ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF URETHANE FUNCTIONAL POLYMERIC RESIN AND INVESTIGATION OF ITS HEAVY METAL SORPTION PROPERTIES

M.Sc. THESIS

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Department of Chemistry

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

ÜRETAN FONKSİYONLU POLİMERİK REÇİNENİN SENTEZLENMESİ VE AĞIR METALLERİ ADSORPLAMA ÖZELLİKLERİNİN İNCELENMESİ

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To my family and friends,

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ABBREVIATIONS

AIBN : 2,2′-Azobis(2-methylpropionitrile)

DMF : Dimethylformamide

DVB : Divinyl benzene

EDTA : Ethylenediaminetetraacetic acid

EDX : Energy dispersive X-Ray analysis

EGDMA : Ethylene glycol dimethacrylate

TEGDA : Tetraethylene glycol diacrylate

FT-IR : Fourier transform infrared spectroscopy

PS : Polystyrene

PS-UR-resin : Urethane functional polymeric resin

PVBC : Poly(vinylbenzyl chloride)

SEM : Scanning electron microscope

UV-vis : Ultraviolet visible

SYMBOLS

C	**:** Concentration
t	**:** Time
q_e	**:** Amount of adsorption at equilibrium
q_t	**:** Amount of adsorption at time t
k_1 , k_2	**:** Rate constants
k_i	**:** Diffusion rate constant
$q_{experimental}$	**:** Experimental adsorption capacity
$q_{theoritical}$	**:** Theoretical adsorption capacity
R^2	**:** Coefficient of determination
q_m	**:** Maximum adsorption capacity
K_L	**:** Langmuir isotherm constant
K_F , n	**:** Freundlich isotherm constants
R	**:** Universal gas constant
A, b	**:** Temkin isotherm constants
T	**:** Temperature

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SYNTHESIS OF URETHANE FUNCTIONAL POLYMERIC RESIN AND INVESTIGATION OF ITS HEAVY METAL SORPTION PROPERTIES

SUMMARY

Metals are very important for continuity of life and ecosystems. For instance, sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) are essential for many organisms. However, some metals show toxic properties for the humans and pose a hazard for the environment. They are named "heavy metals" and have a density equal to or greater than 5. Manganese (Mn), iron (Fe), copper (Cu), cobalt (Co) and zinc (Zn) are some of the heavy metals that are essential for life but they can be toxic in case of high amount of exposure. On the other hand, arsenic (As), lead (Pb), mercury (Hg) and Cadmium (Cd) are nonessential and toxic heavy metals. They have very negative effects at low concentrations and can be lethal at high concentrations.

Mercury (Hg) is one of the toxic heavy metals with −38.8°C melting point and 356.7°C boiling point. As a leading environmental pollutant, mercury exists in elemental (Hg^0), inorganic (Hg^+ and Hg^{2+}) and organic (methyl, ethyl and phenyl mercury) forms in the environmental mercury cycle. Mercury is released to the environment by volcanoes, fires, geothermal systems. Also, gold mining, production of batteries, switches, thermometers and fossil fuel combustion are some anthropogenic sources of mercury.

Humans, animals and plants can be exposed to mercury by different ways. Dietary consumption of fish and other seafoods is an important source for exposure. Besides, drinking water, ambient air, dental amalgam fillings and medical/cosmetic products containing mercury are the other sources of exposure to mercury forms. Mercury causes many damages on mostly kidneys, the liver and neurological tissues. At high amounts, exposure to mercury leads to death.

The global Hg emission by anthropogenic sources is predicted as about 2000 tonnes/year. Furthermore, maximum mercury level in drinking water should be 2 μg/L according to the US Environmental Protection Agency. Therefore, treatment of mercury pollution and removal of mercury are considerable topics for research.

Various methods have been reported until today for removal of mercury such as chemical precipitation, membrane separation, ion exchange and adsorption. Among these methods, adsorption is considered as a remarkable technique due to its simplicity, low cost, reversibility and removal efficiency. In terms of removal of mercury from solutions, adsorption is all about chemical and physical interactions among the functional groups on the adsorbent surface and mercury in the solution. Temperature, initial adsorbate concentration, pH and chemical nature of the adsorbate and adsorbent are the factors that affect the adsorption process.

Activated carbon, bioadsorbents obtained from different sources, silicates, clays and polymers can be used as adsorbent materials for removal applications of mercury. In particular, polymeric adsorbents with specific functional groups are very important materials used for the removal of mercury. Polymeric adsorbents have high

efficiency in heavy metal removal and can be regenerated. Amines, amides and thiols are the functional groups often used in mercury selective polymeric sorbents.

In this thesis, a cross-linked polymeric resin was prepared by suspension polymerization of vinyl benzyl chloride as a monomer EGDMA as a crosslinker. Prepared polymer (PVBC) is modified with diethanolamine to obtain aminated resin. Then, the aminated resin was reacted with butyl isocyanate in the presence of DMF and dibutyltin dilaurate (DBTL) as a catalyst to obtain urethane modified resin (PS-UR-resin). The PS-UR-resin was characterized by FTIR and analytical methods.

Mercury adsorption from aqueous solutions were studied at different conditions. $HgCl_2$ salt was used in all adsorption experiments at room temperature.

In the first part of the study, optimum amount of PS-UR-resin was found 0.075 g resin and used for Hg(II) sorption experiments. In the sorption experiments depending on different initial mercury concentration, maximum mercury loading capacity of the PS-UR-resin was 2.50 $mmol.g^{-1}$ at non-buffered conditions. Moreover, pH=7 was determined as optimum pH for maximum mercury sorption capacity among different pH mediums.

In the second part of the study, Freundlich, Langmuir and Temkin adsorption isotherm models were examined for mercury sorption of PS-UR-resin. Pseudo-first, pseudo-second and intra-particle diffusion kinetics models were applied to the PS-UR-resin.

In the last part of the study, amount of mercury, which was recovered from the loaded resin, is 2.32 $mmol.g^{-1}$ indicating regeneration ability of PS-UR-resin. Furthermore, sorption capacities of PS-UR-resin were investigated for different heavy metal ions.

ÜRETAN FONKSİYONLU POLİMERİK REÇİNENİN SENTEZLENMESİ VE AĞIR METALLERİ ADSORPLAMA ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Metaller biyolojik hayatın ve ekosistemlerin devamlılığı açısından oldukça önemlidir. Sodyum (Na), potasyum (K), kalsiyum (Ca) ve magnezyum (Mg) gibi metaller birçok canlı için önemlidir. Ancak ağır metaller insanlar için toksik özellik gösterir ve çevre için risk teşkil eder. Yoğunluğu 5'e eşit veya 5'ten büyük olan bu metaller "ağır metaller" olarak bilinirler. Örneğin, manganez (Mn), demir (Fe), bakır (Cu), kobalt (Co) ve çinko (Zn), canlılar için önemli olan ancak fazla miktarlarda toksik etki gösteren ağır metallerden bazılarıdır. Öte yandan, arsenik (As), kurşun (Pb), cıva (Hg) ve kadmiyum (Cd) gibi ağır metaller düşük konsantrasyonlarda bile toksik etki göstermekle birlikte, yüksek konsantrasyonlarda ölümcül etki gösterirler.

Cıva (Hg), -38,8°C erime noktası ve 356,7°C kaynama noktası ile bu toksik ağır metallerin en önemlilerinden biridir. Çevreyi kirleten metallerin başında gelen cıva, doğadaki cıva döngüsü içinde elementel (Hg^0), inorganik (Hg^+ and Hg^{2+}) ve organik (metil, etil ve fenil cıva) cıva formlarında bulunmaktadır.

Cıva, doğal kaynaklı veya insan kaynaklı olmak üzere iki türlü doğaya salınabilir. Volkanlar, yangınlar ve jeotermal sistemler cıvanın doğal kaynaklarına örnek olarak verilebilir. Bunun yanında, altın madenciliği, batarya üretimi, fosil yakıtların kullanımı, metal ve çimento üretimleri ve termometreler gibi insan kaynaklı bazı faaliyetler ve ürünler de cıvanın doğaya salınması için birer kaynaktır.

İnsanlar, hayvanlar ve bitkiler birçok farklı yoldan cıvaya maruz kalabilirler. Balık ve diğer deniz ürünlerinin düzenli olarak tüketimi, en önemli cıva maruziyeti yollarından biridir. Gıdalarla vücuda alınan cıvanın günlük ortalamasının yaklaşık 2-20 μg olduğu düşünülmektedir ve deniz ürünlerini fazla tüketen insanlar için bu miktar çok daha fazladır. Bunun dışında, içme suları, solunan hava, amalgam diş dolguları ve cilt beyazlatıcı kremler gibi cıva içeren tıbbi ve kozmetik ürünler, cıvanın farklı formlarına maruz kalınmasına neden olur.

İnsan vücuduna alınan cıvanın miktarı, saç, idrar, kan ve kordon kanından alınan örneklere yapılan çeşitli testlerle belirlenebilir. Cıva insan vücudunda sitotoksik, nörotoksik, nefrotoksik ve immünotoksik etkilere sahiptir. Cıvanın bütün formları toksiktir ve insan vücuduna girdikten sonra, dışarı atılma oranları çok düşüktür. Cıva, böbrekler başta olmak üzere, karaciğer ve nörolojik dokularda ciddi hasarlar yaratır. Cıvanın yüksek miktarlı alımı, ölüme sebep olur. Öyle ki, 1956 ve 1965 yıllarında Japonya'da cıva maruziyetine bağlı bir salgın literatüre geçmiştir. Denge kaybı, konuşma ve işitme güçlüğü, duyu ve hareket bozukluğu, görme alanının daralması gibi belirtilerle ortaya çıkan bu hastalık, "Minamata hastalığı" olarak bilinir ve o tarihlerde birçok insanın ölümüne sebep olmuştur.

İnsan kaynaklı ürün ve faaliyetlere bağlı cıva emisyonlarının dünya genelinde yaklaşık olarak 2000 ton/yıl olduğu tahmin edilmektedir. Atmosfere yapılan

antropojenik emisyonların %56'sından Çin, Hindistan, Endonezya, Güney Afrika, Kolombiya, Gana, Rusya ve ABD sorumludur. Topraktaki cıva birikiminin ise global olarak 250-1000 Gg civarında olduğu düşünülmektedir. Ayrıca, cıvanın yarattığı su kirliliği göz önüne alınarak, ABD Çevre Koruma Ajansı tarafından içme sularındaki maksimum cıva seviyesinin 2 µg/L olması gerektiği belirlenmiştir. Cıvanın sebep olduğu bu çevresel etkilerin boyutları düşünüldüğünde, cıva kirliliğinin giderilmesi oldukça önemli ve dikkat çekici bir araştırma konusudur.

Bu zamana kadar cıvanın giderilmesinde birçok farklı yöntem denenmiş ve kullanılmıştır. Kimyasal çöktürme, membran ayırma, iyon değiştirme, biyolojik ayırma ve adsorpsiyon bunlardan bazılarıdır. Tüm bu yöntemlerin içinde, adsorpsiyon yaygın olarak kullanılanlardan biridir. Basit bir yöntem olması, düşük maliyeti, ağır metal giderimindeki verimliliği ve tersinir olması dolayısıyla ağır metalin geri kazanımına ve aynı zamanda adsorbentin tekrar kullanımına izin vermesi bu yöntemin avantajları olarak sayılabilir.

Çözeltilerden cıva giderimi açısından bakıldığında adsorpsiyon, adsorbent yüzeyindeki fonksiyonel gruplar ile çözelti içerisindeki cıva iyonlarının kimyasal ve fiziksel etkileşimlerinden ibarettir. Sıcaklık, adsorbatın başlangıç konsantrasyonu ve pH adsorpsiyon prosesini etkileyen en önemli parametrelerdir. Adsorbatın ve adsorbentin kimyasal nitelikleri de adsorpsiyonu oldukça etkiler. Adsorbentin yüzey alanı, por hacmi ve partikül boyutu, adsorpsiyon prosesi açısından dikkate alınmalıdır. Ayrıca, adsorbentin hazırlanışında kullanılan materyal ve metotların ucuz olması ve adsorbentin rejenerasyon kabiliyeti, değerlendirilmesi gereken diğer faktörlerdir.

Aktif karbon, pirinç samanı, ceviz kabuğu, kitosan ve lignin gibi farklı kaynaklardan elde edilmiş biyoadsorbentler, silikatlar, killer ve polimerler, cıva adsorpsiyonu uygulamalarında adsorbent materyali olarak kullanılabilir. Özellikle de, spesifik fonksiyonel gruplara sahip polimerik adsorbentler, cıva gideriminde çokça kullanılmaktadır. Cıva seçimli polimerik sorbentlerde amin, amid ve tiyol grupları fonksiyonel grup olarak sıklıkla kullanılır. Ağır metal giderimi çalışmalarında yüksek verime sahip olmaları ve rejenerasyona uygun olmaları, polimerik adsorbentlerin en önemli avantajlarıdır.

Bu tezde, vinil benzil klorür (%90) ve EGDMA (%10)'nın süspansiyon polimerizasyonu ile çapraz bağlı bir polimerik reçine hazırlanmıştır. Elde edilen polimerik sorbent (PVBC), dietanolamin ile aminlenmiştir. Aminlenmiş olan reçine, DMF varlığında ve dibütiltin dilaurat katalizörlüğünde bütil izosiyanat ile reaksiyona sokulmuştur. Böylece üretan fonksiyonlu polimerik reçine (PS-UR-reçine) elde edilmiştir. PS-UR-reçine, FTIR ve analitik yöntemlerle karakterize edilmiştir.

Sulu çözeltilerden cıvanın PS-UR-reçine ile adsorpsiyonu, farklı koşullarda çalışılmıştır. Tüm adsorpsiyon deneyleri oda sıcaklığında yapılmıştır ve cıva çözeltilerinin hazırlanmasında $HgCl_2$ tuzu kullanılmıştır.

Çalışmanın ilk kısmında, 0,050 g-0,125 g arasındaki kütlelerde PS-UR-reçineler, cıva çözeltisi ile 24 saat boyunca etkileştirilmiş ve optimum reçine miktarı 0,075 g olarak bulunmuştur. Tüm adsorpsiyon deneylerinde bu reçine miktarı kullanılmıştır. Sonrasında, PS-UR-reçine, farklı cıva başlangıç konsantrasyonlarındaki çözeltilerilerle (0,005 M-0,100 M) 24 saat boyunca etkileştirilmiştir. Cıva başlangıç konsantrasyonu arttıkça, reçinenin cıva tutma kapasitesinin arttığı gözlemlenmiş ve maksimum cıva tutma kapasitesi 2,50 $mmol.g^{-1}$ olarak bulunmuştur.

Çalışmanın ikinci kısmıda, Freundlich, Langmuir ve Temkin adsorpsiyon izotermleri, PS-UR-reçinenin cıva adsorplama davranışının özelliklerini belirlemek amacıyla incelenmiştir. Sonuç olarak, PS-UR-reçinenin Langmuir adsorpsiyon izotermine uygun davrandığı görülmüştür. Bunun yanında, reçinenin cıva adsorpsiyonu açısından kinetik davranışını belirleme çalışması yapılmıştır. Bunun için düşük cıva konsantrasyonuna sahip çözeltilerle ($1.0x10^{-4}$ M), 0,025 g PS-UR-reçine en uzunu 1 saat olmak üzere farklı sürelerde etkileştirilmiştir. Zaman ilerledikçe reçinenin cıva adsorplama kapasitesinin arttığı ve nihayetinde sabitlendiği görülmüştür. Bu çalışmada, reçine için yalancı birinci dereceden, yalancı ikinci dereceden ve parçaçık içi difüzyon kinetik modelleri uygulanmış ve PS-UR-reçinenin yalancı ikinci dereceden kinetik modeline uygun davrandığı bulunmuştur.

Çalışmanın son kısmında, 0,100 M cıva çözeltisiyle önceden etkileştirilmiş yüklü reçine, asetik asit ortamında 1,5 saat boyunca karıştırılarak desorpsiyon çalışması yürütülmüştür. Bu çalışma sonucunda, 2,32 $mmol.g^{-1}$ cıvanın geri kazanıldığı bulunmuş ve PS-UR-reçinenin iyi bir rejenerasyon yeteneğine sahip olduğu ve tekrar tekrar kullanılabileceği görülmüştür. Son olarak, PS-UR-reçine Zn^{2+}, Pb^{2+} ve Cd^{2+} iyonlarını içeren 0,100 M'lık çözeltilerle 24 saat boyunca etkileştirilmiştir. PS-UR-reçinenin cıva dışındaki bu ağır metalleri adsorplama özelliğinin çok düşük olduğu görülmüştür.

1. INTRODUCTION

Many metals are essential to human body and ecosystems in the right amounts. However, metals can cause important health and environmental effects with chronic low exposures. Moreover, they can be toxic due to high exposures. The main toxic metals are heavy metals such as lead, cadmium, arsenic and mercury. Heavy metals are prone to accumulate in the environment and also in human, animal and plant cells, leading to many negative effects. Therefore, heavy metal polution is one of the main concerns all over the world. Hence, treatment of heavy metal pollution is an important and remarkable topic for research [1].

Mercury, as one of these toxic heavy metals, has a lot of different chemical properties, bioavailabilities and toxicities. Nowadays, Hg emission to the atmosphere is globally about (5.5−8.9) × 10^6 kg/year. Mercury exists in the forms of elemental mercury (Hg^0), inorganic mercury (Hg^{1+} or Hg^{2+}) and organic mercury (such as methylmercury) and these forms can transform each other in the environmental mercury cycle. Environmental release of mercury is originated from both natural sources like volcanoes and anthropogenic sources like coal-burning and gold-mining. Mercury forms have nephrotoxic, hepatotoxic, immunotoxic and neurotoxic effects in case of exposure of human body. Also, consumption of seafoods is the best-known exposure pathway [2].

Various techniques have been reported so far for removal of mercury such as chemical precipitation, membrane separation, ion exchange and adsorption [3]. Among these techniques, adsorption is quite popular due to its low cost, simplicity, reversibility, efficiency for removal of the metal ion from water and ability for recovery of the metal ion [4]. Furthermore, polymeric adsorbents with specific functional groups are very important materials used for the removal of mercury [5].

In this study, removal of mercury from water was achieved by a cross-linked polymeric resin. For this purpose, suspension polymerization of vinyl benzyl chloride-co-EGDMA was performed. After amination of PVBC beads with diethanol

amine, aminated polymeric sorbent was modified with urethane groups by using butyl isocyanate in the presence of dibutyltin dilaurate as catalyst. This urethane-modified polymeric resin (PS-UR-resin) was characterized by using analytical and spectroscopic methods. Then, the capacity of mercury adsorption, adsorption kinetics, regeneration capacity and the adsorption capacity for different metal ions were investigated colorimetrically and titrimetrically for PS-UR-resin.

2. THEORY

2.1 Heavy Metals and Their Importance

Metals can be classified as essential light metals, essential heavy metals and toxic heavy metals in terms of their importance for human life. Sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) are highly important for continuity of biological life and therefore essential light metals. The amount of these four metals are much higher than other metals in human body and these metals have significant functions in metabolic processes [6].

The term “heavy metal” generally refers to metals which have a density equal to or greater than 5 and pose a hazard for the environment or for the humans [7]. Manganese (Mn), iron (Fe), copper (Cu), cobalt (Co), zinc (Zn), selenium (Se), chromium (Cr), molybdenum (Mo) and nickel (Ni) are included in the group of essential heavy metals. They are necessary in small quantities for human health and usually utilized in enzymatic activities. However, these metals become toxic when the intake into the human body is excessive compared to the required amount. Toxic heavy metals are nonessential and harmful for human body and arsenic (As), lead (Pb), mercury (Hg) and Cadmium (Cd) are placed in this group of heavy metals. They have negative effects at even low concentrations for human metabolism and can be ocassionally lethal for greater amount of exposure [6]. Moreover, most of the heavy metals and their compounds have potential to cause mutations and cancer [8].

Heavy metals are evaluated as leading environmental pollutants as a result of rapid industrialization, transportation and agricultural activities. They affect air, water, soil, plants and various organisms. The heavy metals which are responsible for soil pollution are Cu, Cd, Zn, Ni, Cr and especially Pb as the most widespread one. Pesticides and oil drilling sites are main sources of heavy metals in soils. The plants and soil microorganisms absorb these metals via their metabolic activities. Considering that the soil meets the need of more than 90% of human foods, these heavy metals easily find their way to human body through plants. Besides, heavy

metals pass from soils into ground waters and directly endanger drinking waters [8]. Fish and shellfish species are also seriously affected by heavy metals in soils and waters and their consumption is another way to take heavy metals into the human body [7]. Table 2.1 shows anthropogenic sources of some important heavy metals and their health effects on humans.

Table 2.1 : Main anthropogenic sources of some heavy metals and their effects on humans [9-12].

Heavy metal	Anthropogenic sources	Effects on humans
Pb [9]	• Auto emissions from cars with leaded gasolines to air • Water and soil pollution near metal mining areas	• Dysfunction in kidneys, reproductive system, brain, liver, and nervous system • Anemia, gastrointestinal problems, anorexia • Mental retardation in children
Cu [10]	• Soil, air and water pollution due to incineration and metal smelting sites, foundries and power plants	• Acute hemolysis and hemoglobinuria, gastrointestinal ulcerations and bleeding • Nephropathy, cardiotoxicity, tachycardia, tachypnea
Zn [10]	• Soil and water pollution due to zinc mining, purification and decomposition • Usage of zinc-based products such as paints and batteries	• Hematological effects with oral exposure • Gastrointestinal effects such as nausea and vomiting with oral exposure • Fever, sweating, headache and weakness with inhalation
As [11]	• Mining, smelting, combustion of fossil fuels • Usage as wood preservative and pigment • Usage as a component of agricultural insecticides	• Acute gastrointestinal syndrome with a dysphagia followed by organ damage • Symptoms from darkening of skin to cancer with chronic poisoning in years

Table 2.1 (continued): Main anthropogenic sources of some heavy metals and their effects on humans [9-12].

Heavy metal	Anthropogenic sources	Effects on humans
Cd [12]	• Ni–Cd batteries, coatings and platings, stabilizers for plastics, fertilizers • Fossil fuel combustion, incineration, mining and cement production • Smoking cigarettes	• Bronchitis, chemical pneumonitis, gastrointestinal symptoms as acute effect • Renal failure, anemia, impaired lung function, osteoporosis and bone fractures as chronic affect
Hg [12]	• Gold mining • Coal combustion, metal and cement production • Pesticides and fertilizers	• Severe pneumonitis and acute necrotizing bronchitis as acute effect • Gastrointestinal tract, kidney and central nervous system damage as chronic effect

Not only anthropogenic activities but also some natural activities cause spread of the heavy metals on earth. For instance, rock weathering events, volcanic eruptions and microbial colonizations contribute to the increase of As level in the environment. Similarly, contamination of Cd is resulted from dust storms, volcanic activities, erosions and wildfires in addition to anthropogenic sources. Hg and Pb contaminations are also originated from volcanoes and natural fires [12].

2.1.1 Characteristics of mercury

Mercury (Hg) is a metal with − 38.8 °C melting point and 356.7 °C boiling point. It is considered as a risk for global public health because of its toxicity [13]. Mercury exists in elemental, inorganic and organic (alkyl) forms. Elemental or metallic mercury (Hg^0) is a liquid with silver color at room temperature. This form is the best known form and found in thermometers, dental amalgam fillings and fluorescent lamps. It is also used in traditional rituals and medicines in different cultures [14]. Inorganic mercury is found in the oxidation state (I) and oxidation state (II). They are mercury salts in the form of powder or crystal. Due to their antimicrobial functions,

mercury salts have been used in disinfectants and some folk medicines. Mercurous compounds consist of mercury with oxidation state (I) which is formed by two linked Hg(II) ions. Hg(I) ions are stable in acidic medium, while it readily turns into mercuric or elemental forms at higher pH. Mercuric compounds consist of mercury with oxidation state (II) such as $HgCl_2$, HgO, HgI_2. The most important inorganic mercury source is mercury(II) sulfide (HgS). This compound has two crystalline structure including cubic metacinnabar (black) and the hexagonal cinnabar (red). Mercury mines are rich in cinnabar ores. Both are soluble in aqua regia, but insoluble in water, alcohol and mineral acids. [14, 15]. Two forms of mercury, elemental mercury and cinnabar, are shown in the Figure 2.1.

Figure 2.1 : Elemental mercury, which also known as “quicksilver” (left) [14] and red hexagonal cinnabar (right) [16].

Organic mercury compounds include mercury compounds with methyl, ethyl or phenyl groups. Methylmercury is transported by bioaccumulation in food chain after it is taken up as inorganic mercury from aquatic mediums and methylated by microorganisms. Ethyl mercury has been included in vaccine preservatives such as thiomersal (or thimerosal) for years. However, it has removed from most of the vaccines in the USA because of its neurotoxicity. Phenyl mercury has been added in biocides. It has as the same toxic behaviour as inorganic mercury [14].

2.1.2 Environmental release of mercury

Mercury is released to the environment by both anthropogenic sources and natural sources. Natural sources of volatized mercury are volcanoes, fires, geothermal systems and mercury evaporated from the seas. Mercury levels in the atmosphere have risen above natural levels because of anthropogenic emissions since industrial evolution. Main anthropogenic sources of mercury are gold mining, fossil fuel combustion, solid waste incineration and various industrial processes [17]. Production of switches, thermostats, batteries in electrical industry, production of caustic soda and nuclear reactors are some of the examples for industrial usage of

mercury. Mercury is also used as a solvent for some reactive and precious metals, as antifungal agents for wood processing and as a preservative in pharmaceutical products. After the widespread use of mercury which peaked in 1964, industrial demand for mercury decreased between 1980 and 1994 due to legal regulations on reducing mercury use [18].

Mercury forms circulating in the environment include elemental mercury (Hg^0) and inorganic mercury with two oxidation states (Hg(I) and Hg(II)). Mercury participates in the environmental cycle through numerous chemical and physical transformations in the land, water and air. Figure 2.2 describes mercury cycles in the environment. The elemental mercury vapor released into the atmosphere via natural and antropogenic sources is transported by the wind for a year or more and accumulates in soil and water. Hg^0 vapor is oxidated to Hg(II) photochemically. This oxidated form of mercury returns to the Earth's surface with water vapor as rain [17].

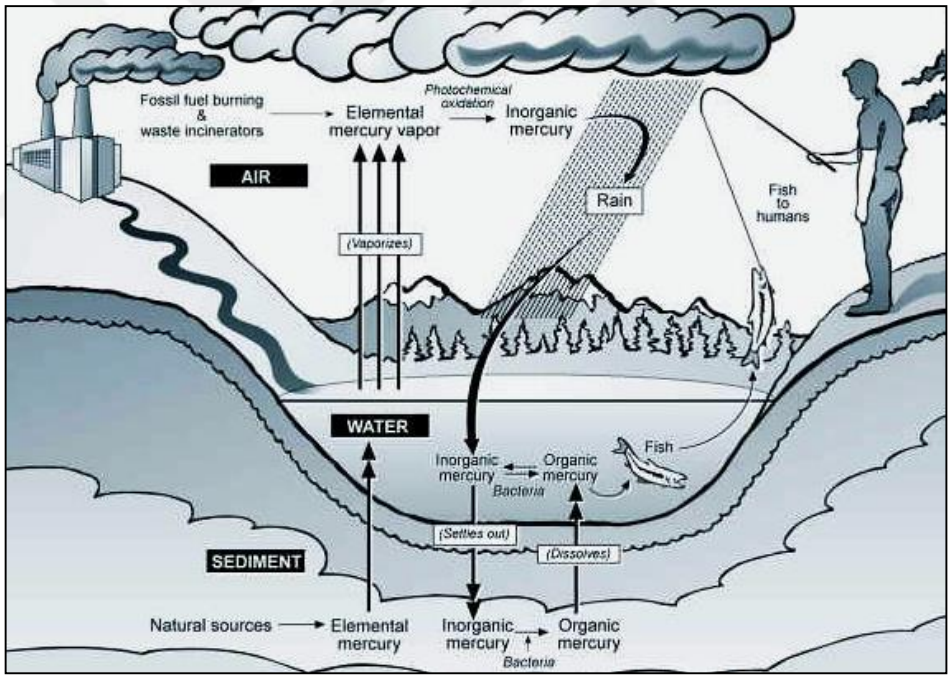


Figure 2.2 : Mercury cycles in the environment [19].

Inorganic mercury is converted into barely soluble mercury sulfide and then more soluble methylmercury by sulfate-reducing bacteria in anaerobic conditions such as well-buried muddy sediments of rivers, lakes, and oceans. Methylmercury is more toxic than inorganic mercury and biologically accumulates in higher amounts than other forms of mercury due to prolonged elimination process by organisms [17]. Methylmercury-processing bacteria can be consumed by bigger organisms so

methylmercury can enter the food chain. In another way, methylmercury can stick to planktons and similarly carried in the food chain. Therefore, methylmercury is finally eaten by bigger and bigger organisms such as fish species, other animals and humans. Methylmercury can also vaporize and enter the atmosphere as a part of environmental cycle [19].

The global Hg emission by anthropogenic sources is calculated as approximately 2000 tonnes/year. The Hg emissions of China, India, Indonesia, South Africa, Columbia, Ghana, Russia, and the USA are responsible for 56% of global anthropogenic emission to the atmosphere. Furthermore, Hg accumulation in the soil is thought to be globally 250-1000 Gg (1 Gg $=10^3$ tonnes) [13]. Over the last decades, anthropogenic Hg emissions have been decreased by half but contamination of Hg continues to be a global problem today [17]. Table 2.2 gives some examples of mercury levels in ambient air and water sources and clarifies how anthropogenic sources contribute to mercury contamination.

Table 2.2 : Examples of mercury levels in ambient air and some water sources [20,21].

Source	Mercury level (per litre)
Ambient air [20]	0.002 - 0.01 ng
Ambient air near mercury mines, refineries, and agricultural fields treated with mercury-containing fungicides [21]	10 – 15 ng
Unpolluted marine water [21]	2 ng
Coastal area near the industrial areas (New York)[21]	90 ng
Rainwater [20]	5 - 100 ng

2.1.3 Toxicokinetics of mercury

Humans, animals and plants are incapable of avoiding exposure to mercury forms as a result of that mercury is an omnipresent environmental pollutant and toxicant [18]. Humans can be exposed to elemental and inorganic mercury in occupational areas such as gold mining and dentistry. Products which cause direct body contact such as dental amalgams, skin-lightening creams, broken mercury-containing materials are also other ways of exposure to mercury. Besides, dietary consumption of seafoods, especially tuna, swordfish, grouper, mackerel and shellfish species is a major source of methylmercury exposure. Rice and some other foods which are grown in mercury-

contaminated areas are also evaluated as reasons for exposure to mercury [22]. Average daily mercury intake from food is about 2-20 μg and this level can be higher for people with high proportion of fish consumption. Drinking water and inhalation of ambient air are also other sources for exposure to mercury. Nearly all of the mercury in uncontaminated drinking water is thought to be Hg(II) form. Maximum mercury level in drinking water is determined as 2 μg/L by the US Environmental Protection Agency [20].

All of the mercury forms are toxic and mercury excretion rate is higly low when it is taken to the human body. Mercury mostly affect the kidneys, the liver and neurological tissues. Methylmercury (CH_3Hg) and elemental mercury (Hg^0) have the highest proportion of absorption to the body among the other forms of mercury. Eating fish is the most important source for methylmercury. CH_3Hg easily enters gastrointestinal system and passes through both the placental and blood–brain barriers because of its lipid solubility. Dental amalgams consist of more than 50% of elemental mercury. Hg^0 vapor enters effectively to the human body through the lung cells and tissues around the mouth due to its lipophilicity. Hg^0 readily cross cell membranes and is oxidized to Hg^{2+} which is very reactive form of mercury by the cell [18].

Methylmercury causes various damages on neurological function, fetal growth, cardiovascular system and immune function for adults and children. Elemental mercury which is converted to Hg^{2+} mostly impairs kidney and brain functions in this form. Cell, animal and plant-based researches on exposure to organic and inorganic mercury show that mercury causes cytotoxicity, neurotoxicity, teratogenicity, nephrotoxicity and immunotoxicity. Mechanism of oxidative response, protein folding, immune response, metabolic processes, DNA repair, hormone and cell apoptosis are targets of the exposure [23]. Minamata disease is a well-known neuropathy caused by methylmercury-contaminated fish and shellfish consumption. It was first reported as an outbreak in Minamata bay area, Japan in 1956 and occurred again in Agano river basin, Japan in 1965. It is characterized by loss of balance, speech and hearing disturbance, sensation and movement disturbance, constriction of visual fields [24].

Mercury concentration in a human body is determined by analysing hair, urine, blood and cord blood samples. Hair analysis provides information about methylmercury

amount in a human body, while urine analysis provides information about elemental and inorganic mercury amounts. Blood samples are used for detecting recent (1 to 2 months) exposures to both methylmercury and inorganic mercury [22]. Mercury level obtained from hair analysis is generally < 1 μg/g for people who do not consume fish and it may increase to >30 μg/g for those who regularly prefer fish in their diet. For instance, a case which causes severe symptoms with 2400 μg/g mercury level in hair and another case which causes death with 1100 μg/g mercury level in hair and 4000 μg/g mercury level in blood are found in the literature [25].

2.2 Removal Technology of Mercury

Mercury pollution is needed to be reduce due to environmental and public health concerns. Therefore, various methods have been developed for removal of mercury. Common methods are chemical precipitation, membrane filtration, oxidation-reduction, adsorption and ion exchange [26,27]. Biological treatment is a method applied for removal of mercury as well [28].

2.2.1 Chemical precipitation

Soft acides and soft bases are defined in Pearson hard-soft acid-base theory and strong covalent bond can occur between them. Mercury is a “soft acid” according to this theory hence it can bind to soft bases such as sulfur and selenium covalently. The bond between mercury and sulfur has higher strength than the bonds between mercury and other elements. Hg-S bond strength is 200 kJ/mol thus sulfur compounds are widely used in this method. In sulfide precipitation method, soluble sulfides are added into mercury-containing wastewater under basic conditions and then mercury sulphides are formed and precipitated (equation 2.1 and 2.2):

$$Hg^{2+} + S^{2-} \rightarrow HgS_{(s)} \quad (2.1)$$

$$Thiol + Hg/Hg^{2+} \rightarrow HgS_{(s)} \quad (2.2)$$

Sulfide precipitation methods are simple and inexpensive. However, they have some disadvantages such as poor selectivity, the necessity of adding high amount of sulphide for effective removal and the possibility of secondary pollution of sulfur. Sulfides and thiol hybrids nanomaterials are also developed in order to removal of mercury ions from aqueous solutions [28].

2.2.2 Membrane filtration

Membrane processes can be sorted as ultrafiltration, microfiltration, nanofiltration and reverse osmosis. This technique is preferred when mercury in wastewater is present in particulate/colloidal form. With selective permeability of the membranes, it is possible to achieve low Hg levels in treated water. The membrane systems require small space and provide high separation selectivity and efficiency. The deficiencies of the method are membrane fouling and high energy consumption [28]. Urgun-Demirtaş *et al.* performed experiments using four different membrane filters which has filtration types of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) to treat an oil refinery effluent. The results indicated that these membrane filtration methods are able to remove colloidal mercury from the effluent [29]. Fouling of a microfiltration membrane and SEM images of the fouling are seen in the Figure 2.3.

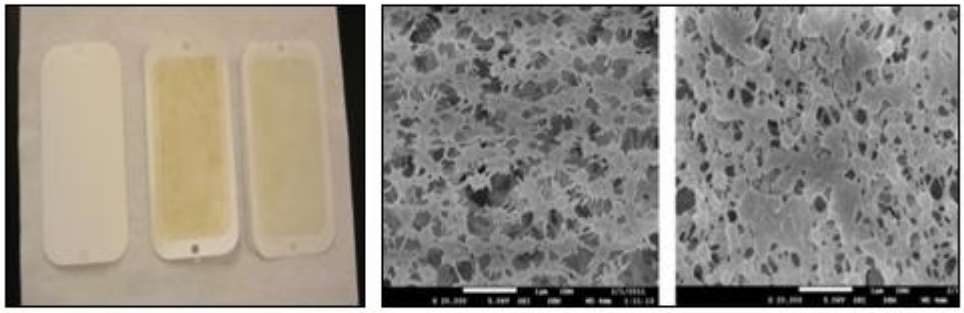


Figure 2.3 : Fouling of microfiltration membrane (MF) (left), SEM image of MF before mercury removal (middle), SEM image of MF after mercury removal (right) [29].

2.2.3 Bio-based separation

Bio-based separations include transport through the cell membrane, biosorption to cell walls and entrapment in the extracellular capsule and oxidation/reduction reactions. Depending on the method, non-living or living organisms can be used. Biological materials such as algae, bacteria, fungi and yeasts are found promising on wastewater treatment. The living microorganisms oxidize or reduce non-biodegradable heavy metal ions in wastewater and convert them less soluble forms via biochemical reactions. Thus, heavy metal ions are adsorbed or precipitated on the extra cellular protein of the microorganisms. This tecniques are attractive and open to be studied more due to being eco-friendliness and being economical. However, efficiency and specificity in metal binding are very low in real industrial wastewaters

when dead or pretreated microorganisms are used. [30]. *Escherichia coli, brown algae, green algae, pseudomonas putida, bacillus* species are tested and successfully applied for removal of mercury from wastewater in the literature [28,30].

2.2.4 Oxidation and reduction

Oxidation methods are used for removal of Hg^0 from flue gas and include catalytic oxidation, photocatalytic oxidation and photochemical oxidation [31]. The basis of the method is that Hg^0 is converted into oxidised mercury Hg^{2+} which is more easily captured by the adsorbents and thereby Hg^0 emissions to the atmosphere is controlled. In photochemical oxidation methods, UV radiation is applied to the flue gas because it breaks up oxygen molecules into two radicals and these radicals oxidize Hg^0 to Hg^{2+} [32]. In photocatalytic oxidation methods, titanium dioxide-based, bismuth-based, silver-based and hybrid catalysts are used [31].

It is also possible to use reduction methods in applications of removal of mercury ion and organic mercury compounds from aqueous solutions. Photoreduction of phenylmercury ($C_6H_5Hg^+$) and methylmercury (CH_3Hg^+) using TiO_2 photocatalyst and UV radiation is reported. The net equation of the photoreduction process is given below (equation 2.3) [27]:

$$Hg^{2+}_{(aq)} + H_2O\ (h\nu\ /\ TiO_2) \rightarrow Hg^0_{(ads)} + 2H^+ + 2O_2 \qquad (2.3)$$

2.2.5 Ion exchange

Ion exchange method is based on reversible interchange of ions between solid phase which serves as ion exchanger and a solution phase in which ion exchanger is insoluble. The basic equation of ion exchange process is shown in the equation 2.4 where M^-A^+ is ion exchanger, M^- is fixed anion of the ion exchanger, A^+ cation is the exchanger ion and B^+ cation is the cation in the solution phase. The equation represents “cation exchange”:

$$M^-A^+_{\ (solid)} + B^+_{(solution)} \rightleftharpoons M^-B^+_{\ (solid)} + A^+_{\ (solution)} \qquad (2.4)$$

In the aforementioned equation, A^+ and B^+ are called “counter ions”. Similarly, “anion exchange” is also possible and the equation is written as in equation 2.5 [33]:

$$M^+A^-_{\ (solid)} + B^-_{(solution)} \rightleftharpoons M^+B^-_{\ (solid)} + A^-_{\ (solution)} \qquad (2.5)$$

Ion exchangers generally do not require pretreatments in their applications except pH adjustment. A pH value between 4 and 7 is usually favorable. Regeneration is one of the most important advantages of the ion exchangers for providing reusability [34].

Many types of selective ion exchangers can be used for the removal of mercury from drinking water as well as wastewater. This process can be applied using inorganic materials. Zinc sulfide (ZnS), Copper sulfide (CuS) and Copper (I) sulfide (Cu_2S) are some typical examples of ion-exchanger inorganic materials used for removal of mercury [28]. Inorganic ion exchangers can be preferred in places where temperature and radiation resistances are needed. However, they have some disadvantages such as nonsuitability for column operation and low chemical stability [34].

Ion exchange process is also applied using organic materials known as ion exchange resins. The ion exchange resins can work as cation-exchanger (acidic ion exchanger) or anion-exchanger (basic anion exchanger). They are generally classified as strongly acidic, strongly basic, weakly acidic and weakly basic by their functional groups. Strongly acidic resins contain sulfonic acid groups ($-SO_3^- H^+$), while weakly acidic ones contain carboxylic acid groups ($-COO^- H^+$). Strongly basic resins have quaternary amino groups ($-N(R)_3^+ OH^-$) and weakly basic ones have primary, secondary and/or tertiary amino groups ($-NH_3^+OH^-$, $-NH_2(R)^+OH$ and/or $-NH(R)_2^+OH^-$) [35]. Figure 2.4 describes chemical structure of ion exchange resins.

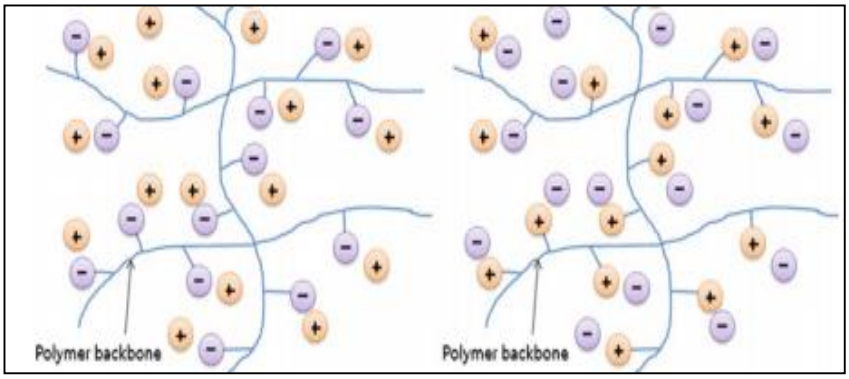


Figure 2.4 : Schematic diagram of ion exchange resins, cation exchangers (left) and anion-exchangers (right) [35].

Ion exchange resins are mostly synthetic and produced in powdered or bead forms. High capacity, wide versatility, wide applicability and low cost are advantages of the ion exchange resins. Low thermal stability and low radiation stability are considered as disadvantages of these resins. For example, a strongly acidic polystyrene-

divinylbenzene cationic resin with $–SO_3H$ functional groups is reported as selective for Hg^+ and Hg^{2+} in the literature [34].

Ion exchange resins can also be chelating ion exchangers and chelating resins which have iminodiacetate groups, thiourea groups or dithiocarbamate groups have selectivity for Hg(II) ions [36].

2.2.6 Adsorption

Adsorption is a preffered method and gives very good results for removal of heavy metals, especially treatment of industrial effluents. This method has many advantages such as high removal efficiency, low cost, availability of various adsorbents, ease of operation, capability of automatic operation and possibility of recovery of compounds [37,38]. The gradual decrease of adsorbent capacity and energy consumption because of regeneration can said to be disadvantages of the method [38].

The most general definition of adsorption process is the enrichment of one or more of the components at the interface between two bulk phases. One of these two phases is needed to be solid and the other phase is fluid which can be gas or liquid [39].

Adsorption ability of various solids can be explained by the increased free surface energy of the solids because of their extensive surface. Considering the second law of thermodynamics, this energy has to be decreased. When the solid captures molecules or atoms, the surface tension and therefore the increased free surface energy decreases [38].

Adsorption occurs by the interaction between the solid surface and a molecule described as follows: Two influences are mentioned when a molecule comes close to the solid surface. One of the influences is repulsion between the cloud of electrons in the atoms of the surface and the molecule. The other influence is van der Waals nuclear attraction force. The nuclear attraction has a much shorter radius of influence than repulsion between the cloud of electrons. According to the balance of these influences, a potential energy curve can be drawn as seen in the Figure 2.5. When the molecule reachs the point where the potential energy is the lowest at a short distance from the surface (red arrow in Figure 2.5), the molecule is adsorbed by the solid and stays there unless it is desorbed [38].

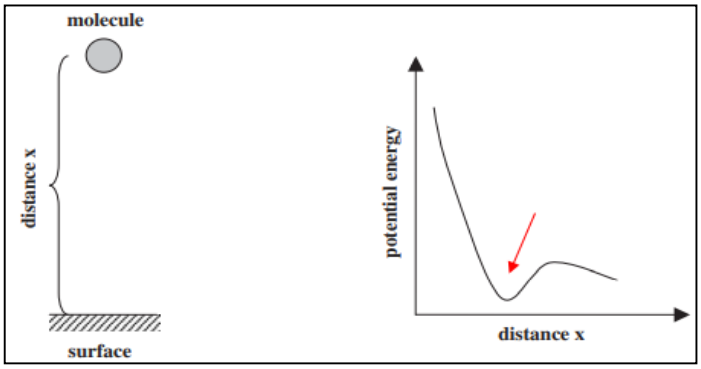


Figure 2.5 : The potential energy versus distance curve in adsorption processes [38].

The solid surface is called "adsorbent" and the material adsorbed is called "adsorbate" in adsorption processes. In the applications of removal of heavy metals, adsorbates are heavy metal ions in the solvent. The adsorption process can also be defined as different kinds of chemical and physical interactions among the functional groups on the adsorbent surface and heavy metals in the solution. Equilibrium is reached between the amount of adsorbate species adsorbed by the adsorbent and the amount of adsorbate species remaining in the solution [37]. Figure 2.6 shows the basic scheme of an adsorption process.

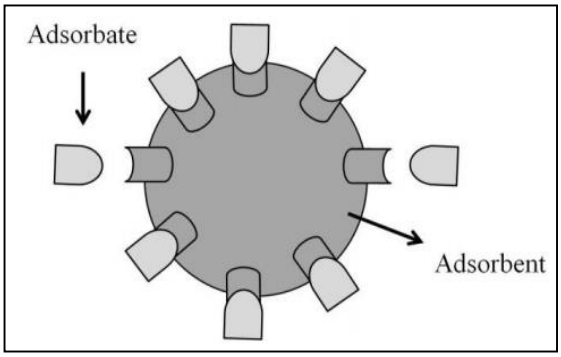


Figure 2.6 : Basic scheme of adsorption [37].

An adsorption process consists of four kinetic steps: (1) transport in the bulk solution, (2) diffusion across the film surrounding the sorbent particles, (3) diffusion in the pores of the sorbent and (4) sorption or desorption on the solid surface, respectively [37]. The rates of diffusion to the external surface of the solid and diffusion through the pores of the solid for accessing the internal surface depend on temperature and differences in concentration [40]. Figure 2.7 schematically explains four kinetic steps of an adsorption process.

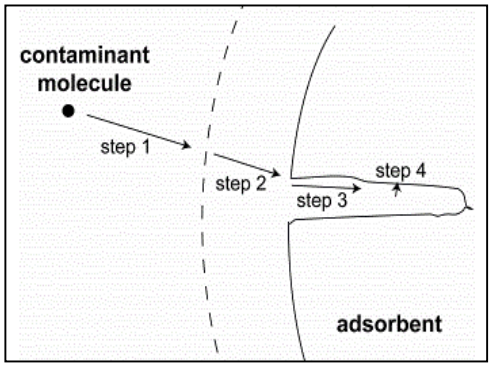


Figure 2.7 : Basic scheme of adsorption steps [41].

There are two types of adsorption called physisorption and chemisorption. Physisorption which is also known as physical adsorption refers to adsorption without chemical bonding. The forces in this process are the same as the forces of condensation of vapours. Chemisorption which is also known as chemical adsorption refers to adsorption involving chemical bonding. The interactions in this process are identical to those forms chemical compounds [39]. The main differences between types of adsorption are summarized in the Table 2.3.

Table 2.3 : Main differences between physisorption and chemisorption [37].

Physisorption	Chemisorption
Low degree of specificity	High degree of specificity depending on the number of actives sites
Low values of enthalpy	High values of enthalpy
Exothermic	Endothermic or exothermic

Adsorption processes depend on various factor relevant to the chemical nature of the adsorbate and adsorbent. Surface and pore volume of the adsorbent affect the amount of adsorption. When particle size of the adsorbent is small, the internal surface is used more efficiently in the adsorption process. [40]. Temperature, initial adsorbate concentration and pH are also the other parameters which influence adsorption performance [37]. Furthermore, efficient regeneration of the adsorbent is very important. Saturated adsorbents are regenerated therefore re-used. Desorption is achieved by changing the temperature, by changing the pressure or by washing with

a suitable reagent. The materials and methods used in the production of adsorbent must be inexpensive as well [37,40].

Activated carbon is one of the adsorbent material for removal of mercury from aqueous solutions and can be made from various sources such as wood, peat, coal, lignite or some industrial waste materials [17,42]. Bioadsorbents are also an option for removing mercury from contaminated solutions via adsorption. Numerous bioadsorbents obtianed from different sources such as rice straw, banana corn, neem leaves, palm oil fuel ash, chitosan, lignin, walnut shell and date pits can be found in the literature of removal of mercury. Besides, silicates, clays, natural minerals, nanoparticles, zeolites and polymers are widely used in adsorption-based removal applications of mercury [17,43].

2.2.6.1 Adsorption isotherm models

Adsorption isotherm is a curve prepared according to a mathematical correlation describing the phenomenon of retention of a substance from a fluid medium to a solid at a constant temperature and pH. Adsorption equilibrium is reached when an adsorbate containing fluid has interacted with the adsorbent for a sufficient time. All adsorption isotherms are obtained by drawing a graph expressing the amount of adsorbate adsorbed at equilibrium (q_e, $mmol.g^{-1}$) against the concentration of adsorbate in solution at equilibrium (C_e, M). These isotherms give information about adsorption mechanism, surface properties and the degree of affinity of the adsorbents. These isotherms have their own advantages and disadvantages respect to the assumptions made in the model [37,44].

Freundlich isotherm is one of the most commonly used isotherms depicting adsorption equilibrium and based on the multilayer adsorption on a heterogeneous surface. It is an empirical equation and explains the adsorption process of organic and inorganic compounds on various adsorbents. The non-linear form and linearized logarithmic form of the isotherm is expressed in the equation 2.6 and 2.7, respectively:

$$q_e = K_F . C_e^{1/n} \tag{2.6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2.7}$$

where K_F and n are Freundlich constant (mmol.g^{-1}) and adsorption affinity parameter, respectively. When n equals to 1, it is linear adsorption due to identical adsorption energies for all sites. When n value is between 1 and 10, the adsorption is considered as favorable. The bigger value of n indicates a stronger interaction between adsorbent and adsorbate. If n < 0, the solvent has more affinity to surface adsorbent than adsorbate. The values of 1/n and $\ln K_F$ are equal to the slope and the intercept of the plot of $\ln q_e$ versus $\ln C_e$, respectively [37].

Langmuir isotherm is also a widely used isotherm and based on the monolayer adsorption on a homogeneous surface. The equation 2.8 expresses the isotherm and it is usually applied as in the form of equation 2.9:

$$q_e = q_m \cdot \frac{K_L\, C_e}{K_L C_e + 1} \tag{2.8}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{2.9}$$

where q_m and K_L are maximum adsorption capacity (mmol.g^{-1}) which is commonly a measure of adsorption ability of an adsorbent and Langmuir constant (L.mmol^{-1}), respectively. When the plot of $\frac{C_e}{q_e}$ versus C_e is prepared, the value of q_m can be calculated from the slope of the plot and the value of K_L can be obtained from the intercept of the plot [37,44].

Temkin isotherm is another isotherm model applied adsorption processes. The model suggests that the heat of adsorption of all molecules in the layer decrease linearly with coverage due to some indirect adsorbate interactions. The isotherm is expressed by equation 2.10. When it is linearized, the equation is written as equation 2.11:

$$q_e = \frac{RT}{b} \ln(A \ln C_e) \tag{2.10}$$

$$q_e = B \ln A + B \ln C_e \tag{2.11}$$

where B = RT/b and b is the Temkin constant related to heat of adsorption (J.mol^{-1}). A is the Temkin isotherm constant (L.g^{-1}), R is the universal gas constant (8.314 J.mol^{-1}K^{-1}) and T is the temperature (K). When the plot of q_e versus lnCe is drawn, B and A are calculated from the slope of the plot and the intercept of the plot, respectively [37].

When an experimental data is needed to be analyzed in terms of adsorption isotherms, the commonly used method is to use the linear regression of the experimental data and obtain a coefficient of determination (R^2). The best fitted isotherm is the one with R^2 value that is closest to 1 [44]. Figure 2.8 represents the plots of the isotherm models in linearized form.

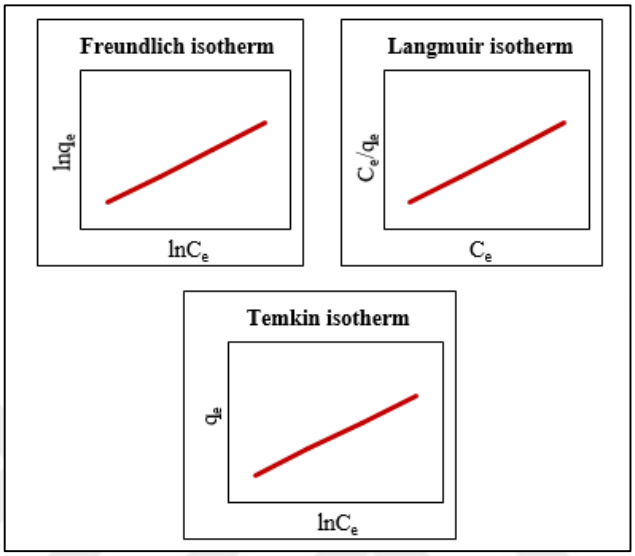


Figure 2.8 : Graphically representation of linearized forms of Freundlich, Langmuir and Temkin isotherm models.

2.2.6.2 Adsorption kinetics models

Kinetics models help to determine the rates of chemical processes and understand the factors that affect the rates. It is very useful to know the reaction rates and the dependent factors in terms of understanding the complex dynamics of the adsorption process and developing adsorbent materials for industrial application [45].

Pseudo first order model is one of the most used kinetics models. Equation 2.12 expresses the model. Equation 2.13 can be written when equation 2.12 is integrated for the boundary conditions of t= 0, q_t= 0 and t= t, q_t= q:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.12}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.13}$$

where q_e is adsorption capacity at equilibrium (mmol.g^{-1}), q_t is adsorption capacity at any time t (mmol.g^{-1}). The rate coefficient k_1 (min^{-1}) is equal to the slope of the plot $\ln(q_e - q_t)$ versus t [45].

Pseudo second order model is also a commonly used kinetics model for adsorption processes. This model is written as in the equation 2.14. Equation 2.15 can be obtained when equation 2.14 is integrated for the boundary conditions of t= 0, q_t= 0 and t= t, q_t= q:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.14}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.15}$$

where q_e is adsorption capacity at equilibrium (mmol.g^{-1}), q_t is adsorption capacity at any time t (mmol.g^{-1}). When a plot of $\frac{t}{q_t}$ versus t is prepared, the rate coefficient k_2 (g.min^{-1}mmol^{-1}) is obtained from the intercept of the slope [45].

Another kinetics model applied to adsorption processes is intra-particle diffusion model. This model is based on the idea that intra-particle diffusion may control the rate of uptake of an adsorbate for porous adsorbents. This model is simply stated by equation 2.16:

$$q_t = k_i . t^{0.5} \tag{2.16}$$

where q_t is adsorption capacity at any time t (mmol.g^{-1}) and k_i is the rate coefficient (mmol.g^{-1}min$^{-0.5}$). The slope of the plot of q_t versus $t^{0.5}$ gives k_i value [45]. Figure 2.9 shows representative plots of these three kinetics models.

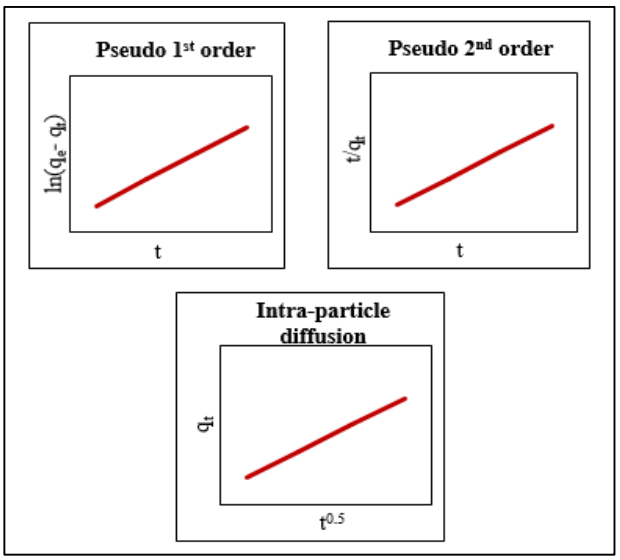


Figure 2.9 : Graphically representation of linearized forms of pseudo first, pseudo second and intra-particle diffusion kinetics models.

2.3 Polymerization

Polymerization is a process which creates a large molecule called “polymer” by binding small chemical units called “monomer” repeatedly. Sequential reactions of monomers lead to polymerization. For example, formation of polystyrene polymer from styrene monomer is shown in the Figure 2.10 and the unit in square brackets is named “repeating unit”. The number of repeating units which are arranged in the polymer chain and represent the length of the polymer is called “degree of polymerization” [46].

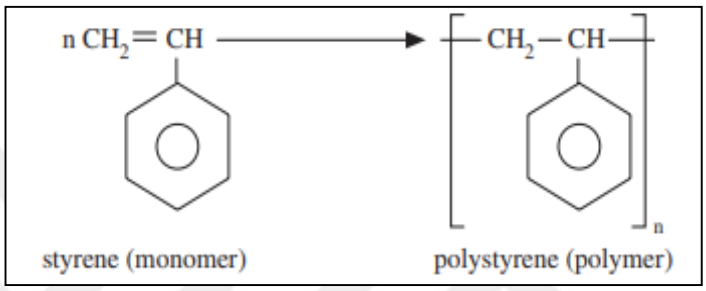


Figure 2.10 : Polymerization of “styrene” monomer to form “polystyrene” polymer [46].

Polymers can be classified in many ways. A polymer may be natural or synthetic in respect to origin of the polymer. For example, starch and cellulose are classified as natural polymers because of their plant origin, while fibers, elastomers, plastics, adhesives are some classes of synthetic polymers with various subgroups. In addition to natural/synthetic classification, polymers can be classified by polymerization mechanism, polymerization technique or polymer structure. When the polymer classification is made according to the polymerization mechanism; chain-reaction (addition) polymerization and step-reaction (condensation) polymerization are seen as two main mechanisms in polymerizations. If the polymers are evaluated in terms of polymerization technique; bulk, solution, suspension and emulsion polymerizations should be mentioned. When the polymers are classified by their structure; linear, branched or cross-linked polymers as well as homopolymers or copolymers are involved in the classification [46].

2.3.1 Chain-reaction polymerization

Chain-reaction polymerization is a polymerization mechanism involving addition of unsaturated molecules to a growing polymer chain. There is an active center at the

end of the growing polymer during the polymerization, thus monomers are sequentially added to this center. Depending on the nature of these active centers, chain-reaction polymerization is classified as free-radical, ionic (anionic/cationic) and coordination polymerization. Olefins are commonly known compounds which polymerizes with this mechanism, as exemplified by the polymerization of a vinyl monomer in the Figure 2.11. In the figure, R group may be halogen, alkyl, ester, phenyl or other groups [46].

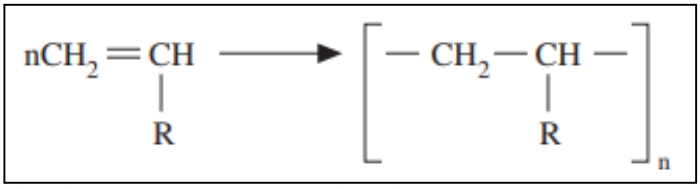


Figure 2.11 : The polymerization of a vinyl monomer [46].

This mechanism involves three main steps: initiation, propagation and termination. These steps are explained for free-radical polymerization in detail below:

- Chain initiation

In this step, a radical is created. Generally, homolytic decomposition of an initiator species I produces primary radicals R· with k_d which is the rate constant for the catalyst dissociation, as shown in the equation 2.17 below:

$$I \xrightarrow{k_d} 2\,R\cdot \tag{2.17}$$

Then, this radical R· is added to the first monomer (M) to yield the chain-initiating species $M_1\cdot$ with k_i which is the rate constant, as given in the equation 2.18:

$$R\cdot + M \xrightarrow{k_i} M_1\cdot \tag{2.18}$$

The rate of radical formation is lower than the rate of the reaction of free radicals with the monomer, therefore it is rate-determining.

- Chain propogation

A large number of monomers (M) are added to $M_1\cdot$ and thus polymer chain starts to grow with the propogation rate constant, k_p. Chain propogation forms a high-molecular-weight polymer very rapidly. Equations 2.19, 2.20 and 2.21 shows the chain propogation steps below:

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot \tag{2.19}$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot \quad (2.20)$$

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \quad (2.21)$$

- Chain termination

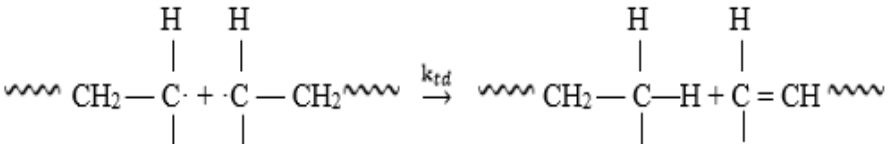
In this step, chain propogation stops and terminates. This step is represented in general form, as shown in the equation 2.22. The termination rate constant is written as k_t.

$$M_x\cdot + M_y\cdot \xrightarrow{k_t} \text{polymer} \quad (2.22)$$

However, termination may happen in different ways. First way is combination (coupling) of two propogating radicals and consequently, the formation of dead polymer. It is shown in the equation 2.23 with rate constant of termination by coupling, k_{tc}.

$$\sim M\cdot + \cdot M \sim \xrightarrow{k_{tc}} \sim M{-}M \sim \quad (2.23)$$

Second way is disproportionation. A hydrogen radical is beta to one radical center and goes to another radical center to form two dead polymer chains. As a result, one chain is saturated and the other chain is unsaturated. It is represented in the equation 2.24 with the rate constant of termination by disproportionation, k_{td}. Also, termination can happen by combination of coupling and disproportionation [47].



(2.24)

In a radical vinyl polymerization, radicals are produced in the aforementioned chain initiation step for starting the process. Free radicals are generally generated in the presence of monomers because they are reactive intermediates with limited life-times and react very fast with the monomers. The substances which provide radicals in the polimerization are named “initiators”. Initiators can be organic compounds, metal-containing compounds or metals [47].

If organic initiators are mentioned, production of free radicals occurs by rupture of atomic bonds of the initiator. Atomic bonds may be broken by three types of reactions: thermally initiated homolytic decomposition, light-induction or radiation-

induction, electron transfer from ions or atoms onto an acceptor molecule which undergoes bond dissociation (redox initiation) [47].

When thermal initiators are used, the bond dissociation energy is in the form of thermal energy. The required temperature for bond homolysis is between 50°C and 140°C. Azo compounds and peroxides are pratically used as thermal initiators. Azo compounds are represented with general formula R-N=N-R′ (R and R′ are either alkyl or aryl). The most important azo initiator is 2,2′-azo (bisisobutyronitrile), abbreviated as AIBN. It is successfully used in industrial polymer synthesis and performed at 50–80°C. When AIBN decomposes, two 2-cyano-2-propyl radicals and molecular nitrogen is formed, as seen in the Figure 2.12. The driving force of this bond dissociation can said to be the generation of the energetically favored and stable nitrogen molecule [47].

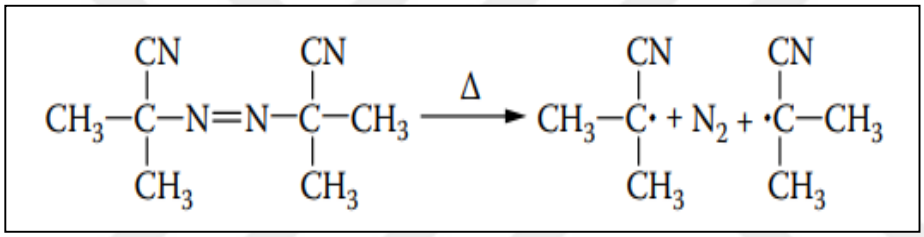


Figure 2.12 : The decomposition of AIBN initiator [47].

2.3.2 Suspension polymerization

Suspension polymerization is a polymerization technique and also known as bead, pearl or granular polymerization because of the form of final product. For instance, polyvinyl cloride (PVC) and polystyrene (PS) polymers are mostly obtained using this technique [48].

This technique was first developed by Hoffman and Delbruch in 1909 and the synthesis of porous polymer particles using free-radical suspension polymerization is applied after 20-30 years. In this technique, polymerization occurs in the monomer droplets. The polymerization medium and organic phase are prepared separately before starting the polymerization. The polymerization medium is liquid phase that is prepared by dissolving surfactant and stabilizer in the solvent. The organic phase contains monomer, initiator, crosslinker molecules and diluents. Organic phase/liquid phase volume ratio can be between 0.1 and 0.5, or even more. Monomer and initiator

are hardly soluble in the polymerization medium, while initiator is easily soluble in the monomer [49].

The monomer phase is mechanically distributed as droplets in the polymerization medium, which is mainly water. Because of the shape of the droplets, spherical polymer particles are obtained [50]. For avoiding agglomeration of the monomer droplets, many types of stabilizers are used such as water-soluble organic polymers, electrolytes and water-insoluble inorganic compounds. Methylcellulose, PVA and gelatin are some stabilizers used in this method. Besides, toluene, THF, n-hexane, n-heptane and MEK are inert diluents, which are added to the organic phase, and serve as porogen. Actually, each monomer droplet (0.01–0.05 cm in diameter) is a small bulk poylmerization system which turns into solid beads at the end. The suspension medium is continuously stirred, therefore heat of the polymerization is easily controlled and distributed during the process [48,49]. A general suspension polymerization process is depicted in Figure 2.13.

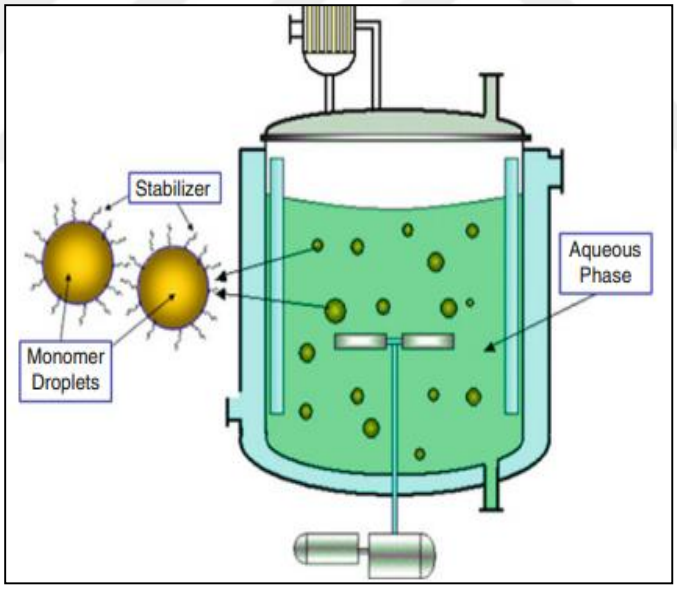


Figure 2.13 : Suspension polymerization process [51].

Before choosing a polymerization technique for the synthesis of polymer particles, some parameters such as particle size, porosity, pore size, particle shape and cost should be considered. Suspension polymerization produces large polymer particles (5–1000 μm), while the other techniques involving emulsion polymerization give polymer products that have smaller particle size [49]. In addition to particle size of the polymer, suspension polymerization and other techniques differ in many other aspects, as summarized in Table 2.4.

Table 2.4 : The differences between suspension polymerization and other polymerization techniques [52].

Polymerization technique	Advantages	Disadvantages
Suspension	Easy heat distribution, low viscosity, polymer in granular form	Requirement of washing/drying, agglomeration, contamination by stabilizer
Emulsion	Easy heat distribution, low viscosity, polymer with high molecular weight	Requirement of washing/drying, contamination by emulsifier, the need of chain transfer agents to control degree of polymerization
Bulk	Simple, no contaminants added	High viscosity
Solution	Easy heat distribution, low viscosity	Added cost of solvent, difficult removal of solvent, possible chain transfer with solvent

2.3.3 Polymer structures

When a polymer is obtained from one kind of monomer, it is named “homopolymer”. A polymer is called “copolymer” when it contains two or more kinds of monomer. Copolymers can be produced in terms of different arangements of repeating units such as random copolymer, alternating copolymer, block copolymer and graft copolymer to provide required properties in various applications [52]. Figure 2.14 shows structure of a homopolymer and different types of copolymers.

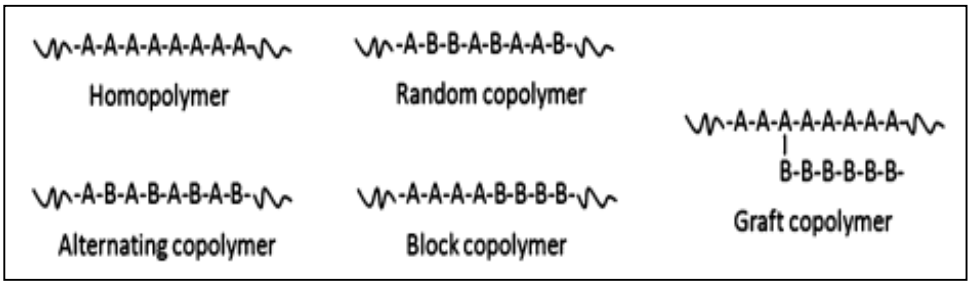


Figure 2.14 : Types of copolymers [52].

These homopolymers and copolymers also can be obtained in terms of different arrangement of molecular segments such as linear polymer, branched polymer and cross-linked polymer, as shown in Figure 2.15 [52].

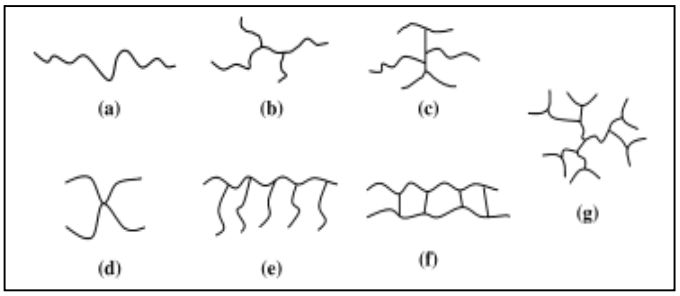


Figure 2.15 : Different arrangements of polymers, (a) linear polymer, (b) branched polymer, (c) cross-linked polymer, (d) star polymer, (e) comb polymer, (f) ladder polymer, (g) dendrimer [52].

Cross-linking is achieved by cross-linking agents in the polymerization and have some effects on polymer properties. DVB, EGDMA and TEGDA are commonly used cross-linkers in polymerizations. Insolubility, rigidity and stiffness can be obtained with cross-linking and these properties enhance advantages of the polymers in numerous applications [49]. Cross-linked polymers are also more resistant to chemicals compared to linear polymers due to their less free volume [52]. Higher cross-linking density increases surface area and pore volume but decreases the pore size. Porous polymer particles can be classified as microporous, mesoporous and macroporous by pore size and the classification is given in the Figure 2.16 [49].

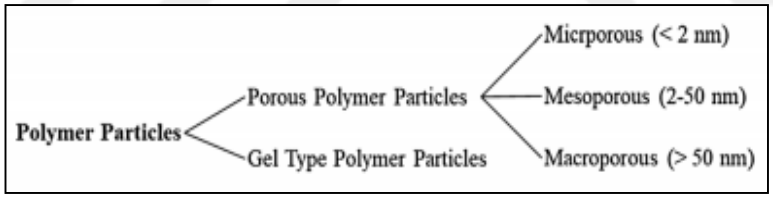


Figure 2.16 : Porous polymers depending on pore size [49].

2.4 Functional Polymers

Functional polymers are the polymers which have some special properties due to their functional group. Functional groups are chemical units which are carefully determined and located on the polymer backbone or side chains for a purpose. Functional groups may be chemically reactive, biologically active, electroactive, photoactive or mesogenic. Mostly, they are ionic, polar or optically active. There are two methods for obtaining a functional polymer. First method is polymerization or copolymerization of functional monomers. This method enables control of the content and latitude about physical properties of the final product. Second method is chemical modification of preformed polymers. This method permits the choice of

molecular weight and the synthesis of polymers unachievable by direct route [46]. These methods are demonstrated in Figure 2.17.

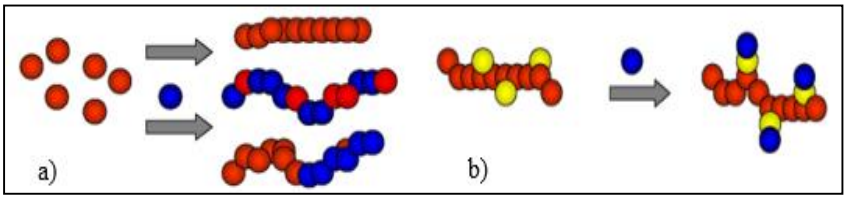


Figure 2.17 : Methods for preparing functional polymers, a) direct polymerization or copolymerization of functional monomer, b) post-polymerization modification of existing polymer [53].

For instance, poly (vinylbenzyl chloride), abbreviated as PVBC, is an important starting material for functionalizing with various simple chemical reactions. Its monomer is vinylbenzyl chloride, as shown in Figure 2.18 [54].

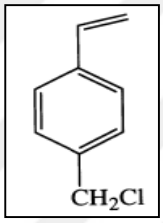


Figure 2.18 : Vinylbenzyl chloride, monomer of PVBC [54].

2.4.1 Polymeric sorbents in metal removal

Polymeric sorbents, also named adsorbent resins, are porous solids with high surface areas and specific adsorption capacities for various metals or organic molecules [55]. Non-soluble polymeric sorbents are generally prepared by functionalization of a polymeric resin and can be produced in the forms of beads, gels, fibers, membranes, foam or sponge. Easy seperation after the sorption step and implementions in packed columns, fixed-beds or membranes are advantages of these polymeric sorbents. Regeneration of a polymeric sorbent is also possible and the desorption of the metallic cations is achieved by the treatment of loaded sorbent with an acidic solution [56].

Polymeric sorbents can be efficiently used for the treatment of process wastewaters and recovery of trace metal ions, because polymer-metal complexes can form for particular metal ions with high selectivity. A polymer-metal complex contains a synthetic polymer ligand that has nitrogen, oxygen or sulphur sites and metal ions bound to this ligand. Typical polymer ligands have functional groups such as –OH, -

COOH, -SH, -NH_2, =NH and ≡N. The most important point is the nature of the functional group and donor atom which create complexes with metal ions. When a polymer ligand is mixed directly with metal ions, the polymer-metal complex can be formed as intra-polymer chelate type or inter-polymer chelate type, as given in Figure 2.19 [57].

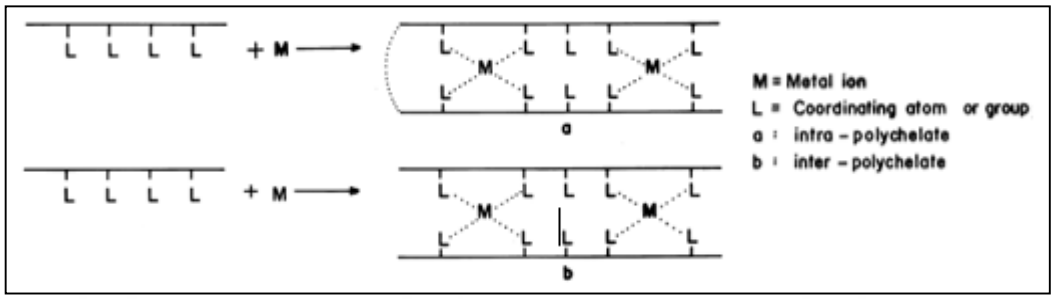


Figure 2.19 : Inter-molecular or intra-molecular brigdes of polymer-metal complexes [57].

2.4.2 Mercury selective resins

In the applications of removal of specific heavy metals, the most common functional groups used are O-donors (alcohol, crown ether) and N-donors (amines, amides). In terms of removal of mercury ions, amines, cyclic amines and amides are the functional moieties often used in polymeric sorbents in the literature, as seen in Figure 2.20 below [56].

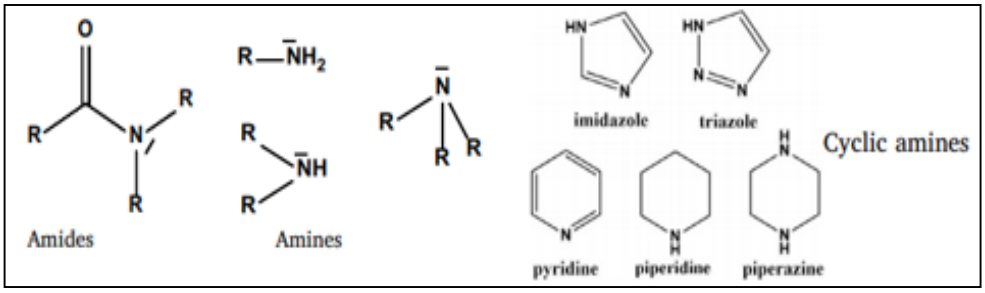


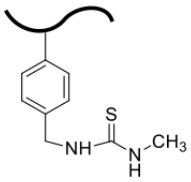
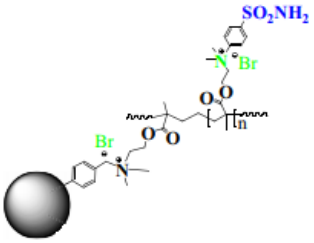
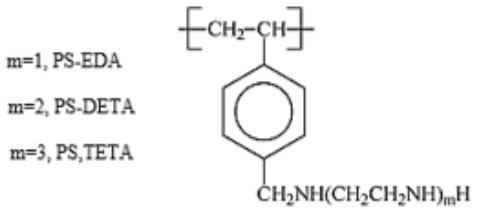
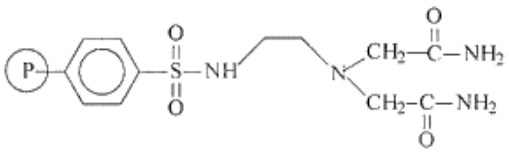
Figure 2.20 : Functional moieties in some polymeric sorbents with sorption properties toward mercury ions [56].

There are numerous mercury selective resins in the literature. Zhuo *et al.* prepared a polystyrene-supported N-methylthiourea resin (DMTUR) in 2017. The maximum adsorption capacity toward Hg(II) of the resin is found as 347 mg/g at pH = 4.0 [58]. Qi *et al.* synthesized a resin, named PDP, by grafting polymerization of functional monomers with sulfamine groups (-SO_2NH_2) onto chloromethylated polystyrene

matrix and studied adsorption characteristics toward Hg(II) in 2013. The maximum adsorption capacity is found as 222.2 mg/g [59].

Furthermore, Qu *et al.* prepared three macroporous polystyrene-co-divinylbenzene beads (ethylenediamine-functionalized PS-EDA, diethylenetriamine-functionalized PS-DETA and triethylenetetramine-functionalized PS-TETA) in 2010. The maximum adsorption capacities toward Hg(II) are 1.55, 1.73 and 1.84 mmol/g for PS-EDA, PS-DETA and PS-TETA, respectively [60]. Senkal *et al.* synthesized polystyrene-co-divinylbenzene beads having sulfone amide and iminodiacetamide groups with 9.6 mmol/g total nitrogen content in 2002. The maximum adsorption capacity toward Hg(II) is found as 4.23 mmol/g under non-buffered conditions [61]. All of these polymeric sorbents mentioned above are summarized in the Table 2.5.

Table 2.5 : Some mercury selective polymeric sorbents in the literature [58-61].

Polymeric sorbent	Chemical structure
DMTUR resin [58]	
PDP resin [59]	
PS-EDA, PS-DETA and PS-TETA resins [60]	
Resin with iminodiacetamide functions [61]	

Also, thiols are able to react with mercury, thus polymers bearing thiol groups are used in the application of removal of mercury. The reaction between thiols and mercury species is given in Figure 2.21 [62]. For instance, Kim *et al.* prepared a porous polymeric adsorbent which is poly(glycidyl methacrylate) (PGMA) grafted with thiol groups, in 2017. Maximum adsorption capacity toward Hg(II) is found as 50.91 mg/g at pH=7 [63].

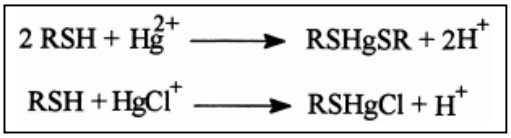


Figure 2.21 : Reaction between thiol group and Hg ions [62].

2.5 Urethane Reactions

Urethane is the widely used name of "carbamate". The preparation of urethane is based on the reaction of isocyanates and alcohols. The reactions between isocyanates and alcohols are very important and beneficial because they are used in production of polyurethane type polymers which have a big economic impact in the industry [64]. Urethane groups are successfully characterized by FTIR and can be recognized by these vibration groups: C-N group at 1530-1580 cm^{-1}, C=O group at 1700-1770 cm^{-1} and N-H group at 3310-3340 cm^{-1} [65]. Figure 2.22 describes the reaction of isocyanate and alcohol forming a urethane.

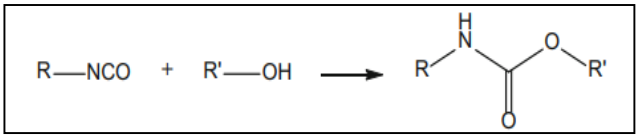


Figure 2.22 : The reaction of an isocyanate and an alcohol forming a urethane [64].

The isocyanate group is strained linear structure and contains two double bonds N=C and C=O. The reactivity of isocyanate group is about the polarization of N and O atoms that have high electronegativity [65]. The electron density is delocalized toward the nitrogen and oxygen atoms and carbon atom have the minimum electron density, as shown in the Figure 2.23:

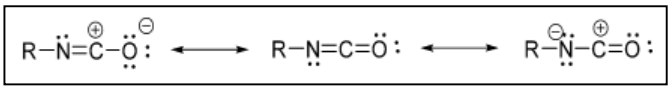


Figure 2.23 : The resonance structures of the isocyanate group [65].

To mention about the general mechanisms of the isocyanate reactions, isocyanate groups easily react with XH groups that act as an active nucleophile. X attacks the electrophilic carbon of isocyanate [65]. Figure 2.24 demonstrates the mechanism of isocyanate reactions.

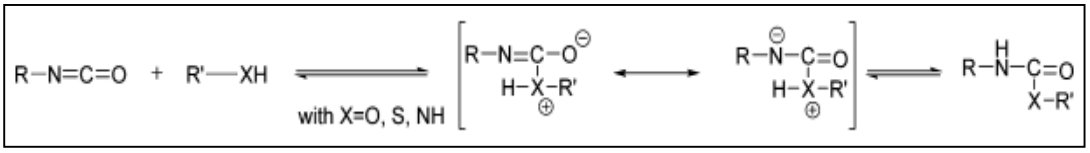


Figure 2.24 : General mechanism of isocyanate reaction [65].

The compound which has XH groups can be alcohol, thiol and amine compounds or water in the reaction. Isocyanate reactions with alcohol, thiol, amine and water compounds give urethane, thiourethane, urea and unstable carbamic acid which decomposes into gaseous carbon dioxide and a primary amine, respectively [65]. Figure 2.25 summarizes common isocyanate reactions.

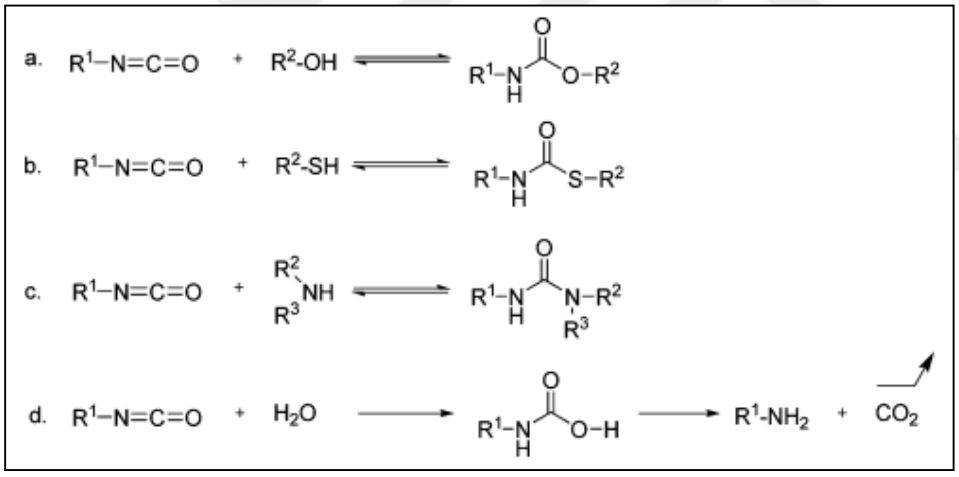


Figure 2.25 : Isocyanate reactions and the products: (a) urethane, (b) thiourethane, (c) urea and (d) unstable carbamic acid which decomposes into gaseous carbon dioxide and a primary amine [65].

It can be generally said that any electron-withdrawing groups attached to the NCO part increase the positive charge on the carbon atom and thus increase the reactivity if steric factors are neglected. The reactivities of isocyanates are sorted as $ClSO_2NCO$ > RSO_2NCO (R = alkyl, aryl) > $O=P(NCO)_3$ > aryl-NCO > alkyl-NCO according to the R-groups attacted to the NCO part [65]. In the reaction of hydroxyl-containing compounds and isocyanates, the reactions of aliphatic isocyanates are slower than those of aromatic isocyanates [66].

If the reactions of isocyanate and alcohol are examined in terms of alcohol, it is seen that primary hydroxyl groups react faster than secondary hydroxyl groups. Secondary hydroxyl groups react faster than tertiary hydroxyl groups in the same way. Urethane linkages obtained with tertiary hydroxyls can said to be less stable [66].

Urethane reactions may occur in the absence of catalyst. However, the reaction rates are too slow to be convenient and useful. Therefore, these reactions are preferred to be performed in the presence of a suitable catalyst. There are two major classes of catalysts employed in these reactions. They are tertiary amines and metal salts and used in combination in many applications. In respect of tertiary amines, a free electron pair present on the nitrogen atom provides catalytic activity. Triethylenediamine and dimethylcyclohexylamine can be given as examples of tertiary amines used in urethane catalysis. Metal salts show more complex catalytic effects than amines. Metal-based catalysts act as Lewis acid toward alcohol or isocyanate to start the reaction. Organometallic salts are based on tin and tin compounds are written with the general formula Bu_2SnX_2 (X is an anion). For instance, stannous octoate, dibutyltin dilaurate (DBTL) and tin mercaptides are generally used. Certain salts of mercury, lead and antimony are used in urethane catalysis as well [65, 67].

When this nucleophilic addition reaction occurs between polyfunctional isocyanates and molecules which have at least two hydroxyl groups, diols or polyols, the product is called “polyurethane”. The properties of polyurethane polymer can be arranged by selection of raw materials and changing of the isocyanate and the polyol components. Polyurethane polymers are utilized in various areas such as automotive systems, construction industry and biomedical applications with annual global consumption of 20 million metric tons [68,69]. Figure 2.26 describes the reaction between a diisocyanate and a polyol forming polyurethane.

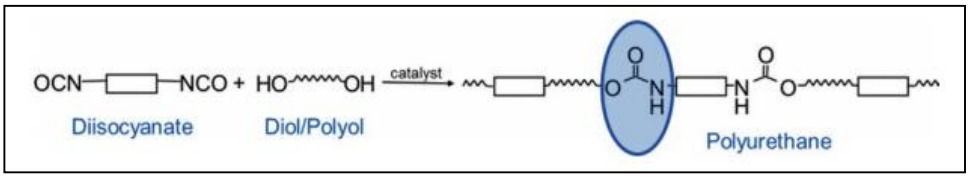


Figure 2.26 : The reaction of a diisocyanate and a polyol forming polyurethane [68].

3. EXPERIMENTAL PART

3.1 Materials and Instruments

3.1.1 Materials

Polyvinyl alcohol (Fluka), vinyl benzyl chloride (Sigma Aldrich), ethyleneglycol dimethacrylate (EGDMA), AIBN (2,2′-Azobis(2-methylpropionitrile)) (Fluka), diethanolamine (Fluka), butyl isocyanate (Sigma Aldrich), dibutyltin dilaurate (Sigma Aldrich), diphenylcarbazide (Merck), mercury(II) chloride (Merck), sulfuric acid (Merck), copper(II) sulfate pentahydrate (Merck), cadmium nitrate tetrahydrate (Sigma Aldrich), zinc sulfate heptahydrate (Merck), lead(II) acetate trihydrate (Merck) and all the other chemicals used were analytical grade commercial products.

3.1.2 Instruments

UV-Vis spektrophotometer (Perkin Elmer 25), FT-IR spektrophotometer (Nicholet), shaker and magnetic stirrer.

3.2 Preparation of Polymeric Sorbent

In this thesis, urethane modified polystyrene based sorbent was synthesized for mercury removal from water.

3.2.1 Preparation of poly (vinyl benzyl chloride) (PVBC) resin

Cross-linked PVBC beads were prepared by suspension polymerization according to literature [70]. The procedure was applied as follows: Vinyl benzyl chloride (VBC) (10 mL, 70.95 mmol), EGDMA (3 mL, 15.90 mmol) as a cross-linker, AIBN (0.24 g, 1.45 mmol) as an initiator were added to toluene (15 mL) to obtain organic mixture. Then, polyvinyl alcohol (0.50 g, 11.35 mmol) as stabilizator was dissolved in water (110 mL).

The organic mixture was added dropwise to the water phase at 80 ^{0}C under nitrogen. Suspension polymerization of VBC-co-EGDMA was performed in a magnetically stirred glass flask at 80 °C for 8 h. After the polymerization, the PVBC beads were

transferred into 250 mL water, washed with excess of water and ethanol, respectively. The spherical beads were filtered and dried under vacuum at 60 °C for 24 h. The yield was 10.22 g.

3.2.2 Amination of PVBC resin

4 g of PVBC resin and diethanolamine (8 mL, 82.90 mmol) were added to 1-methyl-2-pyrrolidone (20 mL) solvent. The mixture was magnetically stirred at room temperature for 48 h and then at 60 °C for 3 h. The reaction content was washed excessively with water and ethanol, respectively. The product was filtered and dried under vacuum at 60 °C for 24 h after washing with ether for once. The yield was 4.30 g.

3.2.3 Determination of amine content of aminated resin

0.10 g of the aminated resin was added to 10 mL of 0.10 M HCl solution. This mixture was shaken for 24 h at room temperature. The resin was filtrated and 3 mL of filtrate was titrated with 0.10 M NaOH solution using phenolphthalein as a colour indicator. 3 mL of 0.10 M HCl solution was also titrated similarly. The difference between NaOH consumptions of two titrations indicated amine content of the resin.

3.2.4 Modification of aminated resin with butyl isocyanate

2 g of aminated resin and 2.50 mL of butyl isocyanate (22.20 mmol) were added to DMF (30 mL). Three drops of dibutyltin dilaurate was added into the reaction mixture as a catalyst. The mixture was magnetically stirred at 60 °C for 48 h. The reaction content was transferred into 250 mL water, washed with excess of water and ethanol, respectively. The urethane modified resin (PS-UR-resin) was filtered and then dried under vacuum at 60 °C for 48 h. The yield was 2.88 g.

3.2.5 Determination of total nitrogen content of PS-UR-resin

Nitrogen content was determined by Kjeldahl method as given in the literature [71]. The procedure was carried out as follows: 0.10 g of PS-UR-resin was added to 20 mL of H_2SO_4 solution (80%). 1 g of copper(II) sulfate pentahydrate was also added to the mixture as a catalyst for Kjeldahl digestion [72].

The mixture was heated at 400 °C for 6 h. Then, the mixture was added dropwise to boiling NaOH solution (12.50 M) and formed ammonia gas was simultaneously

catched by 0.10 M HCl solutions. The consumption of 0.10 M HCl solutions for the neutralization of ammonia demonstrated total nitrogent content of the resin. It was calculated by back titrations of HCl solutions with 0.10 M NaOH solution using phenolphthalein as a colour indicator.

3.3 Adsorption Experiments of Polymeric Sorbent

In this thesis, $HgCl_2$ was used as mercury salt and Hg(II) adsorption experiments of PS-UR-resin were carried out at different conditions.

3.3.1 Optimum amount of resin

The optimum amount of PS-UR-resin for sorption experiments was studied by different weights of the resin as follows: Between 0.050 g to 0.125 g of PS-UR-resin samples were mixed with 10 mL of Hg(II) solution (0.025 M). The mixtures were shaken on a continuous shaker for 24 h at room temperature and filtered.

The Hg(II) concentrations of filtrates were determined colorimetrically by diphenyl carbazide at 542 nm [73]. The optimum amount of PS-UR-resin was found and used for Hg(II) sorption experiments.

3.3.2 Mercury sorption capacity of resin

0.075 g of PS-UR-resin samples were mixed with 10 mL of Hg(II) solutions (0.005 M, 0.010 M, 0.025 M, 0.050 M, 0.075 M and 0.1 M) to determine effect of different Hg(II) concentrations on sorption capacity of the resin. The mixtures were shaken with a continuous shaker for 24 h at room temperature and then they were filtered. The sorption capacities of the resin were examined colorimetrically as described above.

3.3.3 Mercury sorption capacity of resin depending on pH

The Hg(II) solutions (0.1 M) with different pH values (pH = 4, 5, 7) were prepared using 0.10 M HCl and 0.10 M NaOH solutions to arrange pH. 0.075 g of PS-UR-resin samples were mixed with 10 mL of the Hg(II) solutions in various pH. The mixtures were shaken on a continuous shaker for 24 h at room temperature and then filtered. The sorption capacities of the resin were found as described above.

3.3.4 Desorption of mercury from loaded resin

To determine regeneration capability of PS-UR-resin, 0.075 g of mercury loaded PS-UR-resin (loaded in 0.1 M Hg(II) solution) was interacted with 20 mL acetic acid and heated for 1.5 h at 80 °C and then, filtered. 2 M NaOH was used for arranging pH before capacity measurements. The desorption capacity of the resin was found colorimetrically as described above.

After desorption experiments, the residual resin was washed with distilled water and left for drying at room temperature. Then, it was interacted with 10 mL of 0.10 M Hg(II) solution in non-buffered conditions using continuous shaker at room temperature for 24 h in order to determine whether sorption capacity of the resin changed through the process.

3.3.5 Mercury sorption kinetics of resin

0.025 g of PS-UR-resin samples were mixed with 10 mL of diluted Hg(II) solutions ($1.0x10^{-4}$ M) to determine which kinetic model is more suitable for the resin. The mixtures were shaken on a continuous shaker for 2 min, 5 min, 20 min, 40 min and 60 min at room temperature and filtered. The sorption capacities of the resin at different minutes were examined as described above.

3.3.6 Sorption capacity of resin for different metal ions

To examine resin characteristics againist other toxic metal ions, $Cd(NO_3)_2.4H_2O$, $(CH_3COO)_2Pb.3H_2O$ and $ZnSO_4.7H_2O$ metal salts ion solutions were used for in the sorption experiments. 0.075 g of PS-UR-resin samples were mixed with 10 mL of Cd(II), Pb(II) and Zn(II) solutions (0.10 M) to determine sorption capacities of the resin. The mixtures were shaken on a continuous shaker for 24 h at room temperature and filtered.

NH_3/NH_4Cl buffer solution (pH=10) was used in order to arrange pH before titrations. Analyses of the metal content of filtrates were performed by complexometric titration method with 0.050 M EDTA solution using Eriochrome Black T as a colour indicator.

4. RESULT AND DISCUSSION

4.1 Preparation of Polymeric Sorbent

Polymers or reagents which have urethane, urea, amide etc. functional groups capture mercury ions from water via covalent binding. For this purpose, poly (styrene) based urethane modified polymeric sorbent was prepared in this study.

4.1.1 Preparation of cross-linked PVBC resin

The resin was prepared by using suspension polymerization method. Therefore, vinyl benzyl chloride (VBC) (90 % mol) EGDMA (10% mol) as crosslinker were used as monomers and AIBN was used as initiator. This mixure was dissolved in toluene which is used as porogen. Organic mixture was added with a dropping funnel into water which contains polyvinyl alcohol as a stabilizator at 80 ^{0}C.

Reaction apparatus was given below (Figure 4.1):

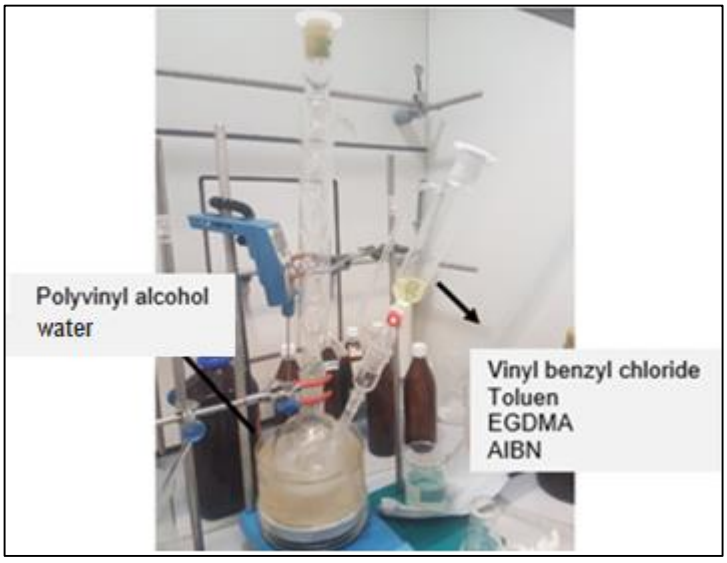


Figure 4.1 : Demonstration of the reaction.

4.1.2 Amination of the PVBC resin

The PVBC resin was modified with excess of diethanolamine to obtain aminated resin in the presence of 1-methyl-2-pyrrolidone as solvent.

The amine content of the resin was determinated titrimetrically and was calculated as 3.00 mmol.g^{-1}. For this purpose, amine group of the resin was interacted with 0.100 M HCl solution for 24 h at room temperature. Amine content of the resin was found titrimetrically with 0.100 M NaOH solution.

4.1.3 Preparation of urethane modified resin (PS-UR-resin)

The aminated resin was reacted with butyl isocyanate in the presence of DMF as solvent using dibutyltin dilaurate as catalyst at 60^0 C for 24 h (Figure 4.2).

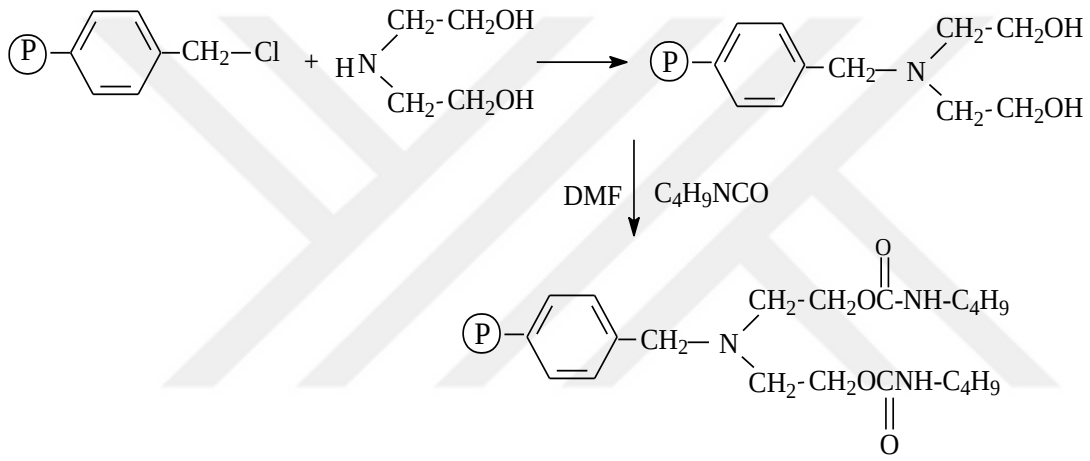


Figure 4.2 : Preparation of urethane modified resin (PS-UR-resin).

The total nitrogen content of the PS-UR-resin was found using Kjeldahl method [71] and total nitrogen content of the resin was calculated as 6.50 mmol.g^{-1}. The final product, PS-UR-resin, were given below (Figure 4.3):

Figure 4.3 : PS-UR-resin, filtration step after reaction (left) and final product after drying under vacuum (right).

The SEM images and EDX spectra before and after adsorption were given in Figure 4.4. SEM images show changes to the surface morphology of the resins. Before adsorption, there are some crevices in the resin surfaces. After mercury sorption, these crevices filled.

The EDX spectrum of the PS-UR-resin contains C, N and O atoms. Pt atom is residue. After interaction with mercury chloride solution, the EDX spectrum of the treated resin shows new peaks and chlorine atoms belong to mercury solutions. Also, both resins do not contain Pt atom, but the device wrongly found Pt.

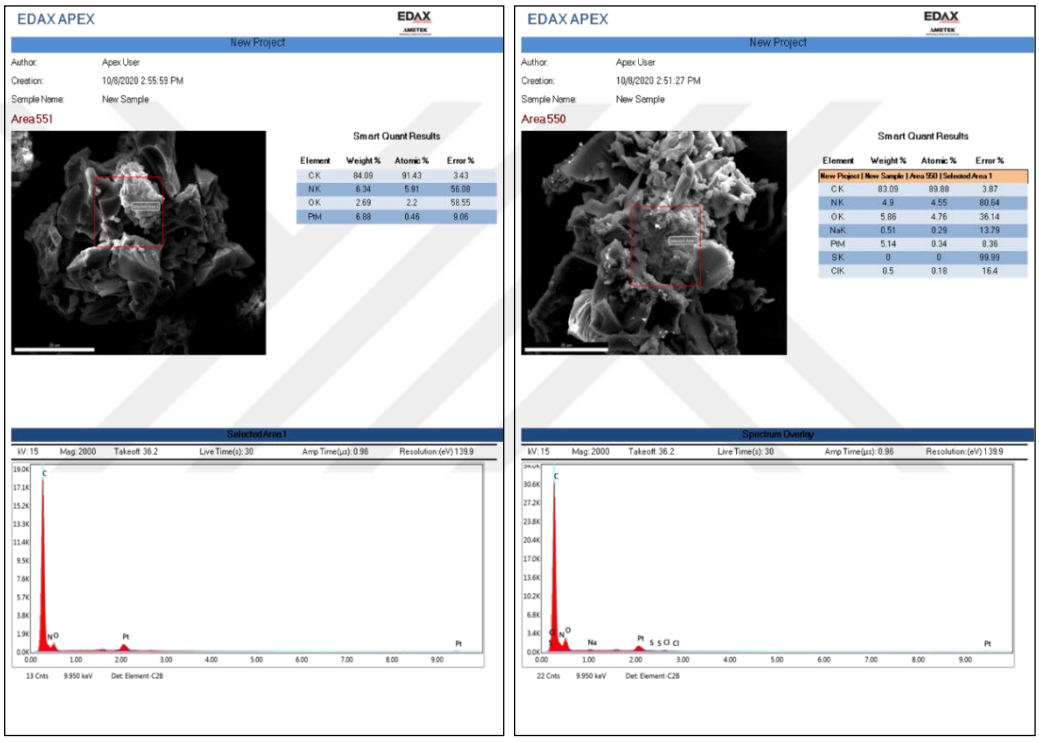


Figure 4.4 : SEM images and EDX spectra of the resin before adsorption of mercury (left) and after adsorption of mercury (right).

Prepared three type of resins were characterized by using FTIR method. PVBC-EGDMA resin shows a sharp band 1720 cm^{-1} belong to the ester carbonyl group of the crosslinking agent. The characteristic stretching C-Cl peak in the PVBC resin was observed at about 668 cm^{-1} (Figure 4.5a). The FTIR spectra of the amine modified resin has strong broad OH stretching absorption which is observed at 3330 cm^{-1}. After amination reaction, the stretching C-Cl peak at 668 cm^{-1} was not observed for amine modified resin (Figure 4.5b). The sharp peaks at 3323 cm^{-1} and

1692 cm^{-1} belong to N-H and carbonyl peak of urethane absorption which are clear evidences of successful modification reaction (Figure 4.5c).

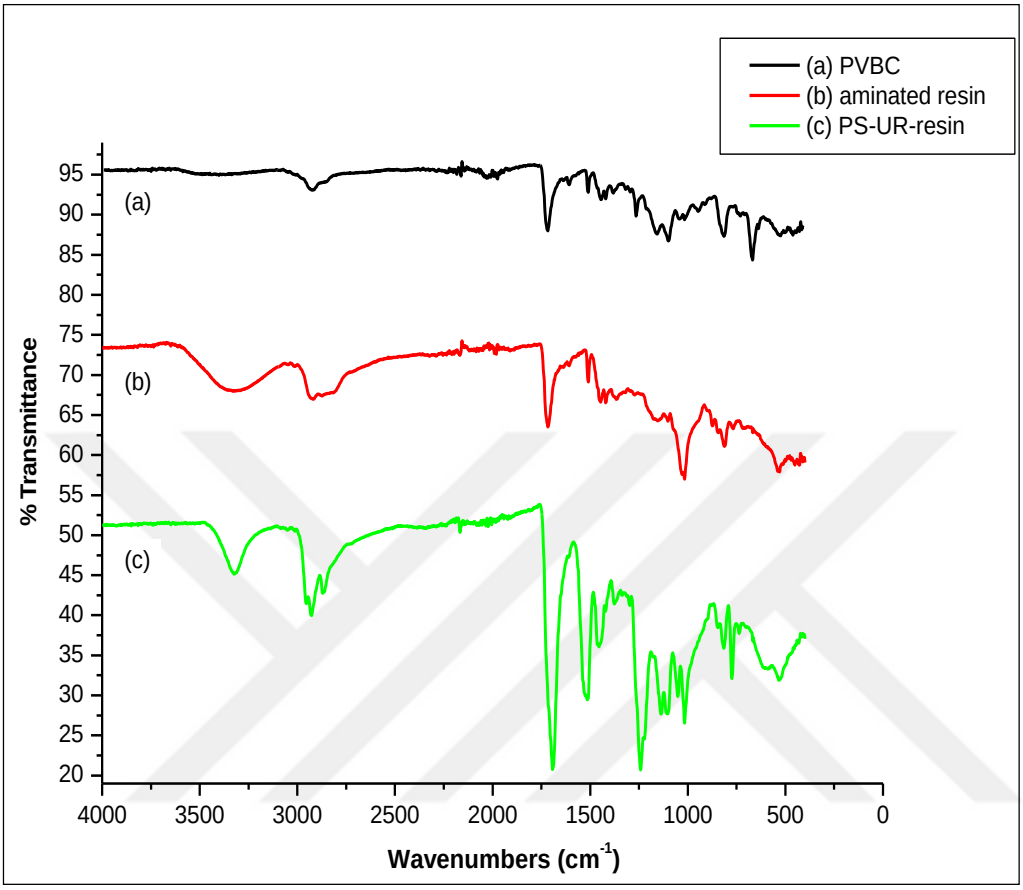


Figure 4.5 : FTIR spectra of the resins.

4.2 Mercury Adsorption Experiments of Polymeric Sorbent

All of experiments were performed at room temperature. $HgCl_2$ salt was used in the sorption experiments. Mercury sorption experiments of the PS-UR-resin were studied depending on different initial concentrations of mercury and different pH values. Also, other toxic metal sorption properties of the resin were investigated.

Mercury sorption capacities of PS-UR-resin were determined colorimetrically with diphenyl carbazide method [73] and calculated with the formula (equation 4.1) given below:

$$q_e = V(C_0 - C_t)/m \qquad (4.1)$$

where, q_e , C_0 and C_t are amount of adsorbed metal ion per 1 gram of resin ($mol.g^{-1}$), initial concentration of metal ion solution ($mol.L^{-1}$) and concentration of metal ion

solution at time t (mol.L^{-1}), respectively. V is volume of metal ion solution (L) and m is mass of the resin (g) [74]. Hg (II) concentrations in water were determined colorimetrically using diphenyl carbazide method, as shown in the Figure 4.6.

Figure 4.6 : Lilac color of Hg(II) and diphenyl carbazide complex, initial Hg(II) solution (darker color-left) and Hg(II) solution after interaction with PS-UR-resin (lighter color-right).

4.2.1 Optimum amount of resin

In this study, optimum amount of PS-UR-resin was determined. The mercury sorption capacities were studied as a function of PS-UR-resin amount. The results were given in Table 4.1 and Figure 4.7.

Table 4.1 : Mercury sorption capacities depending on the amount of PS-UR-resin.

Amount of PS-UR-resin (g)	Capacity (mmol.g^{-1})
0.050	2.28
0.075	2.42
0.100	1.50
0.125	1.14

According to Table 4.1 and Figure 4.7, the highest sorption value for mercury was found for 0.075 g of the resin. Therefore, 0.075 g resin was used in the sorption experiments.

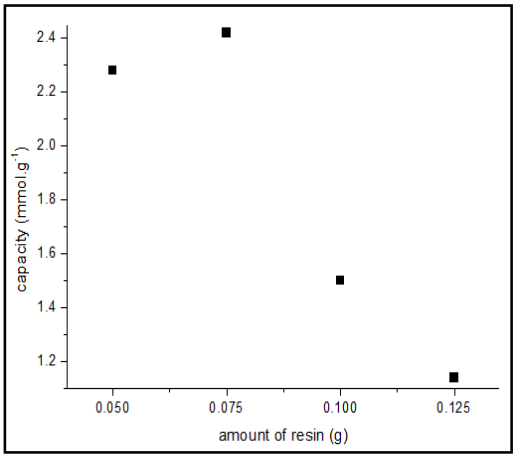


Figure 4.7 : The plot of mercury sorption capacity of PS-UR-resin against amount of resin.

4.2.2 Mercury sorption capacity of resin

To investigate the influence of initial mercury (II) concentration, 0.075 g of the PS-UR-resin was interacted with depending on different initial Hg(II) solutions (0.005 M-0.1 M) in non-buffered conditions at room temperature for 24h.

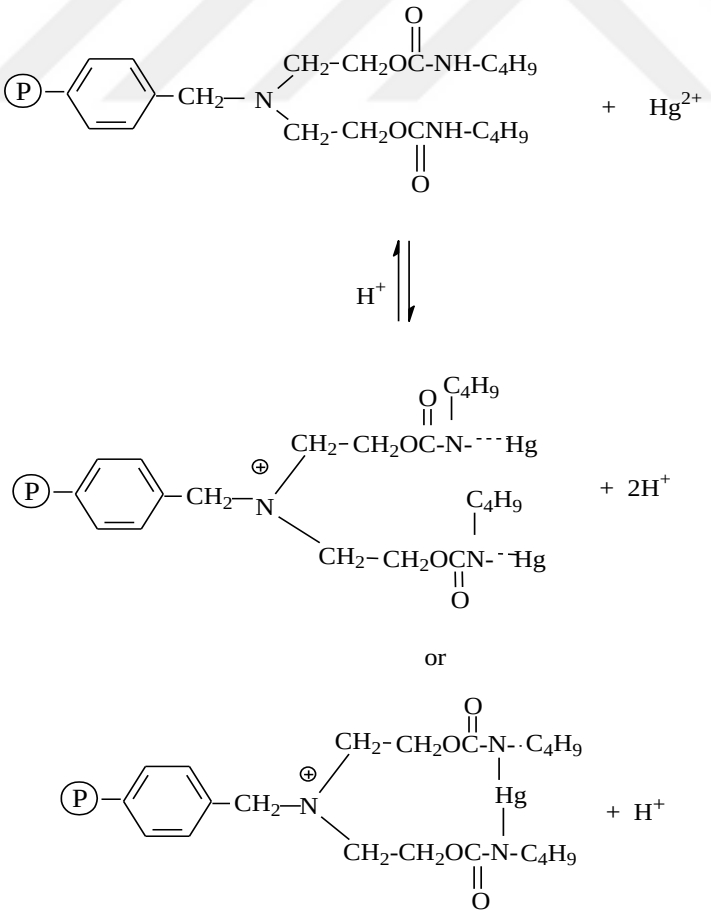


Figure 4.8 : Mercury-resin interaction mechanism.

There are two possible interactions, the binding of Hg(II) ion can occur either by formation of monocarbamate- or dicarbamate-Hg structures (Figure 4.8), which provides removing Hg(II) from aqueous solution.

The sorption experiments give a mercury loading capacity of about 2.50 $mmol.g^{-1}$. Sorption capacity of the resin increases depending on initial mercury concentrations (Table 4.2). The pH's of $HgCl_2$ solutions remain almost constant in the 3.1-3.9 range through the extraction process.

Also, mercury sorption capacities were investigated in different pH values as well (Table 4.2). According to the experimental results, the maximum sorption capacity of the resin was found at pH 7. The sorption amount of the resin increases at high pH values. Because high amount of H^+ present at low pH and protonation of the amino groups on the surface of the resin. In this condition, competitive adsorption occurs between H^+ and Hg (II) [75].

Table 4.2 : Mercury sorption capacities depending on different Hg(II) concentrations and different pH conditions.

Initial Hg(II) concentrations (M)	Capacity ($mmol.g^{-1}$)	Medium condition	Recovered metal ($mmol.g^{-1}$)
0.100	2.50	non-buffered	2.32
0.075	1.95	non-buffered	-
0.050	1.61	non-buffered	-
0.025	0.96	non-buffered	-
0.010	0.43	non-buffered	-
0.005	0.22	non-buffered	-
0.100	2.06	buffered (pH =4)	-
0.100	2.86	buffered (pH =5)	-
0.100	3.13	buffered (pH =7)	-

Furthermore, according to Table 4.2, when mercury-loaded resin was heated at 80 °C in acetic acid, about 92.8% of the mercury was extracted. The remaining mercury was eluted with second acid treatment of the resin.

4.2.3 Mercury sorption isotherms of resin

Adsorption isotherms are description of relationship between amount of adsorbed Hg(II) and concentration of Hg(II) solution after adsorption process. In this study, Freundlich, Langmuir and Temkin isotherm models were analysed for mercury sorption process of the PS-UR-resin.

Freundlich model is used for explaining adsorption processes on heterogeneous surfaces [37]. The linear expression of Freundlich model equation was given below (equation 4.2):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4.2)$$

where q_e is adsorption capacity (mmol Hg(II).g $^{-1}$ resin) and C_e is equilibrium Hg(II) concentration (M) remaining in solution after adsorption process. K_F and n are Freundlich constant (mmol.g^{-1}) and adsorption affinity, respectively and found from intercept and slope of graph of $\ln q_e$ versus $\ln C_e$ [37]. The Freundlich equation graph of PS-UR-resin was given in Figure 4.9.

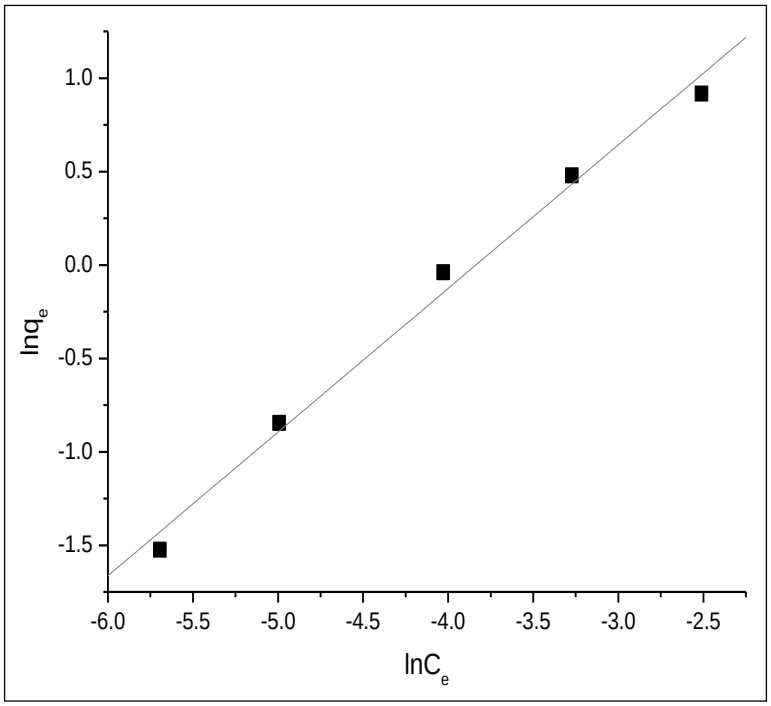


Figure 4.9 : The graph for Freundlich isotherm.

Langmuir model is applied to explain mono-layer adsorption processes on homogeneous surfaces [44]. Langmuir model equation was given below (equation 4.3):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{4.3}$$

where q_e is adsorption capacity (mmol Hg(II).g $^{-1}$ resin) and C_e is equilibrium Hg(II) concentration (M) remaining in solution after adsorption process. K_L and q_m are Langmuir constant (L.mmol^{-1}) and maximum adsorption capacity (mmol.g^{-1}), respectively and found from intercept and slope of graph of $\frac{C_e}{q_e}$ versus C_e [37]. The Langmuir equation graph of PS-UR-resin was given in Figure 4.10.

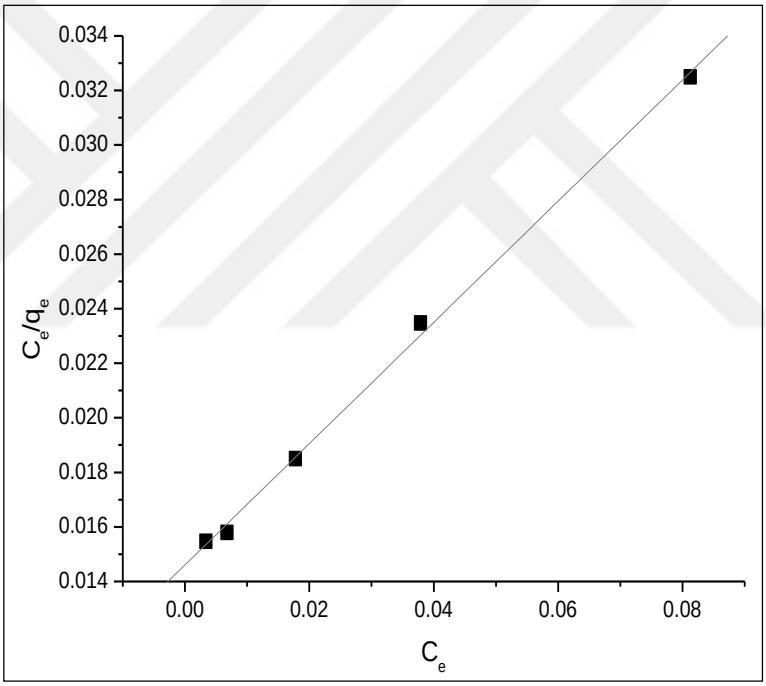


Figure 4.10 : The graph for Langmuir isotherm.

Temkin model is generally used for explaining some adsorbate interactions [37]. Temkin model equation was given below (equation 4.4 and 4.5):

$$q_e = B\ln A + B\ln C_e \tag{4.4}$$

$$B = \frac{RT}{b} \tag{4.5}$$

where q_e is adsorption capacity (mmol Hg(II).g $^{-1}$ resin) and C_e is equilibrium Hg(II) concentration remaining in solution (M) after adsorption process. R is the universal

gas constant (8.314 $J.mol^{-1}.K^{-1}$) and T is the temperature (K). A and B are Temkin isotherm constant ($L.g^{-1}$) and Temkin constant related to heat of adsorption ($J.mol^{-1}$), respectively and found from intercept and slope of graph of q_e versus ln C_e [37]. Temkin equation graph of PS-UR-resin was given in Figure 4.11.

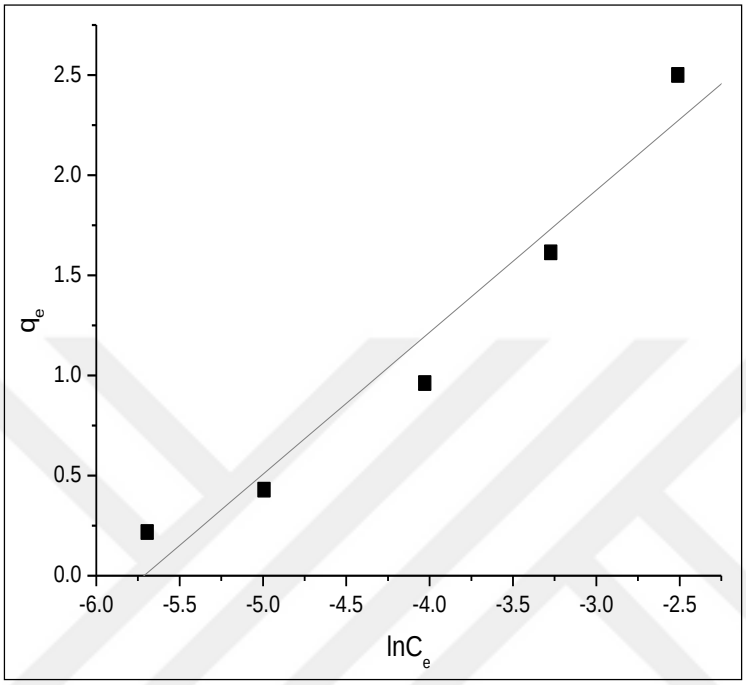


Figure 4.11 : The graph for Temkin isotherm.

For all of the adsorption isotherm models, constants and correlation coefficients were calculated from the graphs above and summarized in Table 4.3.

Table 4.3 : Constants and correlation coefficients of Freundlich, Langmuir and Temkin isotherm models for mercury sorption of PS-UR-resin.

Freundlich			**Langmuir**			**Temkin**		
n	K_F ($mmol.g^{-1}$)	R^2	q_m ($mmol.g^{-1}$)	K_L ($L.mmol^{-1}$)	R^2	A ($L.mol^{-1}$)	b ($J.mol^{-1}$)	R^2
1.30	19.05	0.991	4.50	15.22	0.998	303.12	3494	0.951

According to the Freundlich isotherm, n value which is the adsorption intensity was found 1.30 and K_F was found 19.05. Especially, the larger the K_F and n values show the higher the adsorption amount per unit weight of the sorbent.

The Langmuir isotherm model shows a better fit and the highest R^2 value, suggesting single-layer adsorption on the resin surface. The Hg adsorption capacity was found 4.50 $mmol.g^{-1}$ from this model.

Using Temkin isotherm model, equilibrium binding constant A ($L.mol^{-1}$) and the maximum binding energy, b were calculated as 303.12 and 3.494 $kJ.mol^{-1}$, respectively.

4.2.4 Mercury sorption kinetics of resin

Batch kinetic sorption of the PS-UR-resin experiments were carried out highly diluted mercury solutions ($1.0x10^{-4}$ M).

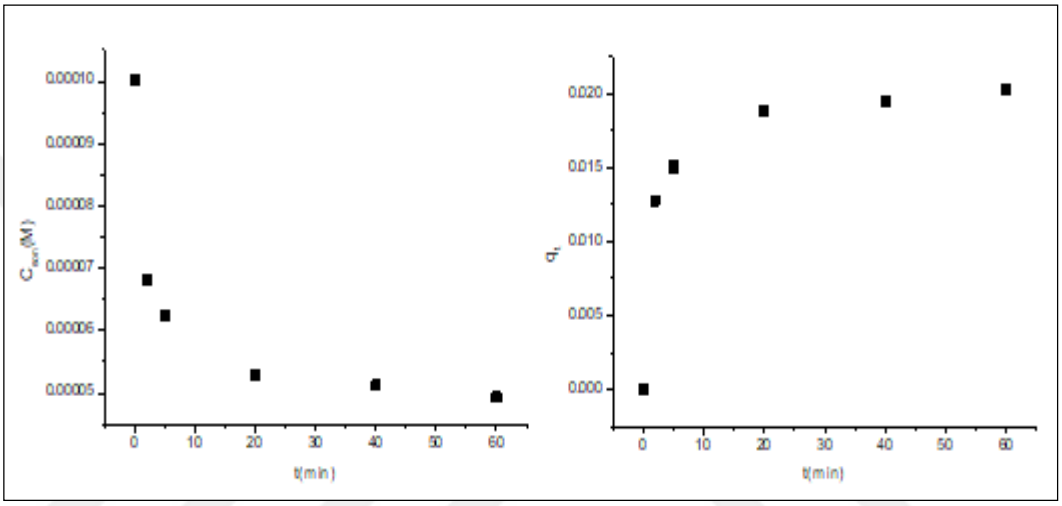


Figure 4.12 : Hg(II) concentration in solution depending on time (left) and Hg(II) sorption capacity depending on time (right).

According to the concentration–time plot in Figure 4.12, within about 60 min of contact time, mercury concentration falls to zero. Also, Figure 4.12 demonstrates that mercury sorption capacity of the resin increases with time.

In this study, pseudo first-order, pseudo second-order and intra-particle diffusion models were analysed for mercury sorption kinetics of PS-UR-resin.
The pseudo first-order kinetic model was represented with equation 4.6:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4.6)$$

where q_e and q_t are amount of adsorption ($mmol.g^{-1}$) at equilibrium and at time t, respectively. The rate constant is k_1 (min^{-1}) in the equation. The slope and intercept of graph of $\ln(q_e-q_t)$ versus t give k_1 and q_e, respectively [45]. Pseudo first-order equation graph of PS-UR-resin was given in Figure 4.13.

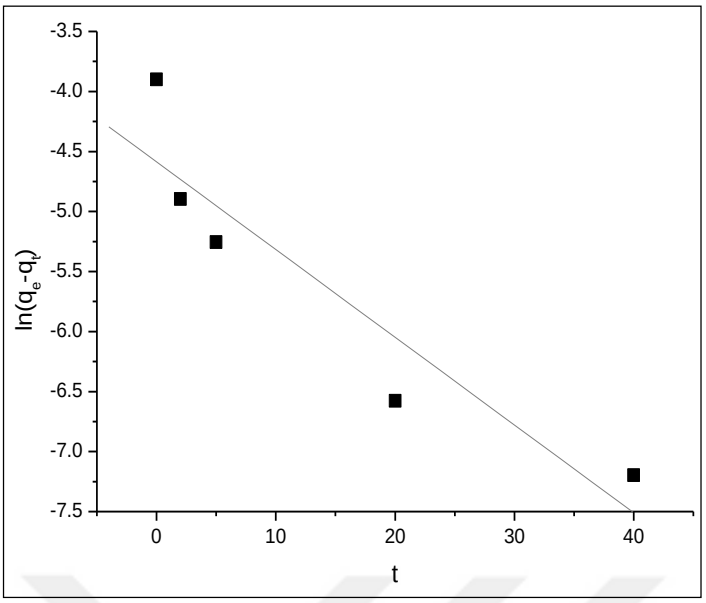


Figure 4.13 : The graph for pseudo first-order kinetic model.

The pseudo second-order kinetic model was formulated with equation 4.7:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4.7)$$

where q_e and q_t are amount of adsorption (mmol.g^{-1}) at equilibrium and at time t, respectively. The rate constant is k_2 (g.min^{-1}mmol^{-1}) in the equation. The slope and intercept of graph of $\frac{t}{q_t}$ versus t give q_e and k_2, respectively [45]. The graph of PS-UR-resin for pseudo second-order model was given in Figure 4.14.

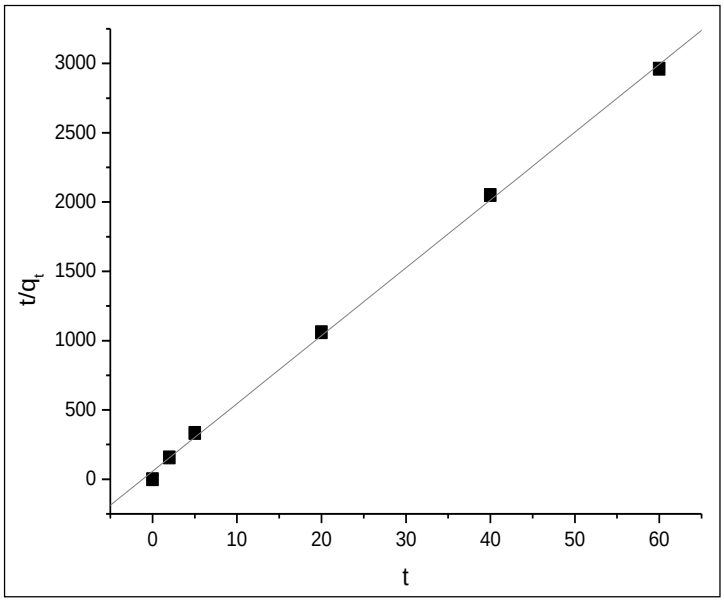


Figure 4.14 : The graph for pseudo second-order kinetic model.

The intra-particle diffusion model was given with equation 4.8:

$$q_t = k_i . t^{0.5} \quad (4.8)$$

where q_t and t are amount of adsorption (mmol.g^{-1}) at any time and time (min), respectively. The rate constant is k_i (mmol.g^{-1}.min$^{-0.5}$) in the equation. The slope of graph of q_t versus $t^{0.5}$ gives k_i value [45]. The graph of PS-UR-resin for intra-particle diffusion model was given in Figure 4.15.

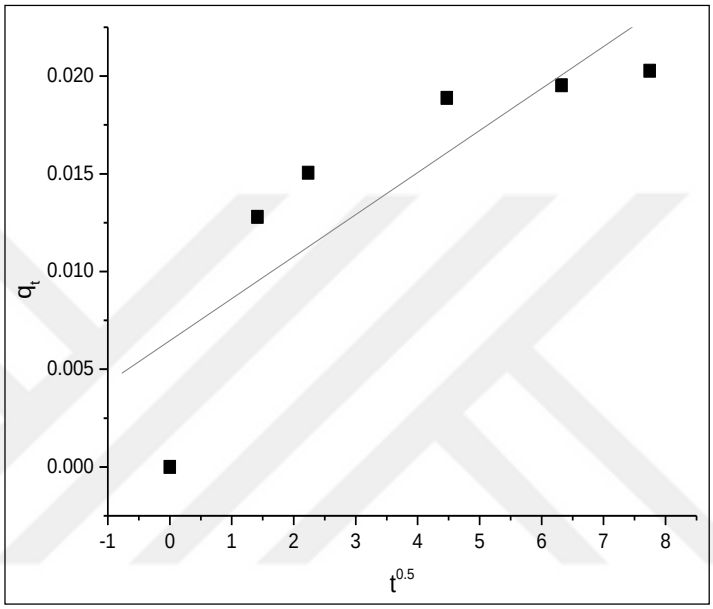


Figure 4.15 : The graph for intra-particle diffusion kinetic model.

For all of the kinetic models, constants and correlation coefficients were obtained from the graphs above and summarized in Table 4.4.

Table 4.4 : Constants and correlation coefficients of pseudo 1st order, pseudo 2nd order and intra-particle diffusion models for mercury sorption of PS-UR-resin.

Kinetic models	$q_{theoric}$ (mmol.g^{-1})	$q_{experimental}$ (mmol.g^{-1})	k	R^2
Pseudo 1st order	0.010	0.020	0.073 min^{-1}	0.862
Pseudo 2nd order	0.020	0.020	42.148 g.min^{-1}.mmol^{-1}	0.999
Intra-particle diffusion	-	0.020	0.002 mmol.g^{-1}.min$^{-0.5}$	0.714

According to results given in Table 4.4 and Figure 4.14, mercury sorption of the resin was found to obey second-order kinetics. Also, the theoretical q_{eq} values for the resin was very close to the experimental q_{eq} value. In addition, higher correlation coefficient value shows that the data fitted the kinetic model well.

The pseudo-second-order model shows that the rate-determining step may be the chemical sorption between adsorbent and adsorbate.

4.2.5 Sorption capacity of resin for different metal ions

The selectivity of the resin against mercury uptake was studied by the testing of the sorption of some toxic ions such as Cd(II), Zn(II) and Pb(II). The experiments show that only minor amounts of sorption were detected from the solutions with 0.10 M initial concentrations (Table 4.5).

Table 4.5 : Sorption capacities of PS-UR-resin for other metal ions.

Metal ion	Initial metal ion concentration (M)	Capacity ($mmol.g^{-1}$)
Hg(II)	0.10	2.50
Zn(II)	0.10	0.67
Cd(II)	0.10	0.17
Pb(II)	0.10	0.00

5. CONCLUSION

In this thesis, a cross-linked polymeric resin (PVBC) was synthesized starting from vinyl benzyl chloride (90%) as a monomer and EGDMA (10%) as a crosslinker by suspension polymerization. The PVBC resin was aminated with diethanolamine and then, this resin was modified with urethane using butyl isocyanate. The purpose of urethane groups is that polymers which have functional groups such as urethane, urea or amide are able to capture mercury ions from aqueous solutions forming covalent binding.

In the experimental part, maximum mercury sorption capacity, pH-dependent mercury sorption capacity, desorption of mercury ions and sorption capacity for different heavy metal ions experiments were performed. Besides, the most suitable adsorption kinetics model and adsorption isotherm model were determined for PS-UR-resin.

According to the results, maximum mercury sorption capacity was found 2.50 $mmol.g^{-1}$ for the resin. The optimum pH medium for mercury sorption was determined as pH=7. Furthermore, mercury sorption of PS-UR-resin fitted well with the Langmuir isotherm model and pseudo-second order kinetics model. Also, it was seen that PS-UR-resin has efficient regeneration ability.

These results indicated that prepared urethane modified polymeric sorbent (PS-UR-resin) has great potential for mercury removal from water.

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