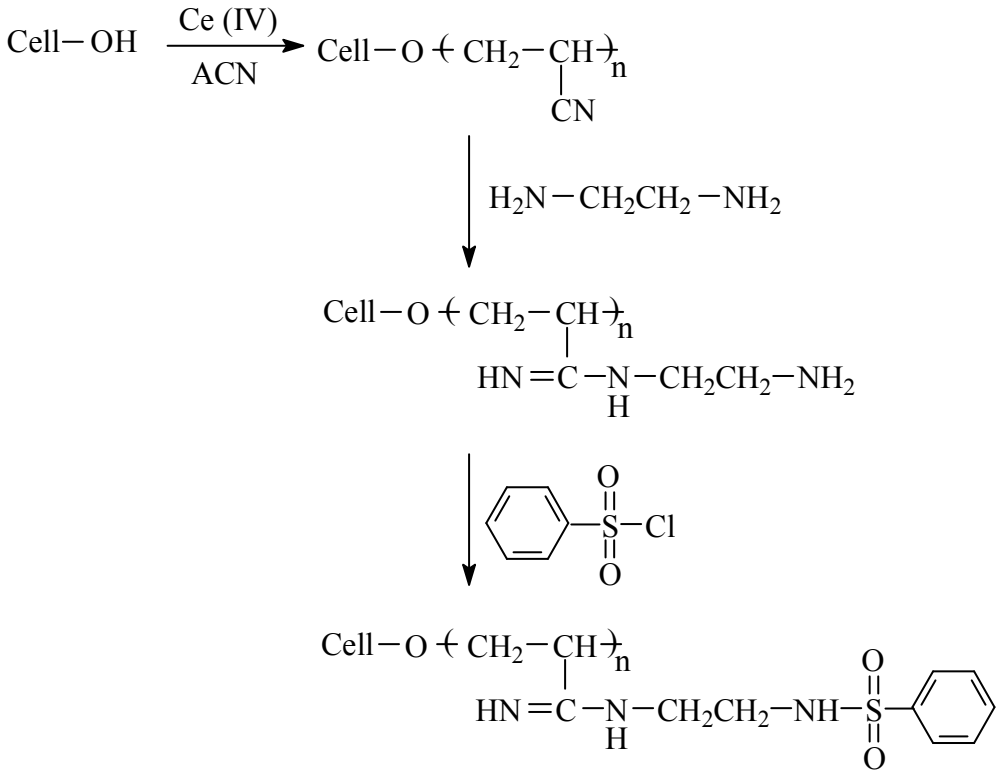


Figure 1 : Preparation of Sorbent 1.

The poly(HEMA-MMA-EGDMA) terpolymer were prepared starting from polymerization of hydroxyethyl methacrylate (HEMA) (50%), methyl methacrylate (MMA) (40%) and ethylene glycol diethacrylate (EGDMA) (10%) by using suspension polymerization method. Grafting of PAN onto beads was carried out by

using redox polymerization method. Grafting reaction is carried out through the hydroxyl groups on HEMA units. The nitrile groups in the PAN grafted poly(HEMA-MMA-EGDMA) beads were converted into amine group by adding ethylene diamine on the polymer. Also, MMA group reacts with ethylene diamine to give amide group by ester aminolysis reaction. Aminated beads was interacted with benzenesulfonyl chloride to obtain sulfonamide modified Sorbent 2.

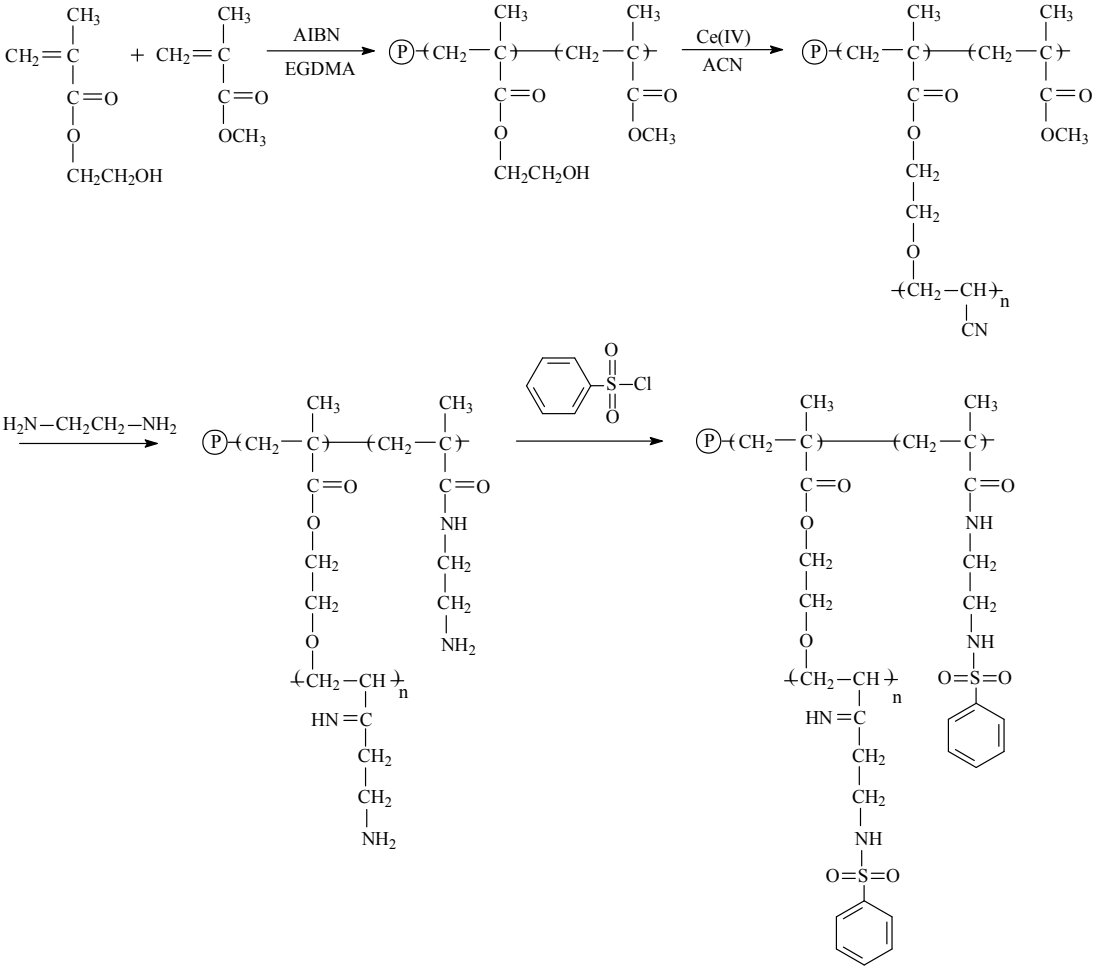


Figure 2 : Preparation of Sorbent 1.

$HgCl_2$ and $Hg(CH_3COO)_2$ salts were used in mercury adsorption experiments. The mercury sorption capacities of the sorbent were determined by mixing weighed amount of 0.2 g polymer sample with 20 mL of 0.074 M aqueous Hg(II) solution. 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. The results were given in Table 1. According to the Table 1, sorption capacities of the Cd(II), Zn(II), Mg(II) and Fe(III) ions are much lower than sorption capacity of Hg(II).

Batch kinetic sorption experiments were performed by using $HgCl_2$ and $Hg(CH_3COO)_2$ salts and in highly dilute Hg(II) solutions ($1.470.10^{-4}$-$0.375.10^{-4}$ M) (147-37.5 ppm). Also, pH depending sorption kinetic measurements were investigated.

Table 1: Metal ion loading capacities (mmol/g sorbent) of sorbents.

Metal Ion	Initial Concentration	Capacity of Sorbent 1	Capacity of Sorbent 2
Hg(II) – $HgCl_2$	0.074	1.95	2.81
Hg(II) – $Hg(CH_3COO)_2$	0.031	2.62	3.10
Cd(II)	0.065	0.06	0.85
Mg(II)	0.017	0.02	0.14
Zn(II)	0.070	0.07	0.10
Fe(III)	0.123	0.46	1.27

According to the Table 2 the mercury binding is reasonable fast for within the pH range of 4.0–6.0. This also suggests that sorbents exhibited a low affinity for Hg(II) at initial pH=2, and a higher affinity between initial pH 4.0 and 6.0. This suggests that the Hg(II) linkage proceeds with deprotonation of the amide groups.

Table 2: Second order rate constant ($M^{-1} \cdot s^{-1}$) of the sorbents.

Metal Solution	Rate Constant of Sorbent 1	Rate Constant of Sorbent 2
$HgCl_2$ in water	40.90	0.042
$Hg(CH_3COO)_2$ in water	476.6	934.8
$HgCl_2$ in pH=2	0.193	4.367
$HgCl_2$ in pH=6	5.872	0.072

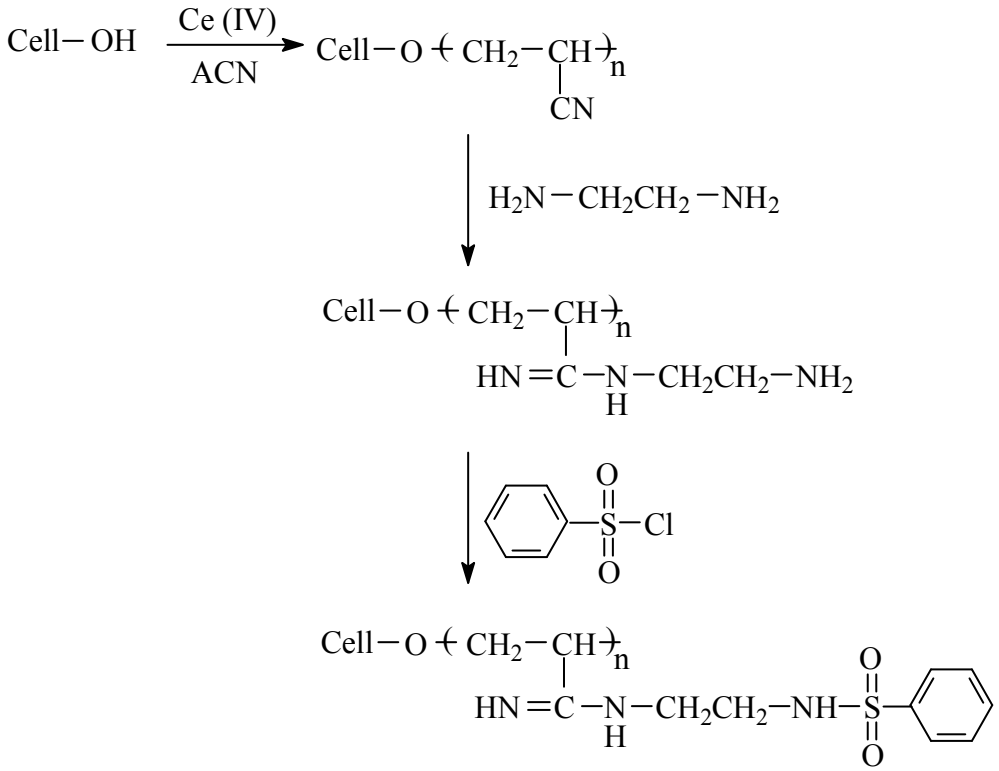
The sorbed mercury in these sorbents can be regenerated by using glacial acetic acid.

SULU ORTAMLARDAN CİVANIN UZAKLAŞTIRILMASI İÇİN SÜLFONAMİD GRUBU İÇEREN SELÜLOZ VE POLY(HEMA-MMA-EGDMA) ESASLI SORBENTLERİN HAZIRLANMASI

ÖZET

Bu çalışmada, sulu ortamlardan civa iyonunun uzaklaştırılmasında kullanılmak üzere iki farklı polimerik sorbent hazırlandı. Bu sorbentlere sırası ile Sorbent 1 ve Sorbent 2 adı verildi.

Sorbent 1 eldesi için ilk olarak selüloz üzerine poli(akrilonitril) PAN aşılanmıştır. Aşılama tepkimesi Ce(IV) varlığında indirgenme-yükseltgenme polimerizasyonu ile gerşekleştirilmiştir. İkinci aşamada PAN aşılanmış selüloz etilen diamine ile aminlenmiştir. Son olarak, sülfonamid fonksiyonel gruplu Sorbent 1 eldesi için sorbent benzensülfonil klorür ile modifiye edilmiştir.

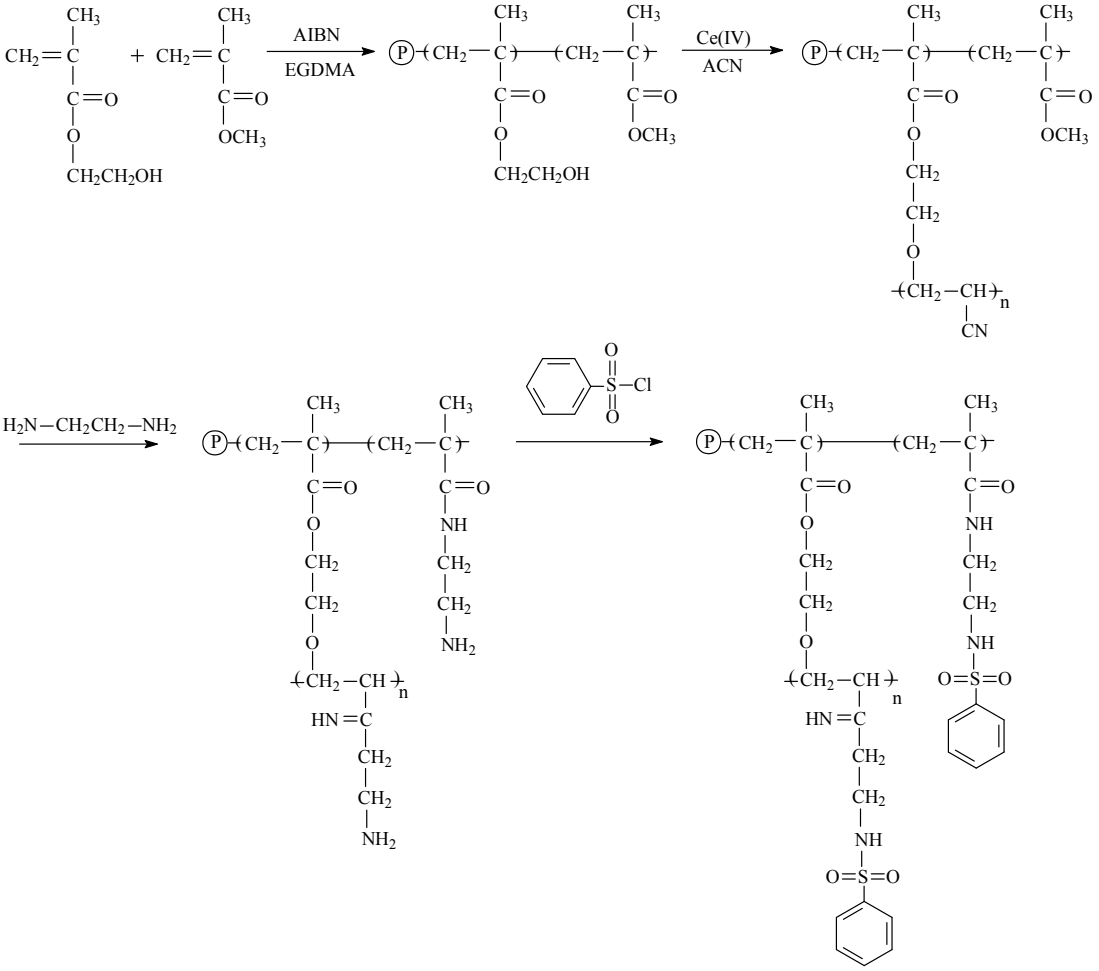


Şekil 1 : Sorbent 1'in hazırlanışı.

Poli(HEMA-MMA-EGDMA) polimeri hidroksietil metakrilat (HEMA) (%50), metil metakrilat (MMA) (%40), etilen glikol dietakrilat (EGDMA) (%10) kullanılarak süspansiyon polimerizasyonu yöntemi ile sentezlenmiştir. Süspansiyon kürelerinin üzerine redoks polimerizasyonu yöntemi kullanılarak PAN aşılanmıştır. PAN aşılı poli(HEMA-MMA-EGDMA) polimeri nitril grupları üzerinden etilen diamin

varlığında aminlenmiştir. Aminleme tepkimesi esnasında MMA ise ester aminolizi sonucu amid gruplarına sahip olmuştur.

Aminlenmiş polimer kürelerinin benzensülfonil klorür ile sülfonamidlenmesi sonucu Sorbent 2 elde dilmiştir.



Şekil 2 : Sorbent 2'nin hazırlanışı.

Civa adsorplama deneyleri $HgCl_2$ and $Hg(CH_3COO)_2$ tuzları kullanılarak gerçekleştirilmiştir. Sorbentlerin civa yükleme kapasiteleri 0,2 g reçinenin 20 mL 0,074 M sulu Hg(II) çözeltilerinin etkileştirilmesi ile bulunmuştur.

Kapasiteler, çözeltilerin etkileşimden önce ve etkileşimden sonra içerdikleri Hg(II) miktarı üzerinden hesaplanmıştır.

Yükleme deneyleri diğer ağır metal iyonlarının bazıları için de gerçekleştirilmiştir. Sonuçlar Çizelge 1 de verilmiştir. Çizelge 1'e göre sorbentlerin Cd(II), Zn(II), Mg(II) ve Fe(III) yükleme kapasiteleri Hg(II) yükleme kapasitelerine göre oldukça düşüktür.

Sorbentlerin civa adsorplama kinetikleri yüksek oranda seyreltik $HgCl_2$ ve $Hg(CH_3COO)_2$ çözeltileri kullanılarak gerçekleştirilmiştir ($1{,}470.10^{-4}$-$0{,}375.10^{-4}$ M) (147-37,5 ppm). Sorbentlerin civa adsorplama kinetiklerine farklı pH ortamlarında da bakılmıştır.

Çizelge 1: Sorbentlerin metal iyonu yükleme kapasiteleri (mmol/g sorbent).

Metal Iyonun Çeşidi	Başlangıç Konsantrasyonu	Sorbent 1 Kapasite	Sorbent 2 Kapasite
Hg(II) – $HgCl_2$	0,074	1,95	2,81
Hg(II) – $Hg(CH_3COO)_2$	0,031	2,62	3,10
Cd(II)	0,065	0,06	0,85
Mg(II)	0,017	0,02	0,14
Zn(II)	0,070	0,07	0,10
Fe(III)	0,123	0,46	1,27

Çizelge 2 ye göre sorbentlerin civa bağlama hızları pH 4,0-6,0 aralığında daha yüksektir. Ayrıca pH=2 civarında sorbentin civaya karşı olan ilgisinin düşük olduğu, pH 4,0-6,0 aralığında ise daha yüksek olduğu Çizelge 2 den çıkarılmış olan sonuçlardır. Bu sonuçlar dikkate alındığında Hg(II) nin sorbente bağlanmasının sorbentten proton ayrılması ile gerçekleştiği sonucu çıkmaktadır.

Çizelge 2: Sorbentlerin ikinci dereceden hız sabitleri ($M^{-1} \cdot s^{-1}$).

Metal Çözeltisi	Sorbent 1 Hız Sabiti	Sorbent 2 Hız Sabiti
$HgCl_2$ (suda)	40,90	0,042
$Hg(CH_3COO)_2$ (suda)	476,6	934,8
$HgCl_2$ (pH=2)	0,193	4,367
$HgCl_2$ (pH=6)	5,872	0,072

Yüklü sorbentlerin rejenerasyonu asetik asit muamelesi ile yapılmaktadır.

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. Thus, metal as a kind of resource is becoming shortage and also brings about serious environmental pollution, threatening human health and ecosystem.

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies [1]. These technologies include chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption. There are several advantages and disadvantages associated with each method.

The most widely used method of removing heavy metals from solution is to increase the pH of the effluent, thus converting the soluble metal into an insoluble form (i.e. its hydroxide). Ion exchange is the second most widely used method for heavy metal removal from aqueous streams. During removal, recovery, or processing of metals, ion exchange acts as a concentrator of metals. The chemistry of the influent stream becomes very important to the success of the ion exchange application. Coagulation–flocculation can also be employed to treat wastewater laden with heavy metals wherein the coagulation process destabilizes colloidal particles by adding a chemical agent (coagulant) and results in sedimentation. Coagulation is followed by flocculation of the unstable particles in order to increase their size and form into bulky floccules which can be settled out. Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment. Adsorptive bubble separation employs foaming to separate the metal impurities. Ion flotation, precipitate flotation and sorptive flotation are the main flotation process mechanisms for removal of metal ions from solution. Membrane filtration has received

considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals.

Amongst all the treatment processes mentioned, adsorption using sorbents is one of the most popular and effective processes for the removal of heavy metals from wastewater. The adsorption process offers flexibility in design and operation and in many cases produces treated effluent suitable for re-use, free of color and odor. In addition, because adsorption is sometimes reversible, the regeneration of the adsorbent with resultant economy of operation may be possible [2].

Designing an adsorption system is one of the most important research areas in sorbent industry. The choice of the effective sorbent in the analytical method is made taking into consideration the nature of functional group, the proper features of the support as well as the characteristics of the sample solution (its pH, metals to be removed, the presence of other cations or anions which might interfere with the process) [3].

Functional group on the sorbent determines the affinity and selectivity of the sorbent to metal ions. In this thesis, sulfonamide functional group containing sorbents were prepared; Sorbent 1 and Sorbent 2. Sorbent 1 was prepared from cellulose and Sorbent 2 was prepared from poly(HEMA-MMA-EGDMA) beads. Initially, poly(acrylonitrile) was grafted onto sorbents for introducing flexible side chains to polymers and increasing both metal sorption velocity and capacity. Modification of PAN grafted sorbents includes amination and sulfonamidation reactions respectively.

Sulfonamide containing sorbents were used for removing Hg(II) ions from aqueous solutions under buffered and non-buffered conditions. Maximum Hg(II) sorption capacities of sorbents and kinetic measurements of sorption were also performed under buffered and non-buffered conditions. In addition, sorption capacities of Cd(II), Mg(II), Zn(II) and Fe(III) were determined. Regeneration experiments of sorbent were also performed and found that sorbents can be effectively regenerated.

2. THEORETICAL PART

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 [4]. 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 [5].

2.1.1 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 ($Hg\text{-}Hg^{++}$). 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 ($C_6H_5\text{-}Hg^{+}$) and methyl ($CH_3\text{-}Hg^{+}$) mercuric cations [6].

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 [7].

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 [8]. 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 [9–11].

2.1.2 Toxicokinetics of mercury

The toxicokinetics (i.e., absorption, distribution, metabolism, and excretion) of mercury is highly dependent on the form of mercury to which a receptor has been exposed. The absorption of elemental mercury vapor occurs rapidly through the lungs, but it is poorly absorbed from the gastrointestinal tract. Once absorbed, elemental mercury is readily distributed throughout the body; it crosses both placental and blood-brain barriers. The distribution of absorbed elemental mercury is limited primarily by the oxidation of elemental mercury to the mercuric ion as the mercuric ion has a limited ability to cross the placental and blood-brain barriers. Once elemental mercury crosses these barriers and is oxidized to the mercuric ion, return to the general circulation is impeded, and mercury can be retained in brain

tissue. Elemental mercury is eliminated from the body via urine, feces, exhaled air, sweat, and saliva. The pattern of excretion changes depending upon the extent the elemental mercury has been oxidized to mercuric mercury.

Absorption of inorganic mercury through the gastrointestinal tract varies with the particular mercuric salt involved; absorption decreases with decreasing solubility. Estimates of the percentage of inorganic mercury that is absorbed vary; as much as 20% may be absorbed. Inorganic mercury has a reduced capacity for penetrating the blood-brain or placental barriers. There is some evidence indicating that mercuric mercury in the body following oral exposures can be reduced to elemental mercury and excreted via exhaled air. Because of the relatively poor absorption of orally administered inorganic mercury, the majority of the ingested dose in humans is excreted through the feces.

Methylmercury is rapidly and extensively absorbed through the gastrointestinal tract. Absorption information following inhalation exposures is limited. This form of mercury is distributed throughout the body and easily penetrates the blood-brain and placental barriers in humans and animals. Methylmercury in the body is considered to be relatively stable and is only slowly demethylated to form mercuric mercury in rats. It is hypothesized that methylmercury metabolism may be related to a latent or silent period observed in epidemiological studies observed as a delay in the onset of specific adverse effects. Methylmercury has a relatively long biological half-life in humans; estimates range from 44 to 80 days. Excretion occurs via the feces, breast milk, and urine [12].

2.2 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 [13].

2.2.1 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 [14].

2.2.2 Cross-linked polymers

Physiosorption, *grafting*, and *crosslinking* are the techniques by which the association of monomers and polymers is described. The term physiosorption signifies that it is related to physical attractive forces. The process is a reversible one and is achieved by the end functionalized polymers on to the solid surface or self - assembly of polymeric surfactants, where *grafting* can be described as the covalent

attachment process and irreversible. Grafting can be accomplished by either "grafting to" or "grafting from" approaches. In "grafting to" approaches, functionalized monomers react with the backbone polymer to form the grafted one. On the other hand, "grafting from" is achieved by treating a substrate with some method to generate immobilized initiators followed by polymerization. High grafting density polymer also can be accomplished using this technique. The schematic presentation of all the processes is depicted in Figure 2.2 A. The *crosslinking* is the association of polymers through a chemical bond. In most cases, the crosslinking is irreversible. It may be intra - and intermolecular (Figure 2.2 B) [15]. In this thesis we grafted poly(acrylonitrile) onto cross-linked poly(HEMA-MMA-EGDMA) beads.

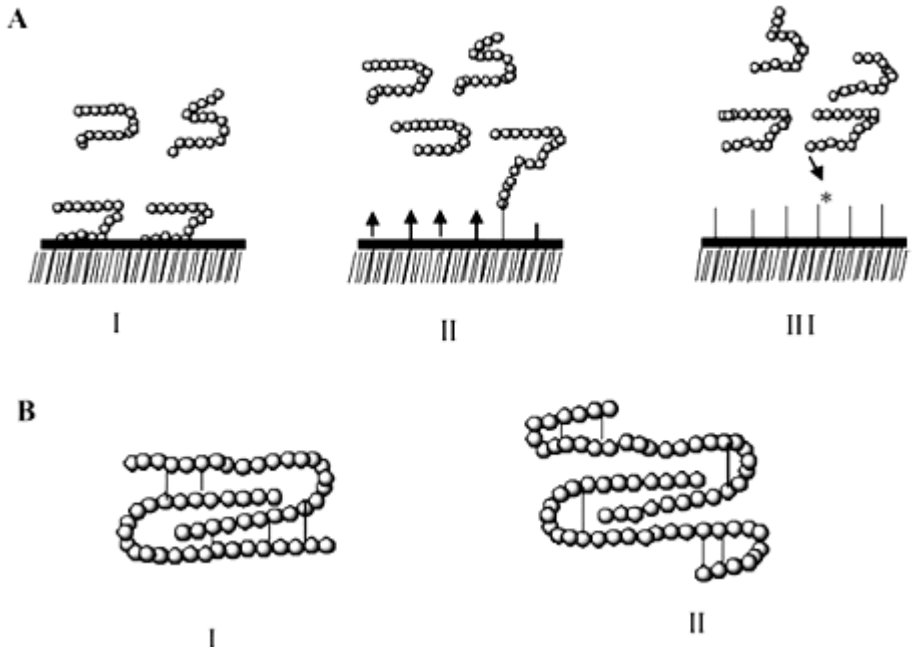


Figure 2.1 : (a) Shematic diagram of (I) physiosorption, (II) grafting to, (III) grafting from (b) Shematic diagram of (I) intermolecular crosslinking and (II) intramolecular crosslinking [15].

2.3 Polymeric Sorbents in Metal Removal

Metal ions are non-biodegradable in nature, and their intakes at a certain level are toxic. Electrochemical methods, chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation and flotation are methods that have been used to treat heavy metal waste waters [16-23]. Conventional methods have limited success in the extraction of trace quantities [24]. Since the target species are

usually in low concentration and in complex mixtures, it is necessary to remove toxic metals by using more efficient polymeric sorbents.

A polymeric sorbent essentially consists of two components: the functional group and the polymeric matrix or the support; the properties of both components determine the features and the applications of the respective material. While chelating group usually determines the selectivity of the sorbent which depends on the nature of the functional group and/or donor atom able to form complexes with metal ions, polymeric matrix determines other analytical properties, namely the capacity, kinetic features, mechanical and chemical strength and regeneration [3].

2.3.1 Physico-chemical properties of polymeric sorbents

Functional group determines the sorption capacity of sorbents which depends on the surface area of the support, the ionic strength and pH of the solution. The property of the sorbent to react with metallic ions under certain favorable conditions is determined by the nature of functional groups and/or donor atom (O, N, S). Selectivity of suitable specific functional groups fixed into the polymeric matrix has been explained on the basis of the concept of strong and weak acids and bases [25].

Functional groups in the sorbents usually act as bases: oxygen containing functional groups have strong, sulphur-containing groups have weak and nitrogen-containing groups have an intermediate character. Equilibriums for the complex formation of chelating sorbents towards some metal ions have been studied by several authors [3,26,27].

Kinetic characteristics of the sorbent depend on the nature and properties of polymeric matrix. Cross-linked polymers are preferred as polymeric support for several reasons. Firstly, cross-linked polymers have high chemical stability, mechanical strength and adjustable chemical surface. Since they are in soluble in solvents, they offer a great processing. In addition, they can be prepared in the form of spherical beads and can be separated from low molecular weight contaminants by simple filtration and washing with very use solvents. Furthermore, polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents. More highly cross-linked resins may be prepared with very porous structures which allow solvents and reagents to penetrate inside of the beads to contact reactive groups [28].

Measurement of the sorption rate under the conditions of diffusion through the particle as the rate-determining process proves the effect of the functional group concentration and of the sorbent structure on its kinetic properties. The time of establishing the sorption equilibrium varies from a few minutes to hours.

Polystyrene-based sorbents exhibit poor kinetic properties because of the hydrophobic nature of the matrix. The sorbents with the best kinetic characteristics are those based on typically hydrophilic matrices, such as cellulose or macro-porous methacrylate copolymers [3, 29].

2.3.2 Complexation of polymeric ligand with 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 [25]. Among the many ligands [30] introduced 8-acryloyloxyquinoline is one of the recent origin.

These kind of polymer-metal complexes are prepared by the chemical reaction of a polymer, containing ligands with metal ions.

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 [28].

2.3.3 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 2.2.

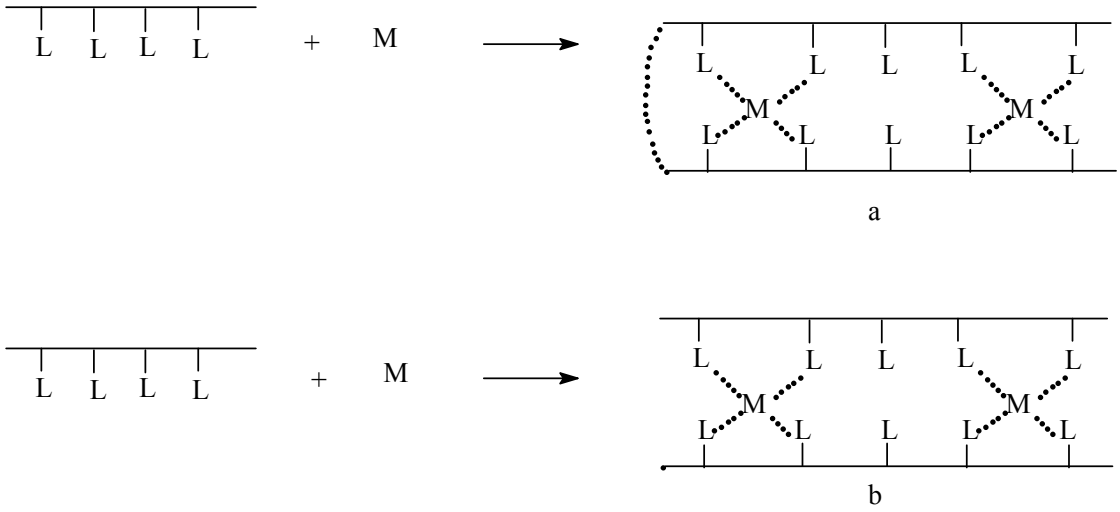


Figure 2.2 : Inter/intra molecular bridged polymer-metal complexes.

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 [31].

2.3.4 Sorbents depending on their backbone

Chelating polymers can be divided into two classes depending on the origin of their backbone: graft adsorbents and graft biosorbants.

2.3.4.1 Graft adsorbents

Graft adsorbents are a class of chelating polymers that have a modified backbone of synthetic polymers containing immobilized functional groups. These adsorbents have the flexibility of being prepared with various combinations of functional group

containing grafts (e.g., polyamines, polyacrylonitrile, polyacrylamides, and polyacrylic acid) and polymer substrates such as polyethylene and polypropylene, thus opening a broad spectrum of prospects for tailor - made applications such as the removal of toxic heavy metals and recovery of precious metals. The adsorption mechanisms in these polymers have generally been attributed to the formation of complexes between the functional groups on the adsorbents and the metal ions to be removed [13].

2.3.4.2 Grafted and cross-linked biosorbants

Grafted and cross-linked biosorbants are a class of chelating polymers that have a modified backbone of biopolymers (polysaccharides) such as chitosan, alignate, starch, and cellulose. These biosorbents are much more selective yet cheaper than traditional ion exchange resins, although their native form shows inferior biosorbance performances caused the instability of physical and chemical properties. Therefore, modification of these polysaccharides has been explored as a way of combining their best attributes with those of synthetic graft polymers. Several functional groups such as amino, phosphate, amido, sulfonate and carboxyl, and hydroxyl groups can be grafted onto the polysaccharides to give them additional ionic characters with their stability further enhanced by crosslinking.

The biosorption mechanism in these grafted and cross-linked materials is a complex process involving (i) ion exchange, (ii) chelation, (iii) complexation, and (iv) adsorption by physical forces such as H-bonding, entrapment in inter -and intrafibrilliar capillaries, and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through the sorbent.

Particularly, chitosan based biosorbents are efficient selective materials that have been frequently used in various separation applications including removal of heavy metals and dyes. For example, beads obtained by the casting of cross-linked and grafted chitosan have high porosity and large surface areas, high stability in acidic media, and are most suitable for industrial applications. Other biopolymers such as starch and cyclodextrins have been also proposed as low-cost biosorbents. The recent developments in the synthesis of biosorbents obtained from modified polysaccharides (starch, cyclodextrin, chitin, and chitosan) were reviewed by Cirni [13].

2.3.5 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 sulfur-hydrogen 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 [32].

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) and removed mercury ions with 5.75 mmol/g sorbent removing capacity [24].

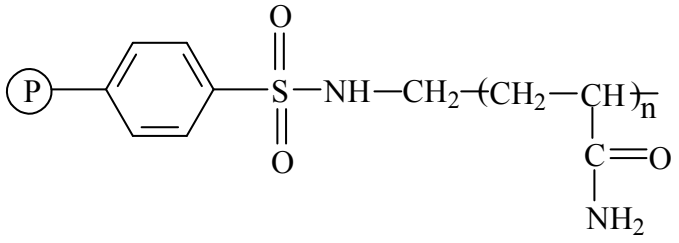


Figure 2.3 : Poly(acrylamide) grafted poly(styrene) [24].

Crosslinked Poly(glycidyl methacrylate) based resin with acetamide functional group 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 [33].

Atia was synthesized cross-linked chitosan polymer by using glutardialdehyde and modified with amine groups for removing of uranyl(III) and mercury ions. Ther mercury sorption capacity of the sorbent was found as 2.0 mmol/g sorbent [34].

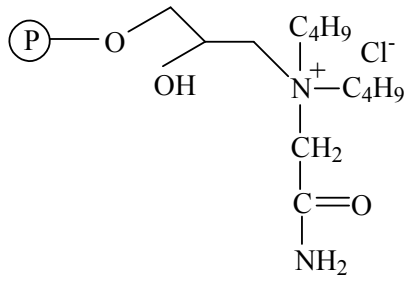


Figure 2.4 : Crosslinked PGMA based resin with acetamide functional group [33].

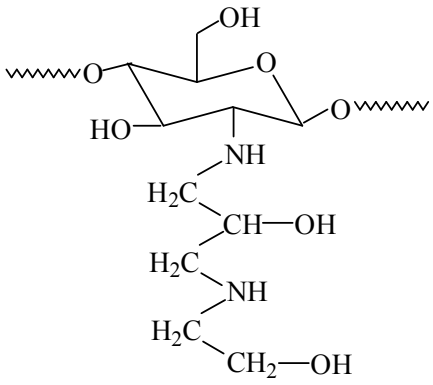


Figure 2.5 : Amine group containing chitosan [34].

2.4 Cellulose

Cellulose is the most abundant organic raw material and finds applications in areas as diverse as composite materials, textiles, drug delivery systems and personal care products.

Since it was first characterised in 1838, this inexpensive, biodegradable and renewable resource has received a great deal of attention for its physical properties and chemical reactivity. The chemical and physical properties of the cellulose biopolymer are largely dependent on its specific structure. The polymeric structure of cellulose was first demonstrated by Staudinger in 1920.

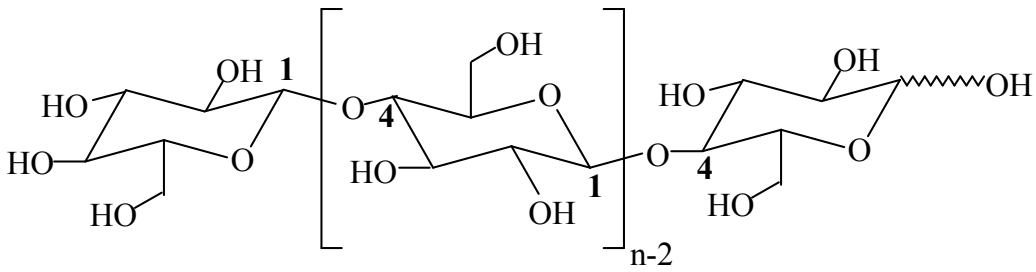


Figure 2.6 : The molecular structure of cellulose.

Understanding the structure of cellulose is a pre-requisite to controlling its modification. Figure 2.6 shows the molecular structure of cellulose generated from repeating β-D-anhydroglucopyranose units that are joined together covalently through acetal functions between the equatorial group of the C4 carbon atom and the C1 carbon atom (b-1,4-glycosidic bonds).

The molecular structure of cellulose suggests that it is a linear-chain polymer with a large number of hydroxyl groups (three -OH groups per anhydroglucose unit (AGU)). The degree of linearity enables the molecules to approach together. Thus, cellulose has a high cohesive energy that is greatly enhanced by the fact that the hydroxyl groups are capable of forming extensive *hydrogen bond networks* between the chains and within the chains. These aspects are responsible for the stiff and straight chain nature of the cellulose molecules. Thus, the physical properties and the chemical reactivity of fibrous cellulose are not only influenced by the chemical constitution of the cellulose molecules but are also determined by the supramolecular structure of cellulose [35].

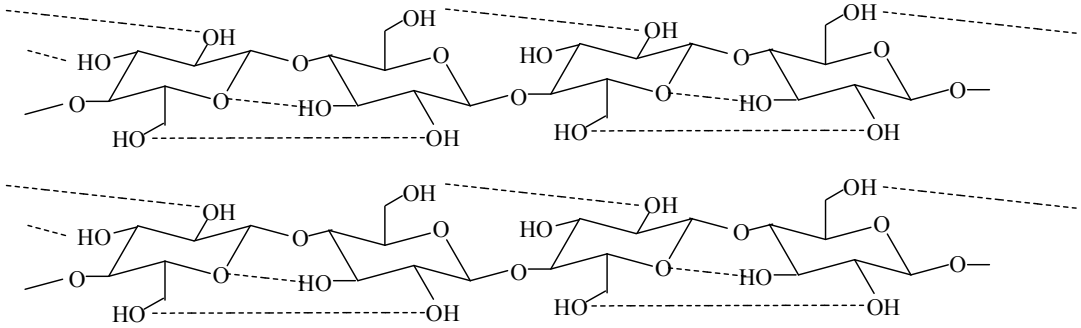


Figure 2.7 : Intramolecular hydrogen bonding in cellulose molecules.

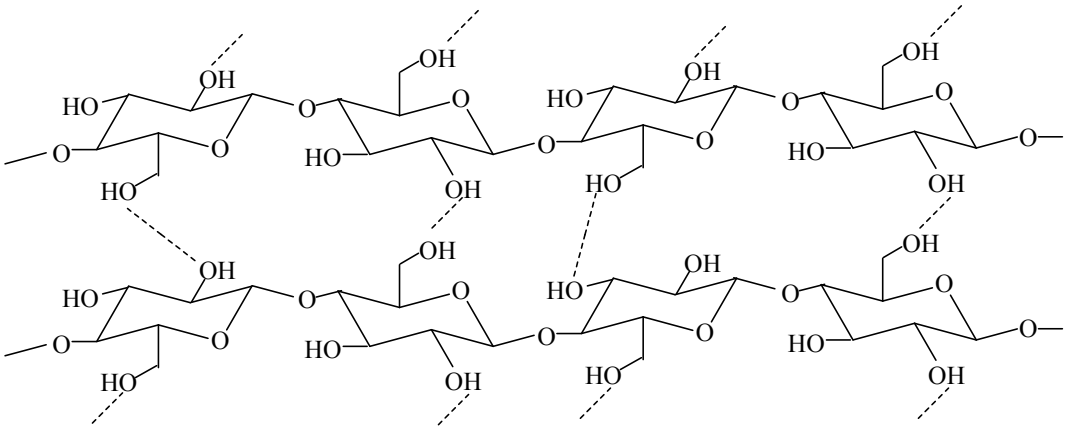


Figure 2.8 : Intermolecular hydrogen bonding in cellulose molecules.

2.4.1 Cellulosic sorbents for removal of metal ions

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. [36] has been demonstrated to be a very efficient selective sorbent for removal of Hg(II) from aqueous solutions.

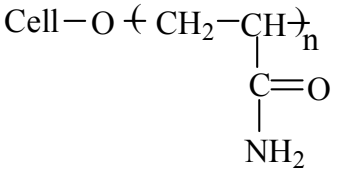


Figure 2.9 : Poly(acrylamide) grafted cellulose [36].

O'Connell et al. [37] have described the glycidyl methacrylate- modified cellulose material functionalised with imidazole (Cellulose-g-GMA-Imidazole) to assess its capacity in the removal of Ni(II) ions from aqueous solution.

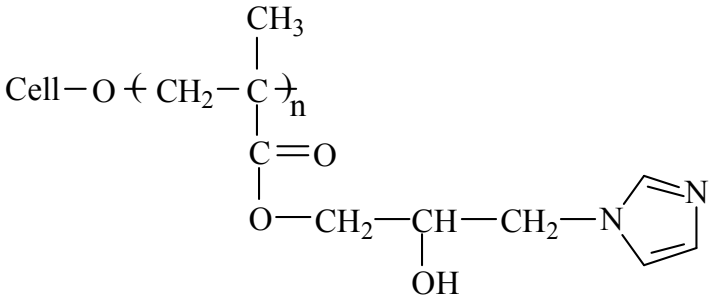


Figure 2.10 : The structure of Cellulose-g-GMA-Imidazole [37].

2.4.2 Poly(HEMA-MMA)

Hydroxyethyl methacrylate (HEMA) is a hydro-soluble monomer, which can polymerize (under various circumstances) at low temperatures (from -20°C to +10°C). It can be used to prepare various copolymers.

The hydroxyethyl pending species of the polymer confer a high hydrophilicity, a good biocompatibility, and these groups can be used (after chemical modification or grafting) to complex various types of molecules or ions [38]. PHEMA is the most widely used hydrogel in medical industry. Nowadays, numerous copolymers of HEMA are used as biomaterials.

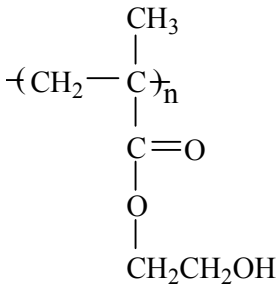


Figure 2.11 : Poly(hydroxyethyl methacrylate).

A large number of alkyl methacrylates, which may be considered as esters of poly(methacrylic acid), have been prepared. By far the most important of these polymers is poly(methyl methacrylate), which is an established major material. PMMA has crystal clear transparency, excellent weatherability and a useful combination of stiffness, density, and moderate toughness. The glass transition temperature of the polymer is 105°C (221°F), and the heat deflection temperatures range from 75 to 100°C (167–212°F). PMMA is widely used for signs, glazing, lighting, fixtures, sanitary wares, solar panels, and automotive tail and stoplight lenses. The low index of refraction (1.49) and high degree of uniformity make PMMA an excellent lens material for optical applications. Methyl methacrylate has been copolymerized with a wide variety of other monomers, such as acrylates, acrylonitrile, styrene, and butadiene [39].

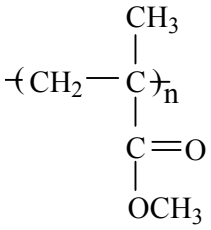


Figure 2.12 : Poly(methyl methacrylate).

Poly(HEMA) copolymers have been of great interest because of the biocompatibility of its copolymers. In the literature there are several studies on poly(HEMA-co-MMA) copolymers, especially in biomedical journals since poly(HEMA-co-MMA) is a biocompatible synthetic co-polymer with adequate mechanical strength for most biomedical and biotechnological applications. In this thesis, the poly(HEMA-MMA-EGDMA) polymer was synthesized where EGDMA was used as cross-linker.

Fang et al. [40] synthesized poly(HEMA-co-MMA), poly(HEMA-co-styrene), poly(HEMA-co- N-vinyl-2-pyrrolidone) copolymers and characterized them in 2007.

In 2002, Congo Red (CR) attached monosize poly(HEMA-co-MMA) microspheres were prepared by Yavuz et al. and used in reversible enzyme immobilization. In this study, Fe(III) adsorption onto both poly(HEMA-co-MMA) and CR modified poly(HEMA-co-MMA) were examined [41].

In the study of Yan et al., type-I collagen and bFGF were immobilized onto the surface of poly(HEMA-co-MMA) hydrogel by grafting [42].

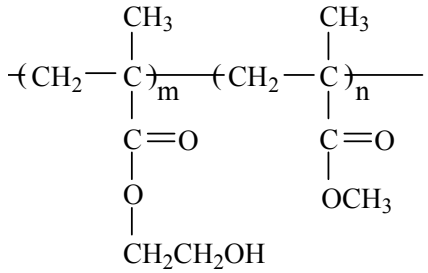


Figure 2.13 : Poly(HEMA-co-MMA).

3. EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

Cotton Cellulose (İpek Pamuk Inc.), Hydroxyethyl Methacrylate (HEMA) (Fluka), Ethyleneglycole dimethacrylate (EGDMA) (Fluka), Azobisisobutyronitrile (AIBN) (Merck), Cerium ammonium nitrate (Fluka), Poly(vinyl alcohol) (80% hydrolyzed, Merck), Acrylonitrile (Aldrich), Ethylene diamine (Fluka), Benzene-sulfonyl chloride (Fluka), Triethyl amine (Fluka), Diphenylcarbazide (Merck), Mercury(II) chloride (Fluka), Mercury(II) acetate (Aldrich), Iron(III) chloride (Fluka), Magnesium sulphate (Fluka), Zinc sulphate (Horasan Kimya), Cadmium nitrate (Aldrich), HCl (LabKim), Ethylenediamine tetraacetic acid (EDTA) (Emir Kimya), Eriochrome T, Phenolphtalein (Merck), Dithizone (Merck), Potassium thiocyanate (Fluka), Carbon tetrachloride (Merck), Acetonitrile (Riedel-de Haën), Toluene (Riedel-de Haën), Dimethyl formamide (DMF) (Merck), 2-methyl pyrrolidone (NMP) (Aldrich), Ethanol (Riedel-de Haën), Nitric Acid (Merck), Sulphuric Acid (Fluka).

3.1.2 Instruments

UV-vis spectrophotometer (Perkin Elmer, Lamda 25), Thermo FT-IR (with ATR), Polarized Optic Microscope (POM) (Leica).

3.2 Preparation of Polymeric Sorbents

In the present study two different types of polymeric sorbents were prepared. Sulfonamide containing cellulose based sorbent and sulfonamide containing poly(HEMA-MMA-EGDMA) based sorbent were prepared according to following procedures.

3.2.1 Preparation of sulfonamide containing cellulose based Sorbent (Sorbent 1)

Poly(acrylonitrile) grafted cotton cellulose was prepared and modified with ethylene diamine and benzene-sulfonyl chloride respectively.

3.2.1.1 Grafting of poly(acrylonitrile) (PAN) onto cotton cellulose

Grafting of acrylonitrile onto cellulose was carried out via redox polymerization of Ce(IV) and HNO_3 redox initiator system. For this purpose, 1.0 g of cellulose was dipped into 10 mL of distilled water. Cerium ammonium nitrate (0.8 g) was dissolved in 5 mL of acetonitrile and 3 drops of HNO_3. The mixture was poured into the wetted cotton. Finally, 10 mL of acetonitrile and 10 mL of acrylonitrile mixture was added to the reaction media at room temperature. The mixture was shaken with a continuous shaker for 24 hours at room temperature.

To remove homopolymer fraction of PAN, the reaction content was poured into DMF (100 mL) and was stirred for 24 hours. Then this mixture was filtered and washed with excess of water and ethanol. The product was dried under vacuum at 40^{o}C for 24 hours. The yield was 9. 72 g.

3.2.1.2 Amination of the PAN grafted polymer

The grafted polymer was aminated using excess of ethylene diamine as described in the literature [43]. 3 g of PAN grafted cellulose was left in contact with 20 mL of ethylene diamine and continuously shaken at room temperature for 24 hours. Then amination reaction was carried out at 95^{o}C for 24 hours in 30 mL DMF solvent. The reaction content was filtered and washed with distilled water and ethanol respectively. The product was dried under vacuum at 40^{o}C for 24 hours. The yield was 2.43 g.

3.2.1.3 Sulfonamidation of the grafted polymer

2 g of aminated cellulose based sorbent was placed in 40 mL on NMP and 6 mL of triethylamine as acid scavenger. 6 mL of benzene-sulfonyl chloride was added drop wise into the reaction mixture. The reaction was stirred at room temperature for 24 hours. The reaction content was poured into 100 mL of water and filtered and washed with distilled water and ethanol respectively. The product was dried under vacuum at 40^{o}C for 24 hours. The yield was 2.051 g.

3.2.2 Preparation of sulfonamide containing poly(HEMA-MMA-EGDMA) based sorbent (Sorbent 2)

The cross-linked poly(HEMA-MMA-EGDMA) was synthesized and modified with sulfonamide according to the procedures described above.

3.2.2.1 Preparation of poly(HEMA-MMA-EGDMA) beads

Poly(HEMA-MMA-EGDMA) beads were prepared by suspension polymerization of HEMA (6.1 mL, 0.05 mol), MMA (4.3 mL, 0.04 mol), EGDMA (1.9 mL, 0.01mol) as a cross-linker and AIBN (0.16 g, $9.74x10^{-4}$mol) as initiator in toluene (50 mL), using 50 mL of aqueous poly(vinyl alcohol) (0.2 g) as stabilizer. The reaction carried out at 65^{o}C for 4 hours. The yield was 9.65 g.

3.2.2.2 Preparation of poly(acrylonitrile) grafted poly(HEMA-MMA-EGDMA) core-shell beads

Grafting of poly(acrylonitrile) onto poly(HEMA-MMA-EGDMA) beads was carried out by using redox polymerization method as mentioned previously. 1.0 g of cross-linked polymer was interacted with 5 mL of acetonitrile. 0.8 g of cerium ammonium nitrate as initiator in 5 mL of acetonitrile and 1 drop of HNO_3 was added to the reaction mixture. Then 10 mL of acetonitrile and 10 mL of acrylonitrile mixture was added to this mixture at room temperature. The mixture was shaken with a continuous shaker for 24 hours at room temperature.

To remove homopolymer fraction of PAN, the reaction content was poured into DMF (100 mL) and was stirred for 24 hours. Then this mixture was filtered and washed with excess of water and ethanol. The product was dried under vacuum at 40^{o}C for 24 hours. The yield was 8.18 g.

3.2.2.3 Amination of the PAN grafted beads

The grafted polymer beads were aminated using excess of ethylene diamine as described in the literature. 3 g of PAN grafted beads were left in contact with 20 mL of ethylene diamine and continuously shaken at room temperature for 24 hours. Then amination reaction was carried out at 95^{o}C for 24 hours in 30 mL DMF. The reaction content was filtered and washed with distilled water and ethanol respectively. The product was dried under vacuum at 40^{o}C for 24 hours. The yield was 2.12 g.

3.2.2.4 Sulfonamidation of the grafted beads

2 g of aminated poly(HEMA-MMA-EGDMA) based sorbent was placed in 40 mL on NMP and 8 mL of triethylamine as acid scavenger. 6.5 mL of benzene-sulfonyl chloride was added drop wise into the reaction mixture. The reaction was stirred at room temperature for 24 hours. The reaction content was poured into 100 mL of water and filtered and washed with distilled water and ethanol respectively. The product was dried under vacuum at 40^{o}C for 24 hours. The yield was 3.1917 g.

3.3 Experimental Characterization of Sorbents

In addition to instrumental analysis, experimental methods were used to characterize polymeric sorbents after grafting and modifying. Experiments are described below.

3.3.1 Determination of nitrogen content

Nitrogen contents of the grafted polymers were determined by Kjeldahl nitrogen analysis method as given in the literature [44]. 0.2 g of polymer samples were placed in 20 ml of 80% H_2SO_4 solution and refluxed for 8 hours. The mixtures were filtered and diluted to 50 ml with distilled water. The total nitrogen contents of the filtrates were assayed by the Kjeldahl method.

3.3.2 Determination of the amine content

For determination of the amine content, 0.1 g of the aminated polymer samples were left in contact with 10 mL of 0.1 M HCl solutions and continuously shaken at room temperature for 24 hours. After filtration, 2 ml of the filtrates were taken and the acid content of the solutions were determined by titration with 0.05 M NaOH solution in the presence of phenol-phatalein color indicator.

3.3.3 Determination of the sulfonamide content

Sulfonamide contents of the sorbents were determined titrimetrically. For this purpose, the sulfonaminated polymer samples (0.1 g) were added to 10 mL of 0.5 M NaOH solutions and continuously shaken for 24 hours. After filtration the sulfonamide content was titrated with 0.1 M HCl solution. The sulfonamide contents of the sorbents were found by comparison with the result of the unreacted solution.

3.4 Adsorption Experiments

Mercury removal characteristics of sorbents (Sorbent 1, Sorbent 2) were studied by conducting adsorption experiments of Hg(II) under buffered and non-buffered conditions, other metals under non-buffered conditions and Hg(II) in the presence of Fe(III) ions. In addition regeneration capacities of sorbents were studied. Adsorption and desorption experiments are described in this chapter.

3.4.1 Loading capacity of the mercury ion

Mercury sorption capacities of the sulfonamidated sorbents were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous $HgCl_2$(0.074 M) and $Hg(CH_3COO)_2$ (0.0314 M) solutions. The mixtures were stirred for 24 hours and then filtered. The Hg(II) concentrations were determined colorimetrically using diphenylcarbazide [45]. The mercury loading capacities were calculated from the initial and final Hg(II) contents of the solutions.

3.4.2 Loading capacity of other metal ions

In order to examine the selectivity of Hg (II) binding, sorption capacity of Cd(II), Mg(II) and Zn(II) were determined. 20 mL of 0.0648 M of Cd(II), 0.166 M of Mg(II), 0.0695 M Zn(II), and 0.123 M of Fe(III) ion solutions were contacted with 0.2 g polymer samples. The mixtures were stirred for 24 hours and then filtered. Analyses of the residual metal contents of the supernatant solutions were performed by a complexometric titration method using EDTA solution (0.05 M).

3.4.3 Mercury sorption kinetics of the sorbents

In order to estimate efficiency of the sorbents for trace mercury batch kinetic experiments were performed using high diluted $HgCl_2$($1.47x10^{-4}$ M) and $Hg(CH_3COO)_2$ ($6.276x10^{-5}$ M) solutions. For this purpose 0.2 g of sorbents were wetted with 1 mL of distilled water and added to a solution of Hg(II). The mixtures were 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 different pH 2 and pH 6 using high diluted $HgCl_2$ ($3.75x10^{-4}$ M) solutions.

3.4.4 Mercury sorption in the presence of Fe(III) ions

This was performed by the mercury loading experiment being repeated in the presence of Fe(III) ion as follows. A binary mixture of $HgCl_2$ and $FeCl_3$ was prepared so that the final concentration of each component was 0.15 M. 10 mL of this solution was interacted with 0.2 g of the sulfonamidated sorbents for 24 hours at room temperature. The mixture was filtered and 1 mL of the filtrate was treated with 5 mL of 0.3 M of KSCN and 5 mL of a dithizone solution (2 g in 50 mL CCl_4). The mixture was shaken vigorously in a separatory funnel.

The iron was retained as a thiocyanate complex in the aqueous phase. For analysis of the residual iron, 3 mL of the aqueous phase was taken and diluted to 25 mL. Absorption measurements at 460 nm were performed as given in the literature [46].

An analysis of the mercury in the extract phase was performed by monitoring of the absorbance of the mercury-dithizone complex at 496 nm as described in the literature [47].

3.5 Regeneration of the Polymer Sorbents

The mercury loaded sorbents (0.05 g) was interacted with 10 mL of glacial acetic acid and stirred at 80 ^{o}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

In this study, poly(acrylonitrile) (PAN) was grafted onto cotton and cross-linked poly(HEMA-MMA-EGDMA) beads by using redox polymerization method. Sulfonamide and amide containing sorbents were used to remove mercury selectively. Therefore, prepared cellulose and methacrylate based on core-shell type polymeric sorbents were modified sulfonamide group to uptake mercury ions from aqueous solutions.

4.1 Preparation of Sulfonamide Containing Cellulose Based Sorbent (Sorbent 1)

Cellulose based sorbents have many advantages over other polymeric supports because its chemical activity due to the presence of the three hydroxyl groups in each glucose residue. In the present study, sulfonamide functional group containing cellulose was prepared. Cellulose grafted with poly(acrylonitrile) and modified with ethylene diamine and benzene-sulfonyl chloride respectively.

4.1.1 Grafting of poly(acrylonitrile) (PAN) onto cotton cellulose

Acrylonitrile (AN) was grafted onto cotton by using redox polymerization method. The most important feature of the ceric ion initiated polymerization technique for grafting vinyl monomers is that it proceeds via single electron transfer with the formation of free radicals on reducing agent. This method of grafting yields substantially pure graft copolymer since the free radicals are produced exclusively on the backbone [48].

The grafting percentage (GP) was determined by calculating the percentage increase in weight by using following equation:

$$GP = \left[\frac{(m_{gf} - m_0)}{m_0} \right] 100\% \qquad \textbf{(4.1)}$$

where, m_0 and m_{gf} are the weights of the beads before and after grafting, respectively and grafting degree was found as 872 %.

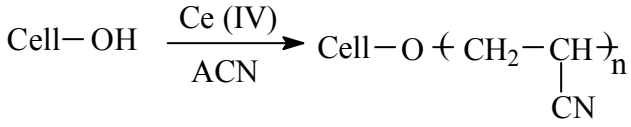


Figure 4.1 : Grafting of PAN onto cellulose.

PAN grafted cotton was characterized by FT-IR spectroscopy and determination of nitrogen content by the Kjeldahl method. The total nitrogen content of the grafted polymer was found as 4.32 mmol.g^{-1}.

According to the FT-IR spectrum in Figure 4.4 A., the peak at 2242 cm^{-1} is the characteristic absorption peak of stretching vibration mode of the nitrile (-C≡N) groups. Most of the other peaks are related to the carbohydrate backbone.

4.1.2 Amination of the PAN grafted cellulose

The nitrile groups in the PAN grafted cellulose were converted into amine group by adding excess of ethylene diamine on the PAN grafted polymer. The amine content of the polymer is found by interaction of polymer with HCl solution. Total amine content of the polymer was calculated as 3.145 mmol.g^{-1} resin.

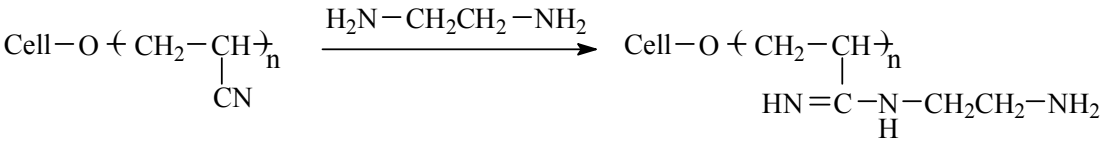


Figure 4.2 : Amination reaction of PAN grafted cellulose.

According to the Figure 4.4 B, after the reaction of PAN with ethylene diamine, the spectra of the obtained amine containing resins show many significant changes. The week peak at 3430 cm^{-1} for the PAN was replaced by a strong broad band for the resins. This strong broad band ranging from 3200-3500 cm^{-1} usually corresponds to the combination of the stretching vibration bands of both -OH and -NH.

4.1.3 Sulfonamidation of the grafted polymer

Sulfonamidation reaction was carried out by reacting the aminated polymer with benzene-sulfonyl chloride. The yield was 2.051 g. Sulfonamide content of the sorbent was determined titrimetrically and found as 3.37 mmol.g^{-1}.

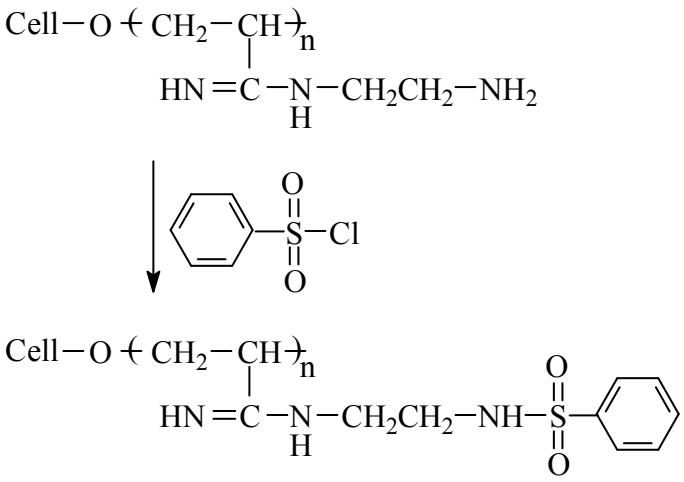


Figure 4.3 : Sulfonamidation of the grafted cellulose.

The sulfonamide containing sorbent was characterized by FT-IR spectroscopy (Figure 4.4 C). In the sulfonamide resin, -S=O stretching vibration occurs at 1122 cm^{-1}.

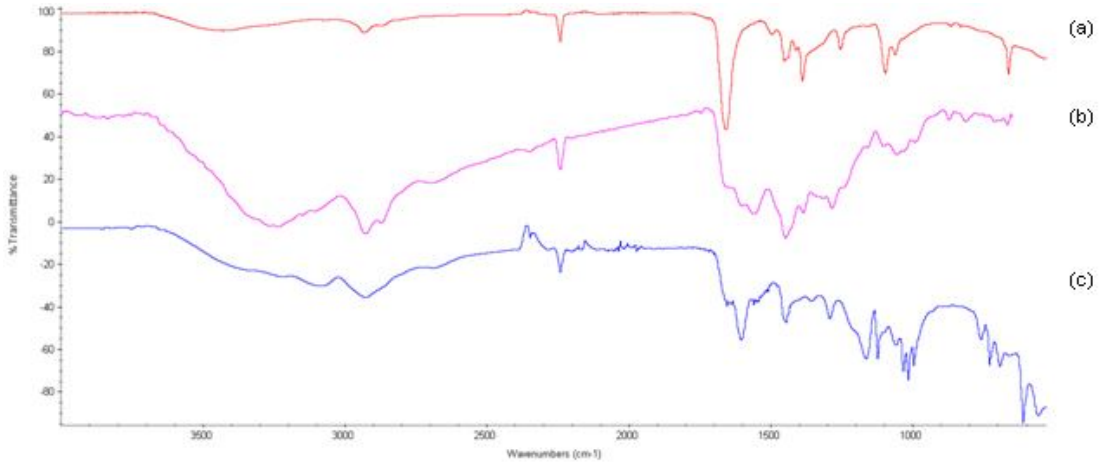
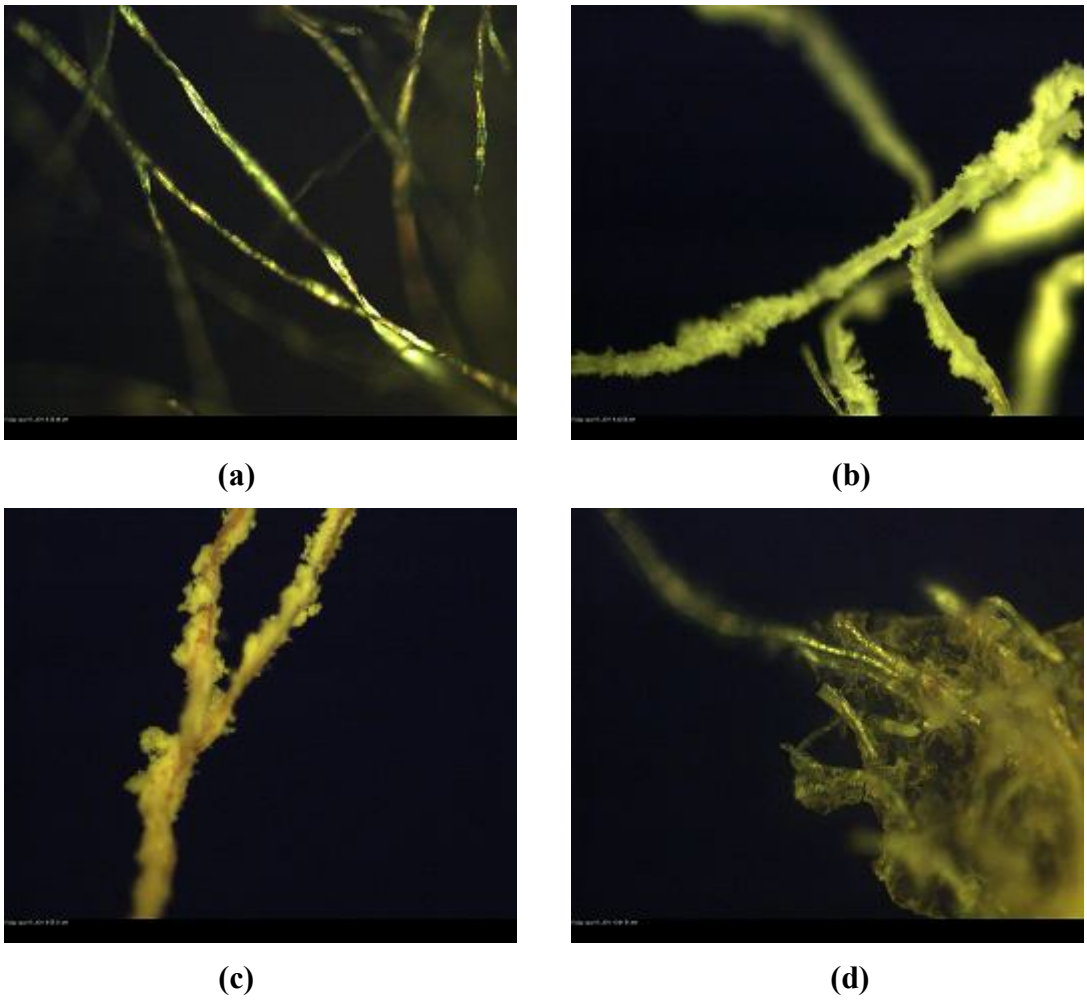


Figure 4.4 : (a) FT-IR spectrum of PAN grafted cellulose (b) FT-IR spectrum of aminated cellulose (c) FT-IR spectrum of sulfonamidated cellulose.

4.1.4 Polarized pptical microscope (POM) images of Sorbent 1

POM images of cotton cellulose, PAN grafted cellulose and modified PAN grafted cellulose are represented below for visualization of the products. In the image of the raw cotton, it can be clearly seen the cellulose fibers. After grafting of PAN onto cotton cellulose it became denser heterogeneously. As a result of sulfonamidation reaction, deformation was observed due to exothermic reaction conditions.



(a) **(b)**

(c) **(d)**

Figure 4.5 : (a) Raw cotton cellulose (b) PAN grafted cellulose (c) Aminated PAN cellulose (d) Sulfonamidated cellulose.

4.2 Preparation of Sulfonamide Containing Core-Shell Poly(HEMA-MMA-EGDMA) Based Sorbent (Sorbent 2)

Hydroxyethyl methacrylate (HEMA) based sorbent was chosen for several reasons. HEMA has hydroxyl groups on it. Hydroxyl and carboxyl functions can be used in redox polymerization as initiating group in the presence of Ce(IV) [36]. Also, remarkable resistance of methacrylate ester linkage to acid and base hydrolysis is an additional advantage to use as a ligand carrying polymer.

The cross-linked poly(HEMA-MMA-EGDMA) terpolymer was synthesized and modified with sulfonamide functional group for removing Hg(II) ions from aqueous media.

4.2.1 Preparation of poly(HEMA-MMA-EGDMA) beads

The poly(HEMA-MMA-EGDMA) beads were prepared starting from polymerization of hydroxyethyl methacrylate (HEMA) (50%), methyl methacrylate (MMA) (40%) and ethylene glycol dimethacrylate (EGDMA) (10%) by using suspension polymerization method.

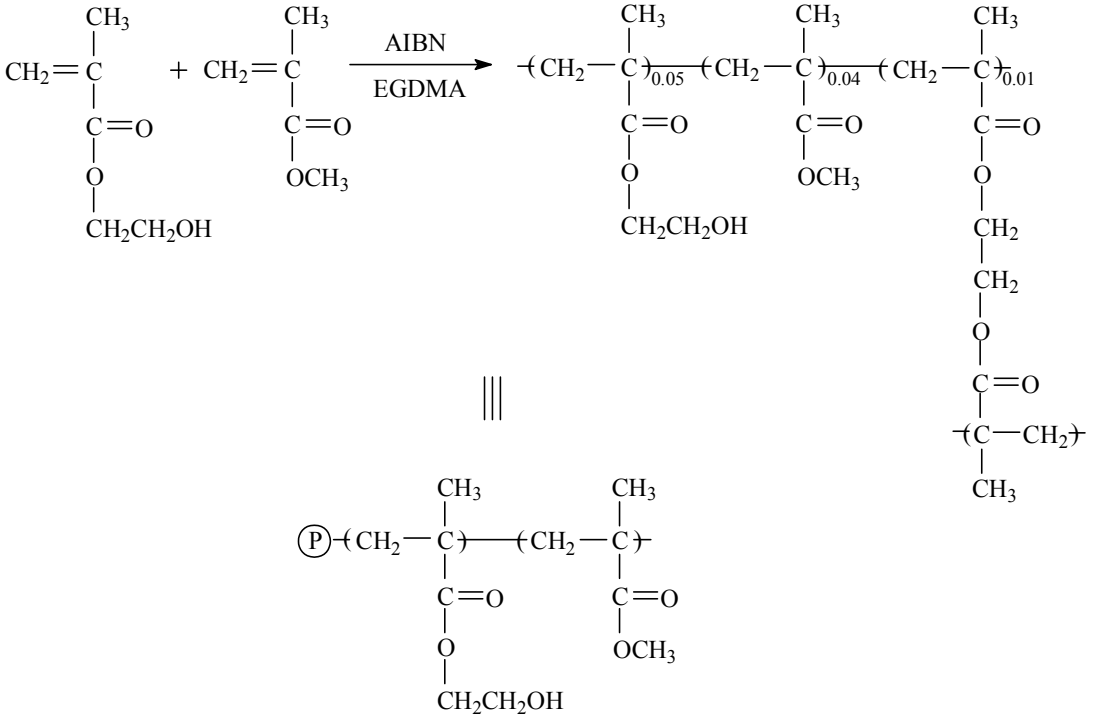


Figure 4.6 : Crosslinked poly(HEMA-co-MMA) beads.

The broad range at 3300-3500 cm^{-1} range in the FT-IR spectrum (Figure 4.11 A) of poly(HEMA-MMA-EGDMA) indicates -OH stretching vibrations in the terpolymer. In addition the sharp peak at 1721 cm^{-1} corresponds to carbonyl groups in monomeric units.

4.2.2 Grafting of poly(acrylonitrile) on poly(HEMA-MMA-EGDMA) beads

Grafting of poly(acrylonitrile) onto poly(HEMA-MMA-EGDMA) beads was carried out by using redox polymerization method. Grafting reaction is carried out through the hydroxyl groups on HEMA units. The total nitrogen content of the grafted polymer was assayed by the Kjeldahl method. Total nitrogen content was found as 3.19 $mmol.g^{-1}$.

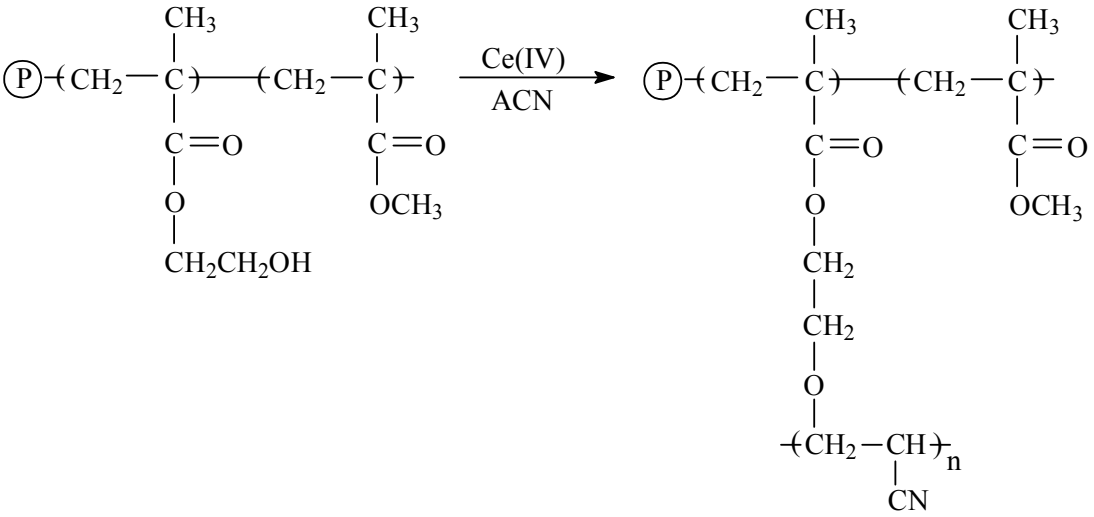


Figure 4.7 : Grafting of PAN onto poly(HEMA-co-MMA) core-shell beads.

The -OH stretching vibration peak at 3300-3500 cm^{-1} range disappeared in the FT-IR spectrum of PAN grafted terpolymer (Figure 4.11 B). Also the peak at 2243 cm^{-1} indicates stretching vibration mode of the nitrile groups of PAN.

By grafting PAN onto beads, core-shell polymeric particles were obtained. A schematic representation of a core-shell cross-linked polymer particle is in Figure 4.8.

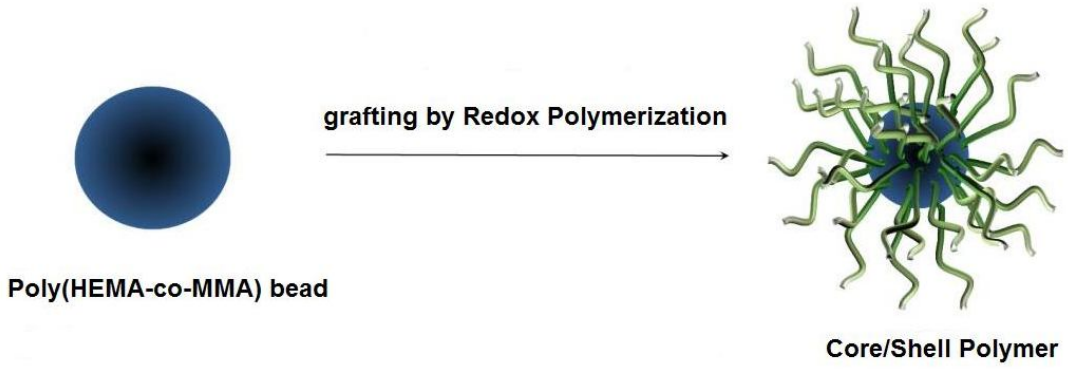


Figure 4.8 : Schematic representation of a core-shell particle.

PAN grafted core-shell beads are anticipated to have superior features over common polymeric supports carrying small reactive sites on their surfaces since, in this structure, bead-shaped support is combined with the flexibility of the suspended graft chains which is providing semihomegeneous reaction conditions. Here, the core controls the type and the size of the particles, whereas the shell provides functionality.

4.2.3 Amination of the PAN grafted beads

The nitrile groups in the PAN grafted poly(HEMA-MMA-EGDMA) beads were converted into amine group by adding ethylene diamine on the polymer. Also, MMA group reacts with ethylene diamine to give amide group by ester aminolysis reaction (Figure 4.9).

The amine content of the polymer is found by interaction of polymer with HCl solution. Total amine content of the polymer was calculated as 3.01 mmol.g^{-1} resin.

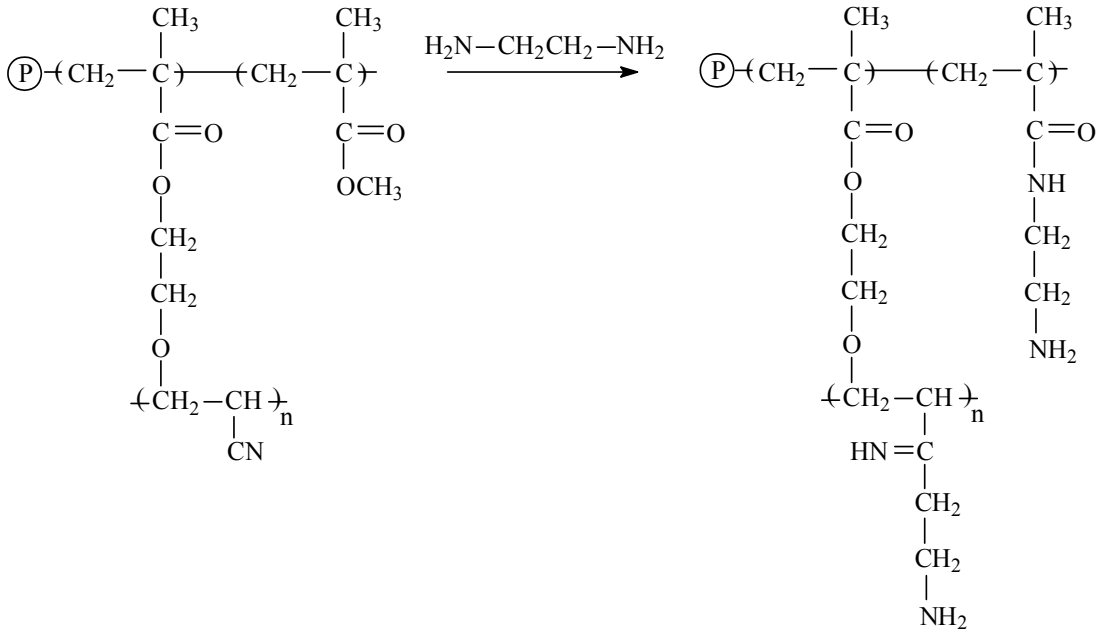


Figure 4.9 : Amination reaction of the PAN grafted terpolymer beads.

In the FT-IT spectrum of amination beads, the -NH stretching vibration band at 3430 cm^{-1} appeared as a result of amination reaction (Figure 4.11 C).

4.2.4 Sulfonamidation of the grafted polymer

Sulfonamidation reaction was carried out by reacting the aminated polymer with benzene-sulfonyl chloride. Sulfonamide content of the sorbent was determined titrimetrically and found as 3.58 mmol.g^{-1}.

In the sulfamidation product, stretching vibration of -S=O appears at 1303 cm^{-1} and 1177 cm^{-1} respectively (Figure 4.11 D).

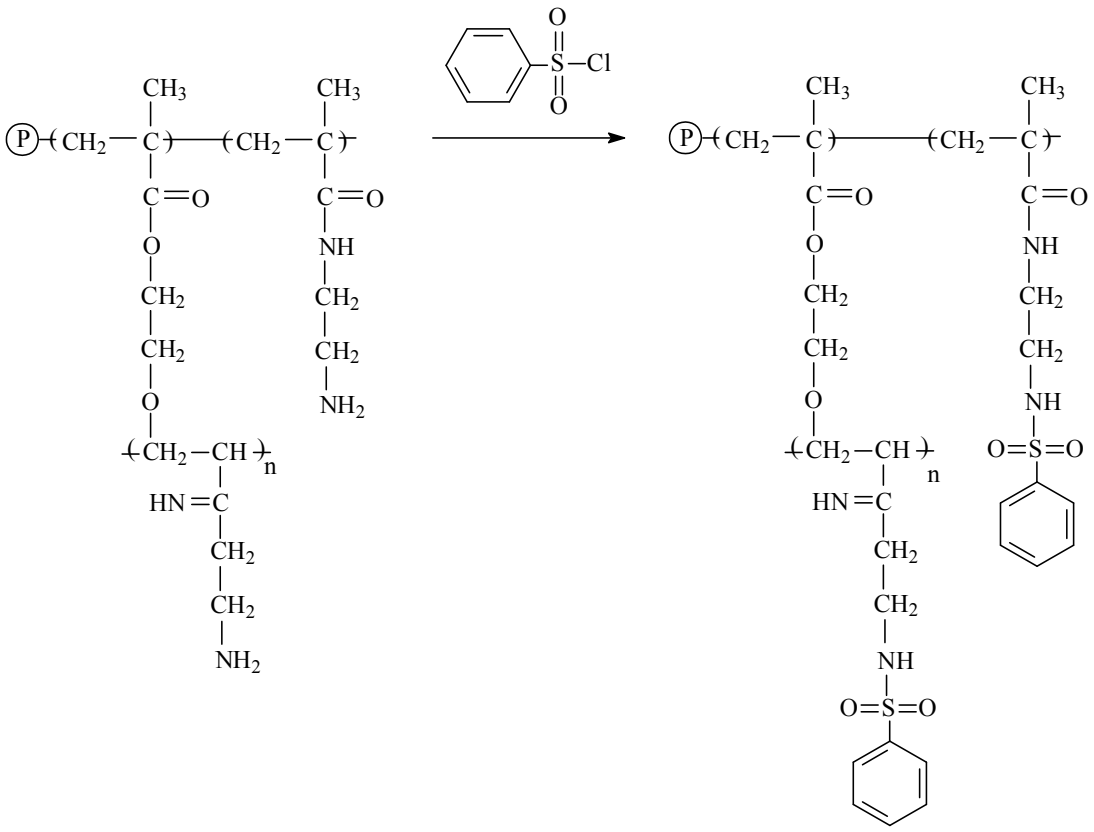


Figure 4.10 : Sulfonamidation of the grafted beads.

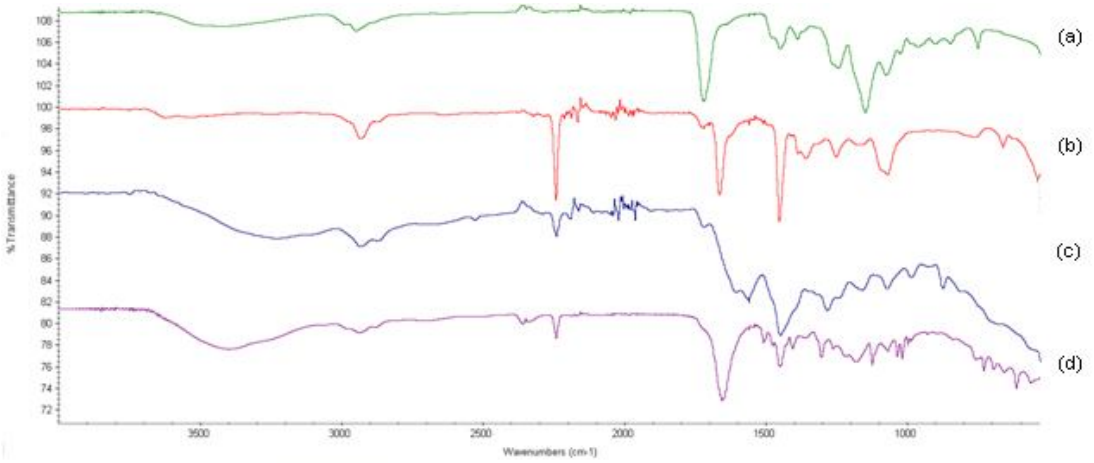


Figure 4.11 : (a) FT-IR spectrum of poly(HEMA-MMA-EGDMA) beads (b) PAN grafted beads (c) Aminated beads (d) Sulfonamidated beads.

4.2.5 Polarized optical microscope (POM) images of sorbent 2

In POM image of poly(HEMA-MMA-EGDMA) terpolymer beads (Figure 4.12 A), the spherical shape of the beads can be clearly seen. After PAN grafting onto beads core-shell polymer particles were obtained (Figure 4.12 B). As a result of grafting, an obvious increase in volume was observed and beads became much denser.

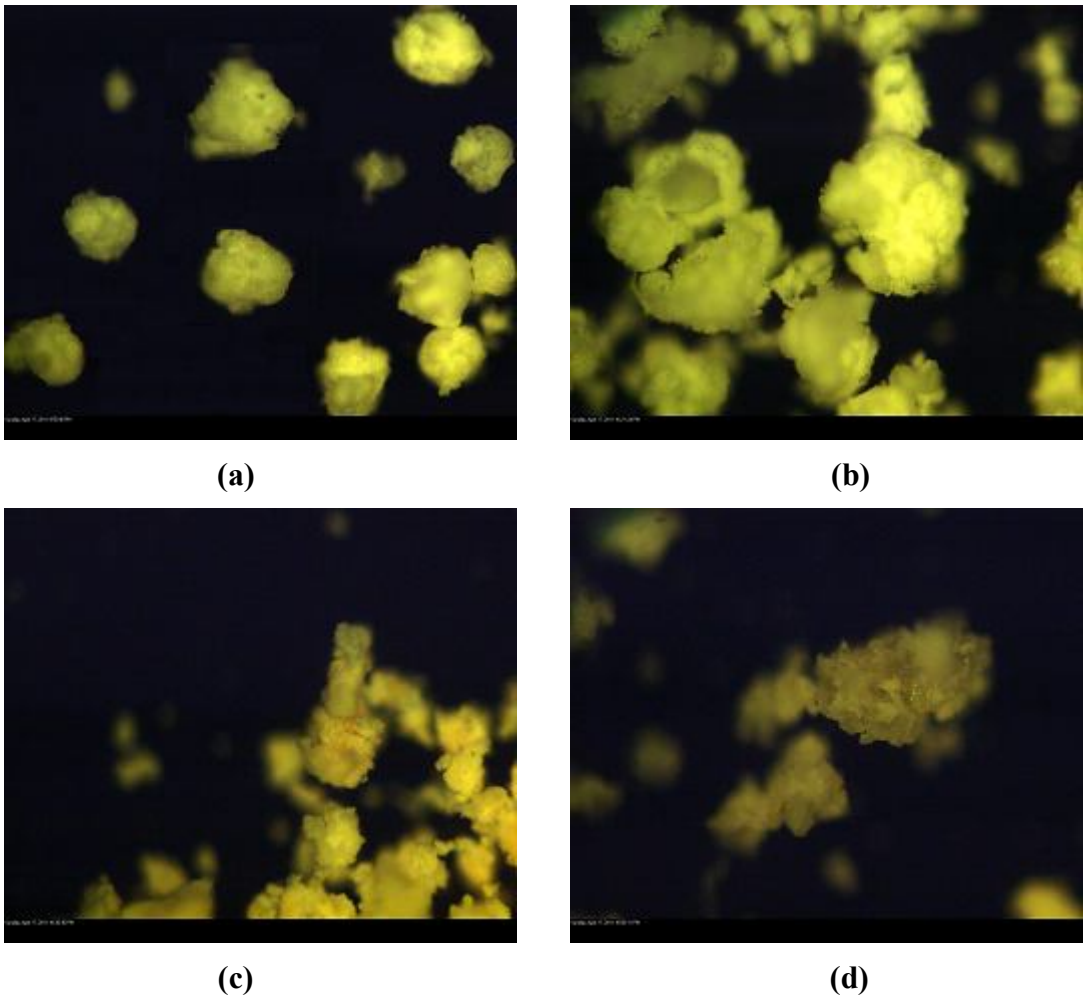


Figure 4.12 : (a) Poly(HEMA-MMA-EGDMA) beads (b) PAN grafted beads (c) Aminated beads (d) Sulfonamidated beads.

4.3 Mercury and Heavy Metal Uptake Measurements for Sorbent 1

$HgCl_2$ and $Hg(CH_3COO)_2$ salts were used in mercury adsorption experiments. The mercury sorption capacities of the sorbent were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous Hg (II) solution (0.074M). 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. The results were given in Table 4.1. According to the Table 4.1., sorption capacities of the Cd (II), Zn(II), Pb(II) and Fe(III) ions are much lower than sorption capacity of Hg(II).

Mercury binding via sulfonamide groups can occur in principle either by formation of monoamide or diamide Hg structures, which provide a means of capturing Hg(II) from aqueous solution (Figure 4.13).

Table 4.1: Metal ion loading capacities of Sorbent 1.

Metal Ion	Initial Concentration	Sorbent Capacity (mmol/g.sorbent)	Recovered metal (mmol/g.sorbent)
Hg(II) – $HgCl_2$	0.074	1.95	1.54
Hg(II) – $Hg(CH_3COO)_2$	0.031	2.62	2.50
Cd(II)	0.065	0.06	-
Mg(II)	0.017	0.02	-
Zn(II)	0.070	0.07	-
Fe(III)	0.123	0.46	-

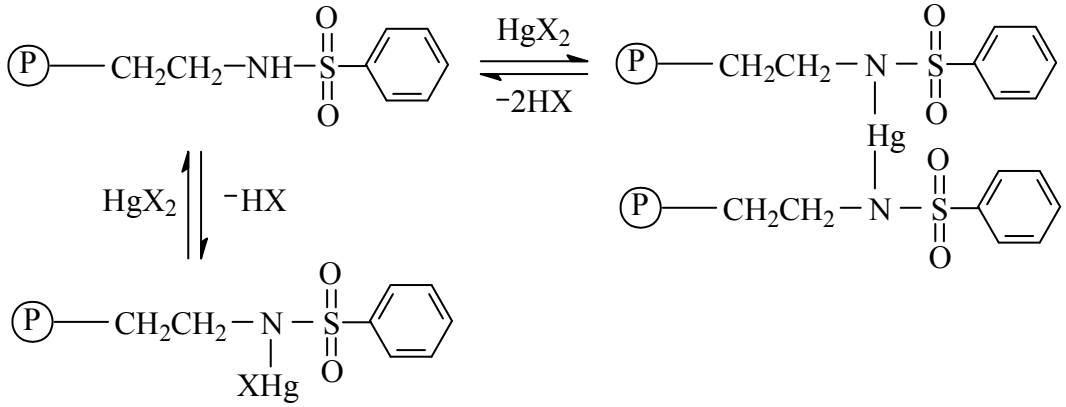


Figure 4.13 : Mercury binding of sorbents.

4.4 Mercury and Heavy Metal Uptake Measurements for Sorbent 2

Maximum loading capacities of metal ions were measured as described previously. The loading capacities were calculated from the initial and final metal contents of the solutions.

Table 4.2: Metal ion loading capacities of sorbent 2.

Metal Ion	Initial Concentration	Sorbent Capacity (mmol/g.sorbent)	Recovered metal (mmol/g.sorbent)
Hg(II) – $HgCl_2$	0.074	2.81	2.79
Hg(II) – $Hg(CH_3COO)_2$	0.031	3.10	3.06
Cd(II)	0.065	0.85	-
Mg(II)	0.017	0.15	-
Zn(II)	0.070	0.10	-
Fe(III)	0.123	1.27	-

Sorbent 2 was expected to show the characteristics of semi homogenous reaction conditions due to core-shell structure. The resulting sorbent with flexible sulfonamide grafts chains should offer the opportunity for rapid interaction with aqueous Hg (II) solutions to form mercury-sulfonamide 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.

4.5 Batch Kinetic Sorption Experiments for Sorbents

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 conducted experiments by the batch method with low mercury concentrations under buffered and non-buffered conditions.

Batch kinetic sorption experiments were performed by using $HgCl_2$ and $Hg(CH_3COO)_2$ salts and in highly dilute Hg(II) solutions ($1.470.10^{-4}$-$0.375.10^{-4}$ M) (147-37.5 ppm).

In the mercury uptake experiments, we used mercury chloride and mercury acetate because the Hg(II) ion has a reasonable affinity to chloride ions. We found mercury uptake to be somewhat higher when mercuric acetate is used.

According to the Figure 4.14 A-B and Figure 4.15 A-B, mercury binding is reasonable fast for within the pH range of 4.0–6.0. In pH depending kinetic experiments, it was investigated that sorbents exhibited a low affinity for Hg(II) at initial pH=2 (Figure 4.14 C, Figure 4.15 C), and a higher affinity between initial pH 4.0 and 6.0.

In ph=6 medium, result indicate relatively fast binding of mercury in water and pH=6 medium. This suggests that the Hg(II) linkage proceeds with deprotonation of the amide groups [36]. Thus, increasing pH of the initial solution favors Hg(II)-amide linkage formation between the reactive groups on the sorbents and Hg(II).

The plots in Fgiure 4.14 and Figure 4.15 show the decrease in Hg(II) concentration after sorbent-mercury solution interaction. The concentration-time plots obey second order kinetics with respect to the Hg (II) concentration. The plots (Figure A.1 to Figure A.8) in Appendix A.1 indicate second order kinetics for each adsorption. Plots and their equations were prepared in OriginPro 7.5.

Table 4.3: Second order rate constant of the sorbents.

Metal Solution	Sorbent 1		Sorbent 2	
	k, M-1.s-1	Correlation Factor	k, M-1.s-1	Correlation Factor
$HgCl_2$ (water)	40.90	0.982	0.042	0.939
$Hg(CH_3COO)_2$ (water)	476.6	0.981	934.8	0.946
$HgCl_2$ (pH=2)	0.193	0.963	4.367	0.938
$HgCl_2$ (pH=6)	5.872	0.994	0.072	0.940

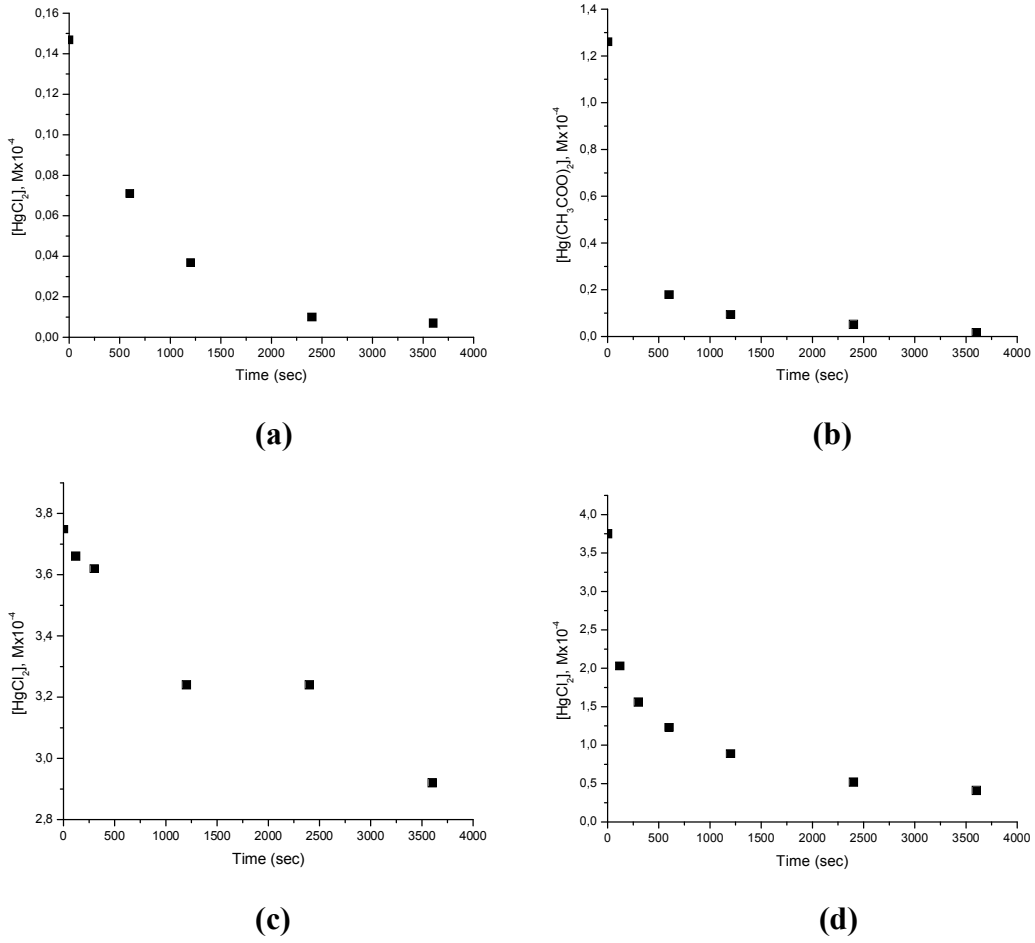


Figure 4.14 : Hg(II) vs. time plots for Sorbent 1 (a) [$HgCl_2$] (water). (b) [$Hg(CH_3COO)_2$] in (water) (c) [$HgCl_2$] (pH=2) (d) [$HgCl_2$] (pH=6).

4.6 Mercury Sorption in the Presence of Fe(III) Ions

Hg(II) sorption capacity of the sorbents in the presence of Fe(III) ions was determined and according to the Table 4.4 , sorption capacity of the mercury of the sorbent1 and sorbent2 were found almost the same. Fe (III) ion is not effect sorption capacity of the sorbents because amide and sulfonamide groups bind mercury selectively.

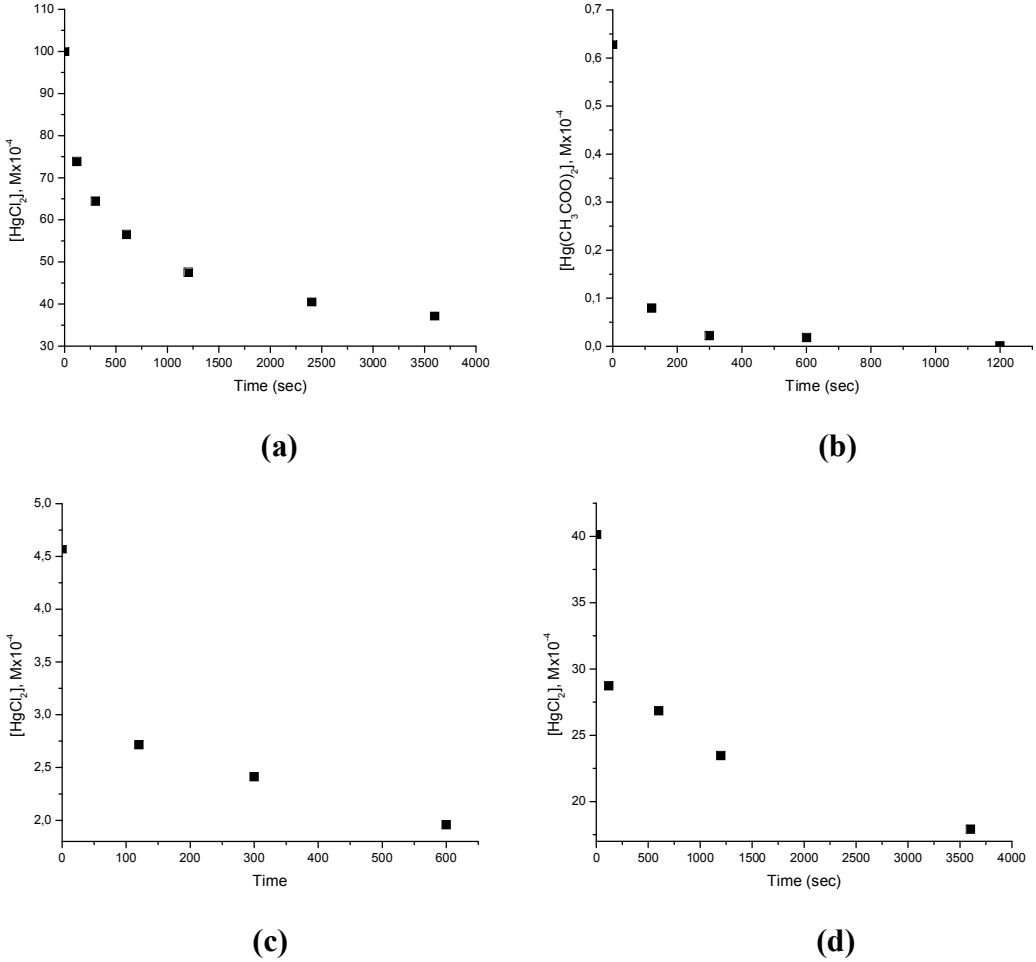


Figure 4.15 : Hg(II) vs. time plots for Sorbent 2 (a) $[HgCl_2]$ (water) (b) $[Hg(CH_3COO)_2]$ in (water) (c) $[HgCl_2]$ (pH=2) (d) $[HgCl_2]$ (pH=6).

Table 4.4: Mercury sorption capacities (mmol/g sorbent) in the presence of Fe (III) ions.

Metal Ion	Sorbent 1	Sorbent 2
Hg(II)	2.25	2.12
Fe(III)	1.37	1.87

4.7 Regeneration of Sorbents

Mercury loaded Sorbent1 and Sorbent2 was regenerated by using glacial acetic acid. Regeneration capacities were found as 2.79 mmol/g sorbent for Sorbent1 and 3.06 mmol/g sorbent for Sorbent2, respectively. According to these results, sorbents were regenerated efficiently.

5. CONCLUSION

In this thesis PAN was grafted onto cellulose and crosslinked poly (HEMA-MMA-EGDMA) terpolymer by using redox polymerization methodology in the presence of Ce(IV). Modification of grafted polymers were performed by amination and sulfonamidation reaction respectively. As a result, sulfonamidated polymer were used for removing Hg(II) ions from aqueous media.

The resulting materials are high capacity mercury sorbents. Under non-buffered conditions, the mercury uptake capacity of the sorbents were found as around 2.0-3.1 mmol/g sorbent respectively for Sorbent 1 and Sorbent 2. Also under buffered condition adsorption measurements were performed. Kinetic measurements indicate that in the range of pH 4.0-6.0 mercury binding is relatively fast.

Results show that sorbents are efficient for trace quantities of mercury, which may be interesting materials for the treatment of drinking and waste waters. Regenerebility of these materials with acetic acid makes them attractive for large scale applications.

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APPENDICES

APPENDIX A.1 : Second order kinetic plots of mercury sorption

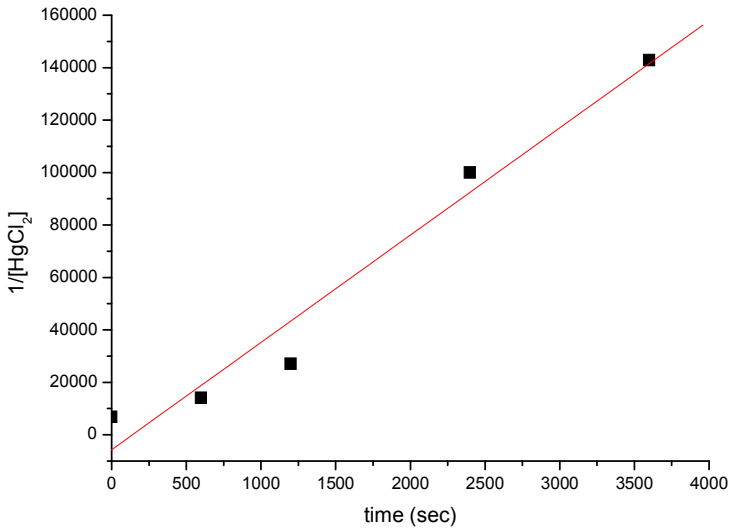

Figure A.1 : Second order kinetic plot of $HgCl_2$ (water) for Sorbent 1.

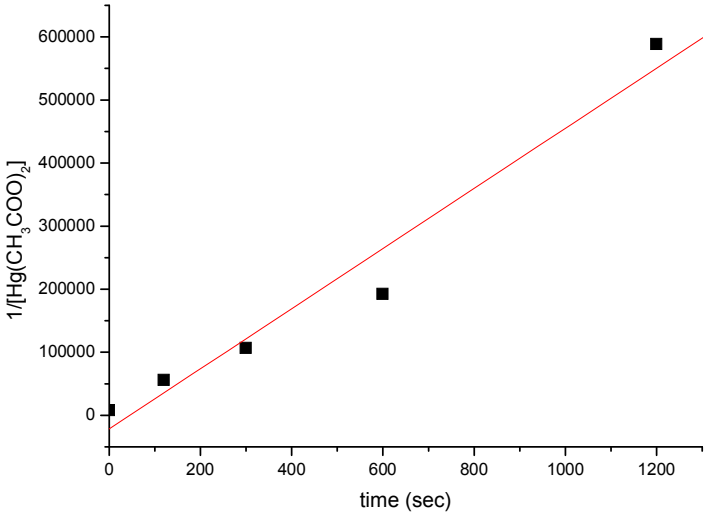

Figure A.2 : Second order kinetic plot of $Hg(CH_3COO)_2$ (water) for Sorbent 1.

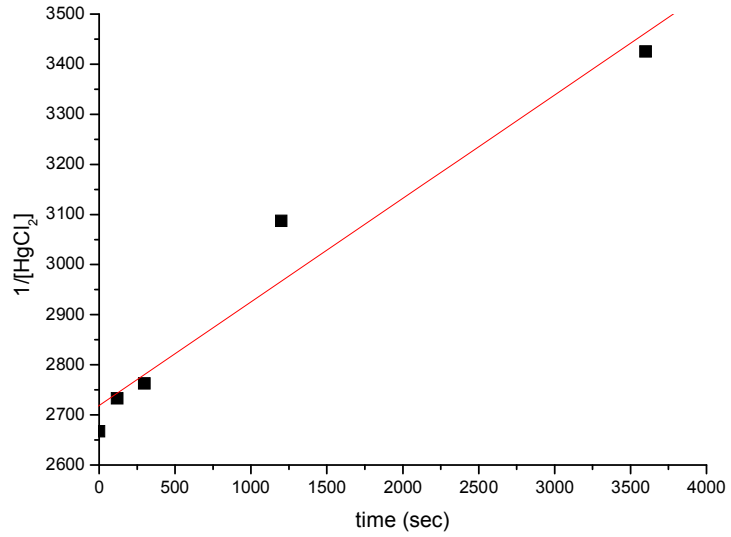

Figure A.3 : Second order kinetic plot of $HgCl_2$ (pH=2) for Sorbent 1.

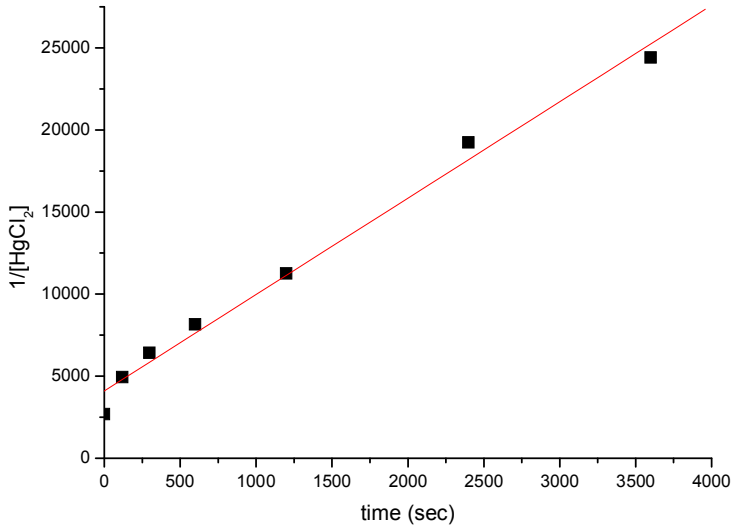

Figure A.4 : Second order kinetic plot of $HgCl_2$ (pH=6) for Sorbent 1.

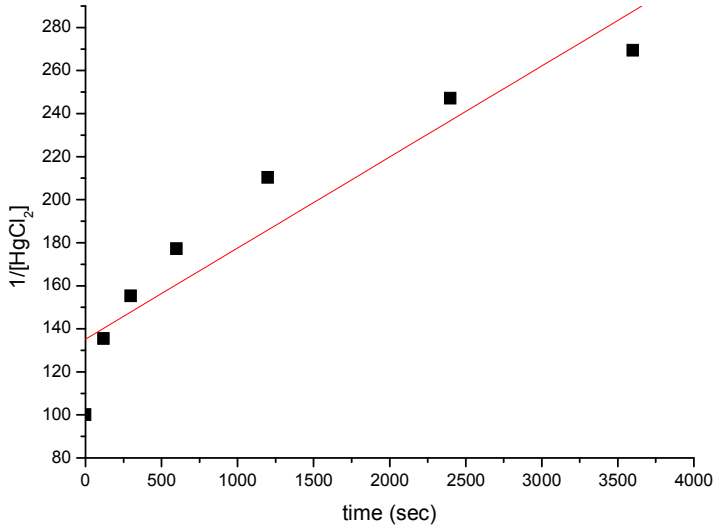

Figure A.5 : Second order kinetic plot of $HgCl_2$ (water) for Sorbent 2.

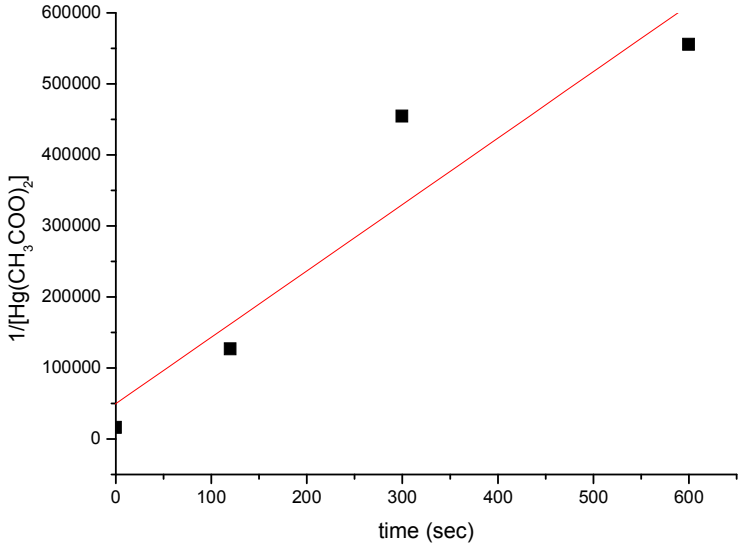

Figure A.6 : Second order kinetic plot of $Hg(CH_3COO)_2$ (water) for Sorbent 2.

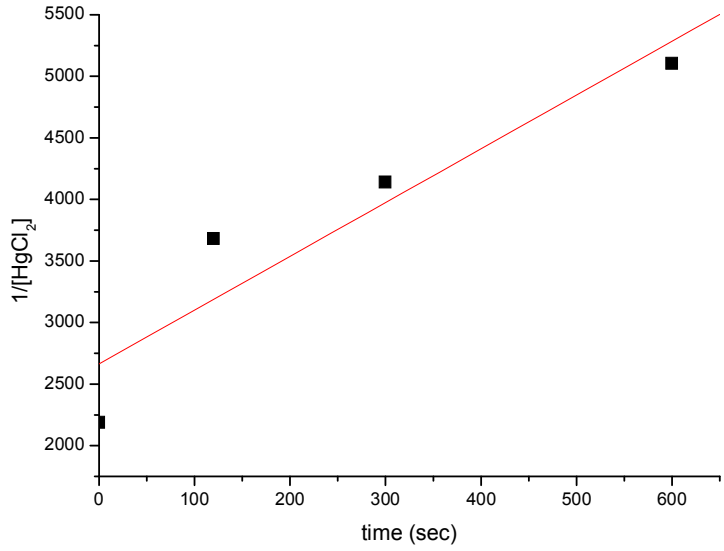

Figure A.7 : Second order kinetic plot of $HgCl_2$ (pH=2) for Sorbent 2

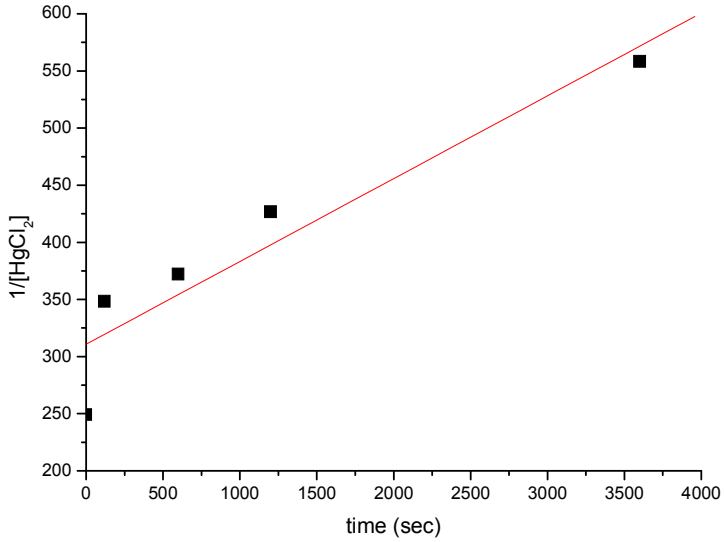

Figure A.8 : Second order kinetic plot of $HgCl_2$ (pH=6) for Sorbent 2

CURRICULUM VITAE

Candidate's full name: SEDA CEKLI

Place and date of birth: Istanbul, 07.08.1986

Permanent Address: Kartaltepe Mah. Buhar Sok. 26/5 Bakirkoy, Istanbul 34144, Turkey

Universities and Colleges attended:

Istanbul Technical University, *Chemistry Department,* (B.Sc.) (2004-2008)

Istanbul Technical University, *Polymer Sci. and Techn.,* (M.Sc.) (2008-2011)

Publications:

- **Cekli, S.,** Yavuz, E., Senkal, B. F., 2010: Sulfonamide Containing Poly(HEMA-co-MMA) Based Sorbent and Selective. *8th Hellenic Polymer Society Symposium (H-POL8)*, October 24-29, Crete, Greece.
- **Cekli, S.,** Yavuz, E., Senkal, B. F., 2008: Preparation of Polyacrylamide Hydrogel for Removal of Mercury ions. *Macro- and Supramolecular Architectures and Materials Symposium (MAM-08),* September 07-11, Düsseldorf, Germany.
- **Cekli, S.,** Yavuz, E., Senkal, B. F., 2011: Preparation of Sulfonamide Containing Cellulose Based Sorbent for Selective Removal of Mercury Ions. *Separation Science – Theory and Practice 2001 (SSTP-11),* June 05-09, Kodowas Zdroj, Poland.