

**SYNTHESIS OF POLYMERIC CHELATES WITH
ENRICHED AMIDOXIME GROUPS FOR THE
ADSORPTION OF HEAVY METAL IONS**

**AĞIR METAL İYONLARININ ADSORPSİYONU İÇİN
AMİDOKSİM GRUPLARINCA ZENGİNLEŞTİRİLMİŞ
POLİMERİK ŞELAT SENTEZLENMESİ**

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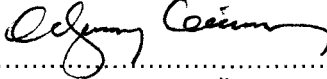


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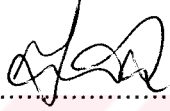
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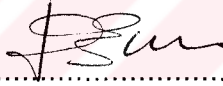
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ABSTRACT

A novel polymer containing double amidoxime groups per repeating unit is synthesized to enhance the metal ion uptake capacity. For this purpose, in the first part of this thesis, N,N'-dipropionitrile acrylamide (DPAAm) monomer was synthesized by the reaction of 3,3'-iminodipropionitrile and acryloyl chloride. The monomer obtained was later polymerized by using AIBN as initiator in ethanol solution at 70 °C and 77 % conversion was obtained. The newly synthesized monomer and polymeric structure were characterized by FT-IR and thermal analysis methods. The polymer was reacted with hydroxylamine to afford a polymer containing two pendant amidoxime groups in each monomeric unit. The conversion of nitrile groups to amidoxime was followed by FT-IR spectrometry. The structure of amidoximated polymer was further characterized by FT-IR and thermal analysis methods. The adsorption properties of this new polymeric adsorbent containing double amidoxime groups per monomeric unit for U, V, Cu, Co and Ni ions were investigated by a batch process at very low concentration levels (ppb). The chelating amidoximated poly(DPAAm) showed high adsorption capacity for uranium ion as well as vanadium ion. In selectivity studies from mixture of metal ions in aqueous solutions, the adsorbent showed high selectivity for U and V ions in the following order: $U > V \gg Cu = Co \gg Ni$ as determined by calculating corresponding distribution coefficients D. The reason for selective adsorption of uranium and vanadium by this new adsorbent was explained to be as due to hard soft acid-base (HSAB) interactions. The adsorption of uranium and vanadium ions from natural seawater for new adsorbent was also examined by flow through mode.

In the second part of this thesis, a non-woven fabric made of polypropylene coated with polyethylene was used as the trunk polymer in the preparation of a highly efficient new adsorbent. Metal ion uptake capacity has been aimed to be increased by introducing double amidoxime groups per repeating unit of the chains grafted to trunk polymer. The base polymer was irradiated by electron beams at a dose of 200 kGy under N₂ atmosphere and glycidyl methacrylate (GMA) was grafted onto irradiated nonwoven fabric. Grafting conditions were optimized, and GMA grafted polymer was modified with 3,3'-iminodipropionitrile in ethanol at

80 °C. Pendant nitrile groups were then amidoximated by using 6 % hydroxylamine in methanol-water mixture (1:1). The all-polymeric structures were characterized by using FT-IR, SEM and thermal analysis methods.

The adsorption properties of amidoximated nonwoven fabric for uranium, vanadium, lead, copper and cobalt ions were investigated by a batch process at very low concentration levels (ppb). The adsorbent showed enhanced adsorption capacity for uranium and vanadium ions. In adsorption studies from a mixture of metal ions in aqueous solutions, the adsorbent showed selectivity for metal ions in the following order: $V > U \gg Cu \geq Pb \gg Co$. The selectivity of the adsorbent has been determined by calculating the distribution coefficient D , for the metal ions studied which showed that U and V ions were up to 6 times more selectively adsorbed onto the polymer than the other metal ions.

In the last part of this thesis, the adsorption properties of amidoximated poly(N, N'-dipropionitrile acrylamide) (poly(DPAAm)) and amidoximated non woven fabric for UO_2^{2+} , Pb^{2+} , Cu^{2+} and Co^{2+} at high concentration levels were investigated by batch process. Metal ion adsorption studies were conducted from different metal ions solutions (100-1500 ppm). It was shown that amidoximated poly(DPAAm) has a higher adsorption capacity than amidoximated nonwoven fabric for all metal ions especially uranyl ions. It was considered that the main reason of this adsorption capacity difference between poly(DPAAm) and nonwoven fabric stem from the synthesis procedure; poly(DPAAm) was obtained as a homopolymer directly from N,N'-dipropionitrile acrylamide monomer but the amidoximated nonwoven fabric firstly grafted with GMA (glycidyl methacrylate) and then functionalized with 3,3'-iminodipropionitrile. The results of the adsorption studies showed that the interaction between UO_2^{2+} and amidoximated groups agree with Langmuir type isotherm. From the Langmuir equation, the adsorption capacities were found as 400 mg UO_2^{2+} /g dry amidoximated poly(DPAAm) and 180 mg UO_2^{2+} /g dry amidoximated nonwoven fabric.

The advantages of these new polymeric adsorbents containing two amidoxime groups per repeating unit are the presence of excess amidoxime groups and an additional diethylene spacer units between the neighboring amidoxime groups in

each monomeric unit. These properties make the new adsorbent more accessible for the adsorption of metal ions in aqueous systems than the conventional adsorbents having only one amidoxime group per repeating unit. From the literature, it was concluded that these new adsorbents have a higher uptake capacity for especially uranyl ion than the other adsorbents containing single amidoxime group per repeating unit.

Keywords: N,N'-dipropionitrile acrylamide, radiation-induced grafting, amidoximation, iminodipropionitrile modified GMA grafts, uranium and vanadium ion selectivity, seawater treatment.

Advisor: Prof. Dr. Olgun GÜVEN, Hacettepe University, Department of Chemistry.



ÖZET

Metal iyon tutma kapasitesini arttırmak için, tekrarlanan birim başına çift amidoksim grubu içeren yeni bir polimer sentezlenmiştir. Bu amaçla, tezin ilk bölümünde, N,N'-dipropionitril akrilamid (DPAAm) monomeri, 3,3'-iminodipropionitril ve akrilol klorür'ün reaksiyonu ile sentezlenmiştir. Elde edilen monomer daha sonra AIBN başlatıcı olarak kullanılarak etanol içerisinde 70 °C'da polimerleştirilmiş ve % 77 dönüşüm elde edilmiştir. Yeni sentezlenmiş monomer ve polimerin yapısı FT-IR ve termal analiz metodları kullanılarak karakterize edilmiştir. Poli(DPAAm)'nin her monomerik birimde çift asılı amidoksim grupları içeren polimere dönüşmesi için hidroksilamin ile reaksiyona sokulmuştur. Nitril gruplarının amidoksim'e dönüşümü, FT-IR spektrometrisi ile izlenmiştir. Amidoksimlenmiş polimerin yapısı FT-IR ve termal analiz metodları ile daha detaylı karakterize edilmiştir. Monomer birimi başına çift amidoksim grubu içeren bu yeni polimerik adsorbentin, U, V, Cu, Co ve Ni iyonları için adsorpsiyon özellikleri çok düşük konsantrasyon seviyelerinde (ppb), kesikli işlem ile incelenmiştir. Şelatlaştırıcı amidoksimlenmiş poli(DPAAm), uranyum iyonları gibi vanadyum iyonlarına da yüksek adsorpsiyon kapasitesi göstermiştir. Sulu çözeltilerdeki metal iyonları karışımından seçicilik çalışmalarında, dağılım katsayısı, D, hesaplanarak adsorbentin U ve V iyonlarına aşağıdaki sıra ile yüksek seçicilik gösterdiği tayin edilmiştir: $U > V \gg Cu = Co \gg Ni$. Bu yeni adsorbent ile uranyum ve vanadyum iyonlarının seçimli adsorpsiyonunun nedeni, sert-yumuşak asit-baz (HSAB) etkileşimlerinden dolayı olduğu açıklanabilir. Yeni adsorbentin doğal deniz suyundan uranyum ve vanadyum iyonları adsorpsiyonu da akışkan sistem ile incelenmiştir.

Tezin ikinci bölümünde, polietilen kaplanmış polipropilenden yapılmış kumaş yüksek verimli yeni adsorbent hazırlamak için, gövde polimer olarak kullanılmıştır. Gövde polimere aşılansız zincirlerin tekrarlanan birimi başına çift amidoksim grupları katılması ile metal iyon adsorblama kapasitesinin yükseltilmesi amaçlanmıştır. Gövde polimer, azot atmosferinde 200 kGy dozda elektron demetleri ile ışınlanmış ve glisidil metakrilat (GMA), ışınlanmış kumaş üzerine aşılansızdır. Aşılama koşulları optimize edilmiş ve GMA ile aşılansız polimer, 3,3'-iminodipropionitril ile etanol içerisinde 80 °C'da modifiye edilmiştir. Daha sonra

asık nitril grupları, metanol su karışımı içerisindeki % 6'lık hidroksil aminle amidoksimleştirilmiştir. Tüm polimerik yapılar FT-IR, SEM ve termal analiz metodları kullanılarak karakterize edilmiştir. Uranyum, vanadyum, kurşun, bakır ve kobalt iyonları için amidoksimlenmiş kumaş elyafların adsorpsiyon özellikleri çok düşük konsantrasyon (ppb) seviyesinde kesikli işlemle incelenmiştir. Adsorbent, uranyum ve vanadyum iyonlarına yüksek adsorpsiyon kapasitesi göstermiştir. Sulu çözeltideki metal iyonları karışımından seçicilik çalışmalarında, adsorbentin metal iyonlarına aşağıdaki sıra ile seçicilik gösterdiği bulunmuştur: $V > U \gg Cu \geq Pb \gg Co$. Adsorbentin seçiciliği, çalışılan metal iyonları için dağılım katsayısının D, hesaplanması ile tayin edilmiş ve adsorbentin U ve V iyonlarını diğer metal iyonlarından 6 kat daha fazla seçimli adsorpladığı gösterilmiştir.

Tezin son bölümünde, amidoksimlenmiş poli(N,N'-dipropionitril akrilamid) (poly(DPAAm)) ve amidoksimlenmiş kumaş elyaf'ın UO_2^{2+} , Pb^{2+} , Cu^{2+} ve Co^{2+} 'ın yüksek konsantrasyonlarında adsorpsiyon özellikleri kesikli prosesle incelenmiştir. Metal iyonları adsorpsiyon çalışmaları değişik metal iyonları çözeltilerinden (100-1500 ppm) yapılmıştır. Amidoksimlenmiş poli(DPAAm)'in, bütün metal iyonları, özellikle uranyum için, amidoksimlenmiş kumaş fiberden daha yüksek adsorpsiyon kapasitesine sahip olduğu görülmüştür. Poli(DPAAm) ve kumaş elyaf arasındaki adsorpsiyon kapasitesi farkının başlıca sebebinin sentez yönteminden kaynaklandığı düşünülmüştür; poli(DPAAm), N,N'-dipropionitril akrilamid monomerinden doğrudan homopolimer olarak fakat amidoksimlenmiş kumaş elyaf, ilk önce kumaş elyaf GMA ile aşılınmış ve sonra 3,3'-iminodipropionitril ile fonksiyonlaştırılarak elde edilmiştir. Adsorpsiyon çalışmalarının sonuçları, UO_2^{2+} ve amidoksim grupları arasındaki etkileşimlerin Langmuir tipi izotermle uyumlu olduğunu göstermiştir. Langmuir eşitliğinden, adsorpsiyon kapasiteleri, 400 mg UO_2^{2+} /g kuru amidoksimlenmiş poli(DPAAm) ve 180 mg UO_2^{2+} /g kuru amidoksimlenmiş kumaş fiber olarak bulunmuştur.

Tekrarlanan birim başına çift amidoksim grupları içeren bu yeni polimerik adsorbentin avantajları, fazla amidoksim gruplarının varlığı ve her bir monomerik birim içerisinde komşu amidoksim grupları arasında diyetilen ara birimlere sahip olmasıdır. Bu özellikler, bu yeni adsorbenti, tekrarlanan birim başına yalnız bir amidoksim grubu içeren geleneksel adsorbentlerden, sulu sistemlerden, metal

iyonları adsorpsiyonu için çok daha etkili yapmıştır. Literatürden, bu yeni adsorbentin tekrarlanan birim başına tek amidoksim grubu içeren diğer adsorbentlerden, özellikle uranyum iyonları için, daha yüksek tutma kapasitesine sahip olduğu sonucuna varılmıştır.

Anahtar kelimeler: N,N'-dipropionitril akrilamid, radyasyonla başlatılmış aşılama, glisidil metakrilat aşılantı kumaş, amidoksimasyon, iminodipropionitril ile modifiye edilmiş GMA aşılması, uranyum ve vanadyum iyonları seçiciliği.

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1. INTRODUCTION

From the age of stone and metals, we have come to the age of nuclear energy and polymers. Indeed, we live in the world of polymers. That is why scientists and technologists have termed this era as the “polymeric age”. In every step of our daily lives, we come across things, which are the fruits of polymer research. The ever widening application of polymers in everyday life over the last several decades has generally been acknowledged as a mixed blessing by scientists and technologists. Though started in the middle of the last century, work in this field of chemistry has been so rapid and the application so useful and versatile, that the number of polymer systems are enormous.

Metals are important raw materials for the traditional machinery industries (tools, equipment, motor vehicles, aviation, marine vessels), for catalyst in the chemical industry, for the electronic industry, for strategic and nuclear energy sources, for the plating industry and for numerous other areas of application. The continuous increase of world needs for most of the known metals, the decrease in grade of available ores, and strict environmental regulations, make it interesting to find effective and efficient methods for processing and recovery. Accordingly, complexation of metal ions is an important technique for recovering precious metals from various sources (hydrometallurgy) and for the removal of metal ions from solutions in municipal and industrial waste streams containing metal ions, even at very low concentrations.

The presence of metal ions in natural or industrial waste water has been a subject of research in environmental science for a long time. Areas throughout the world have been mined for metals, sometimes for thousand of years. Metal-rich wastes resulting from this activity may be deemed to pose a hazard to human health and the quality of the environment. The geological and geochemical literature is rich in accounts of natural, metal-containing waters. While it may not be scientifically reasonable or technically possible, to improve the water to standards with lower metal ion levels than natural background concentrations, processes for wastewater treatment need to be developed. Metal ions such as barium, cadmium, copper, iron, lead or zinc are commonly detected in both natural and industrial

effluents from mineralized areas. Uranium has also interested an increasing number of research programmes. Traditional processes for metal ion decontamination suggest precipitation techniques, or separation on ion exchange resins, but sorption is a well known and much used process. Precipitation involves the production of metal containing mineral sludges which can be hazardous for many years after the landfill of the solid waste. Ion exchange resin processes are justified in the case of high relative content of polluted effluent. For low concentrations, this technique is not valid, so several sorbents have been tested in the last thirty years to remove uranium from low content industrial effluents: fungal or bacterial biomass or organic by-products such as raw or modified chitosan. The cost and ineffectiveness of these sorbents have led to development of other inorganic and organic adsorbents. Inorganic, though inexpensive and easily available, have poor mechanical strength. When made stronger with binders, the loading capacity decreases. They also have an disadvantage in that they cannot be prepared in any form, at times not even as granules. On the other hand, organic sorbents, though relatively more expensive, have the advantage that they can be prepared in any form like, granules, sheets, fiber, etc. Polymeric materials having polyfunctional groups such as carboxylic, amide, nitrile, iminodiacetic acid, amidoxime, and ammonium groups, etc., not only possess good hydrophilic properties, but also have good ion exchange properties which make them suitable for metal recovery from aqueous solutions (Helfferich, 1962; Warshawsky, 1986). For the purpose of separation of metal ions either for purification or enrichment, various kinds of organic chelating resins have been developed. This has been the subject of numerous papers and review papers related to synthesis, characterization and metal ion uptake studies (Hancock and Martell, 1989; Kantipuly et al., 1990; Beauvais and Alexandratos, 1998; Rivas et al., 2003). Polymers with specific functionalities can be obtained by either synthesizing new monomers carrying the special groups capable of interacting with the target metal ions and polymerizing them into practically applicable shapes and forms or by converting some groups on existing polymers or copolymers with suitable reactants into desired forms either by chemical or radiation treatment (Kise and Sato, 1985; Park and Suh, 1996; Choi and Nho, 2000; Zhanhai and Jun, 2002; Rivas et al., 2002).

A polymeric ligand is usually used in an insoluble resin form to separate a specific metal ion from a liquid containing metal ions. For example, uranium is a potential environmental pollutant especially in mining industry wastewater and the migration of uranium in nature is important in this context. In view of the anticipated exhaustion of terrestrial uranium reserve in the near future, research has been directed toward the recovery of uranium from nonconventional sources, such as coal and natural waters (0.1-10 mg U/m³), and especially from seawater (2.8-3.3 mg U/m³). The recovery of uranium from contaminated water of flooded mines (0.1-15 mg U/m³) also presents a very important environmental problem to be solved. Uranium is one of the most valuable metals in sea water. The concentration of the insoluble uranium tricarbonatate in the sea is 3 µg/L and the total calculated reserves are 5x10⁹ tonnes. Uranium exists in seawater mainly in the form of a tricarbonatate complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Saito and Miyauchi, 1981, 1982). The recovery of uranium from seawater has been noted as one of the useful techniques for supplying uranium in the future. The process using specially designed and developed adsorbents is thought to be a very effective method for recovering uranium because of the high selectivity for uranium, the ease of handling, the safe applicability in the environment, etc. Various inorganic and organic adsorbents for the recovery of uranium in seawater have so far been synthesized. Since an early effort to recover uranium from sea water by adsorption on hydrated titania proved uneconomical, (Vernon and Shah, 1983; Sugasaga, et al., 1981), due to physical weakness of the adsorbent, the search for polymers of improved structure has been in progress in many countries. Vernon and Shah have developed resins and fibers by amidoximation of crosslinked acrylonitrile-ethylacrylate copolymers and demonstrated the application of polyamidoxime (PAO)/polyhydroxamic acid (PHA) in continuous extraction of uranium from sea water (Vernon and Shah, 1983). Extensive investigations of adsorbents capable of recovering uranium from seawater and aqueous systems have been carried out during the last two decades especially in Takasaki Radiation Chemistry Research Establishment in Japan and the results compiled recently in a nomogram by Saito and Sugo (Saito and Sugo, 2000). Many types of adsorbents have also been developed and tested for the recovery of uranium from seawater and aqueous media by Güven et al. in Turkey. (Saraydın and Karadağ, 1995; Karadağ and Saraydın, 1995; Akkaş and Güven, 2000).

Adsorbents containing amidoxime groups offer a number of possibilities for the separation and isolation of trace metals from various matrices, including sea water. Chelating resins containing amidoxime groups have been selected for their selectivity towards uranyl ions in the works of Egawa and Harada (Egawa and Harada, 1979; Egawa et al., 1980), and Schenk and Asthemier (Schenk et al., 1982). Amidoxime chelate fiber, with amidoxime chelate groups $[-C=NOH(NH_2)]$, contains functional groups that can chelate some metal ions and create stable chelators, so that very pure metal ions are obtained by elution. Amidoxime chelate fiber is very useful for recovering uranium from seawater and enriching or separating noble metal ions. Egawa et al. prepared a number of macroreticular chelating resins containing amidoxime groups by reacting acrylonitrile-divinyl benzene copolymer beads with hydroxylamine. It was reported that these resins have a high capacity for uranium in seawater (Egawa and Harada, 1979, 1980a, 1980b). Sugo et al. has already investigated a separative elution of uranium from an amidoxime polymer which had been immersed in seawater, and proposed the selective elution of uranium (Kabay et al., 1993; Sekiguchi et al., 1994; Kawai et al., 2000). A number of papers published by Güven et al. which investigated the preparation and properties of new copolymers with balanced hydrophilic and amidoxime group contributions for the uptake of uranyl ions from aqueous solutions (Akkaş and Güven, 2000; Şahiner et al., 2000; Pekel et al., 2000). Research studies involving the adsorption of uranium from seawater with spherical resin or bead and fibrous fiber or nonwoven fabric-chelating adsorbents containing amidoxime group indicate that this group has very high selectivity, strong adsorption ability and a large loading capacity for many metal ions, especially for uranium(VI). Furthermore, it is easy to operate and considerably safe for the environment. So the fibrous polymeric adsorbent containing amidoxime chelating functional group is considered the most promising method for recovering uranium from seawater in the near future.

The aim of the first part of this thesis was to synthesize a new monomer carrying double nitrile groups (N,N'-dipropionitrile acrylamide), preparation of its polymer and finally conversion of nitrile groups into amidoximes. The structure of monomer, polymer and its amidoximated form were characterized by elemental analysis, FT-IR spectroscopy and thermal analysis methods. The adsorption properties of

amidoximated poly(N,N'-dipropionitrile acrylamide) were investigated by batch process for five different metal ions from very dilute aqueous solutions and by using flow-through mode for uranium and vanadium from seawater. The results pertaining to this novel polymer are given herein.

In the second part of thesis, non-woven PP fabric coated with PE was used as the trunk polymer, and by radiation induced graft polymerization (RIGP) of precursor monomer, glycidyl methacrylate (GMA, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CHOCH}_2$), and subsequent chemical modification with 3,3'-iminodipropionitrile ($\text{NH}(-\text{CH}_2-\text{CH}_2-\text{CN})_2$) a copolymer with enriched acrylonitrile groups synthesized and this polymer was reacted with hydroxylamine to obtain graft chains containing two amidoxime groups per repeating unit. The results of metal ion uptake studies from very dilute solutions using this novel adsorbent are reported and compared with the capacities of other adsorbents reported in the literature.

At the final part of this thesis, adsorption capacities of new adsorbents containing double amidoxime group per repeating unit were investigated for uranyl, lead, copper and cobalt ions from concentrated (ppm) aqueous solutions. The binding mechanism of metal ions with amidoxime groups were investigated by using FTIR. Moreover applying the data of uranyl ion adsorption to different equations, adsorption isotherms were constructed for amidoximated poly(DPAAm) and amidoximated nonwoven fiber.

2. GENERAL PROPERTIES OF CHELATING POLYMERS

The lack of selectivity of the conventional ion exchange polymers has led to the discovery and development of a new class of polymers which are now known as specific and selective ion exchange polymers. These polymers are in fact polymeric complexing and chelating compounds which, under certain experimental conditions, are characteristic of one ionic species only. A chelating polymer consists essentially of two components, i.e., a chelating group and a polymeric matrix. The properties of both components have to be taken into account when designing and synthesising a chelating polymer. The chemistry of these new types of complexing polymers began in the late forties when Skogseid (Skogseid, 1947) described the first such polymer, a polystyrene derivative containing dipicrylamine groups and specific for potassium ion. This was followed by advent of chelating ion-exchange polymers incorporating a variety of chelating groups on different types of polymeric matrices (Deuel et al., 1955; Hale, 1956; Osborne, 1955). Since then, the field of chelating ion-exchange polymers possessing ion-selective properties has been developing steadily, incorporating various contemporary refinements of coordination chemistry. At present, a large number of chelating ion-exchange polymers incorporating a host of ligands, such as aminocarboxylic acids (Kiyohara, 1996), hydroxamic acids (Agrawal et al., 1999), phosphonic acids (Zhu and Jyo, 2001), amidoximes (Saito et al., 2000; Güven et al., 2000), dithiocarbamates, thiols (Liu et al., 2002), Schiff bases (Tank et al., 2002), crown ethers (Kavaklı et al., 2002) etc., have been incorporated into a variety of both organic and inorganic polymeric supports or matrices.

The increasing utility and application of complexing and chelating polymers have been in transition metal, as well as, in alkali and alkaline earth metal ion separations, preconcentration and nuclear chemistry, water and waste water treatment, pollution control and industrial processes, hydrometallurgy, polymer drug grafts and various miscellaneous applications in analytical chemistry.

Normally a metal ion exists in sea water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge

must be neutralized and some or all of its water of hydration replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and/or donor atom capable of forming complexes with the metal ions in solution, and it is logical to classify chelating polymers on this basis. Also, for simplicity, it is desirable to classify chelating polymers according to Figure 2.1.

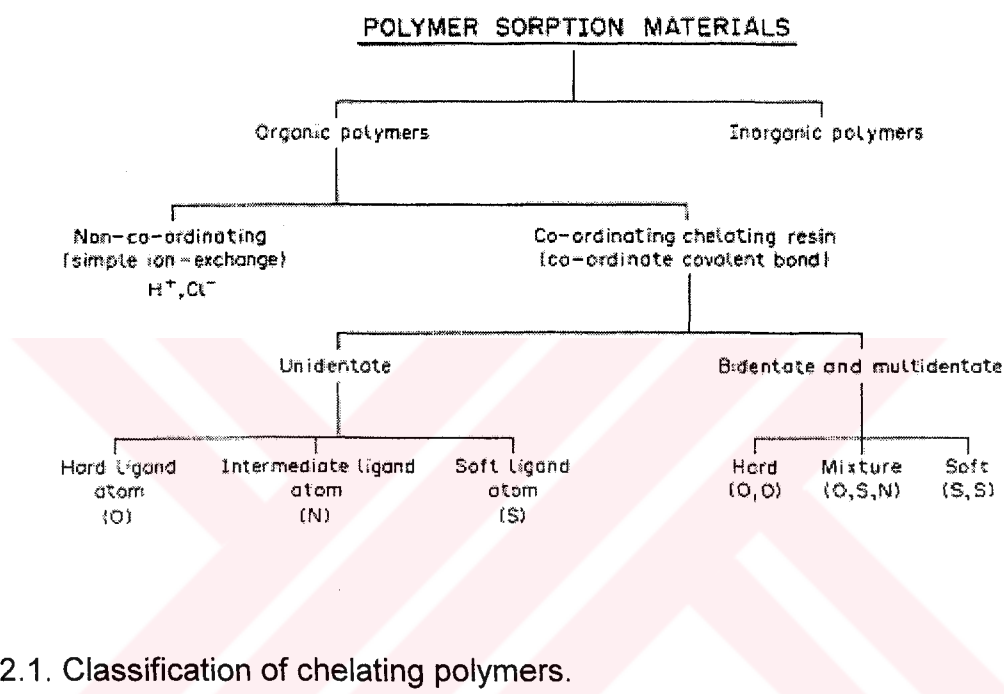


Figure 2.1. Classification of chelating polymers.

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

2.1. Physical Appearance of Chelating Polymers

Polymers can be produced in virtually any physical form, but four forms have become more popular than the others in laboratory as well as in industrial applications. These four are hydrogels, fibers (hollow fiber, nonwoven fabric), spheres and membranes.

2.1.1. Hydrogels

The hydrogels are polymeric materials which exhibit ability to swell in water, i.e. they retain a significant fraction of water within themselves but do not dissolve in water. Hydrogels are produced by the simple reaction of one or more monomers or by association bonds such as hydrogen bonds and strong van der Waals interactions between chains. Hydrogels can be classified into three categories according to their physical structural features: (i) amorphous hydrogels are produced when the macromolecular chains are randomly arranged; (ii) semicrystalline structures are characterized by dense regions of ordered macromolecular chains, known as crystallites; and (iii) hydrogen bonding is often responsible for the three-dimensional structure formed (Güven and Şen, 1991). The polymerization process can be carried out by radiation (electron beams, gamma rays, x-rays, or ultraviolet light), by chemical cross-linking (either using a small molecular weight cross-linking agent that is at least difunctional, or copolymerization with very small quantities of a multifunctional monomer), or by cross-linking monomers and linear polymeric chains via an interlinking agent.

The hydrogels are prepared mostly by using ionising radiation. Upon irradiation of macromolecules, at first macroradicals are formed, when recombined form crosslinks leading to the formation of network structures. If the macroradicals are favourably positioned, new covalent bonds between the polymer chains are formed and thus the hydrogel turns into an insoluble fraction depending upon the amount of these new bonds. On further irradiation, the amount of gel increases, although a part of macromolecules (or their fragments) may still be unbound (sol). However the mechanism is rather complicated in presence of water as a solvent and it has been studied by Davies et al. (Davies et al., 1981).

In the case of hydrogel formation, three-dimensional network is developed and it exhibits higher molecular weight that tends to infinity. The network is schematically represented in Figure 2.2. The circle represented in the figure is accessible for diffusion of solutes. In swollen state, this space contains water or the solvent molecules. The dimension of this region and the mesh size depend on the degree of crosslinking of the polymer chains or the density of junction points. The amount

of water absorption also depends on the degree of crosslinking of polymer chains. The higher degree of crosslinking is, the smaller is the amount of water-solvent absorbed in this space.

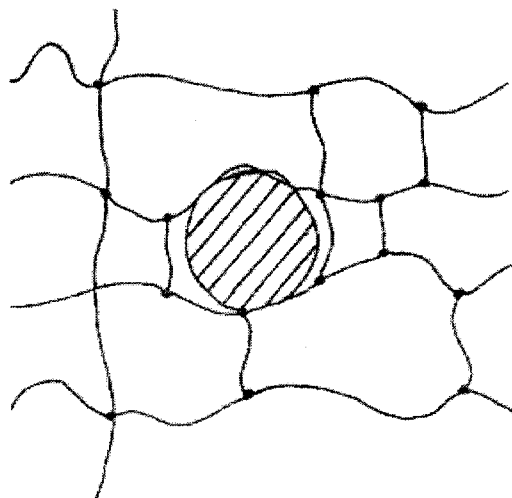


Figure 2.2. Scheme of hydrogel network. Circle denotes available space for diffusion.

2.1.2. Fibers

2.1.2.1. Hollow fibers

The hollow fibers which are generally obtained from polyethylene and polypropylene are produced by a sophisticated melt spinning and drawing process. It is a tough material which has high tenacity and strong resistance to bending fatigue. In addition, it is not affected at all by any microorganisms, is not affected so much by acid or alkali, or by irradiation. Therefore, hollow fibers can be used for various application field. The chemical modification and radiation induced modification of hollow fibers are effective in adding new properties to collect protein and metal ions. Saito and Sugo et al. used many types of hollow fibers for metal ions separation (especially, uranium and vanadium ions) and biotechnological applications (Saito and Sugo, 2000).

2.1.2.2. Nonwoven fabrics

Nonwoven fabrics (NWF) can be produced as sheets by using meltblow technology. Nonwovens are a class of textiles/sheet products, unique in industry. Nonwoven fabrics are different than the conventional textile fabrics and paper. Nonwovens are not based on yarns and (with frequent exceptions) do not contain yarns. They are based on webs of individual fibers. Nonwovens are different than paper in that nonwovens usually consist entirely or at least contain a sizeable proportion of long fibers and/or they are bonded intermittently along the length of the fibers. Although paper consists of fiber webs, the fibers are bonded to each other so completely that the entire sheet comprises one unit. It has an advantage in that a higher flow rate is obtainable at lower operating pressures through the fabric and production cost is relatively economical. Therefore, NWF can be a novel polymeric matrix for immobilizing various moieties such as ion exchange groups, hydrophobic ligands, and affinity ligands. Non-woven fabrics containing amidoxime groups prepared by using radiation induced graft polymerization were extensively studied for accumulating uranium from seawater (Saito and Sugo, 2000).

2.1.3. Spheres

The most widely used of these forms is the (spherical) bead which can be produced in solid or more or less porous form in dimensions from hundreds of nm up to several millimeters or larger. Porous particles were developed to increase the surface area of the beads, thereby increasing the capacity when used as adsorbents, ion exchangers, etc. The porosity of the particles controls, to a large extent, the hydrodynamic properties, as well as reaction kinetics, and it is therefore often crucial to control the size and amount of pores in the material for any particular application. Another important factor, determining the characteristics of synthetic particulate material, is the crosslinking density. The number of crosslinks between the polymer chains determines the ability of the particle to retain its physical form when it is subjected to stress of different kinds. A highly crosslinked particle will be more rigid and mechanically tolerant than its counterparts containing fewer crosslinks. The more highly crosslinked material will also be less

affected by solvents, whereas a low-crosslinked bead will swell to a certain degree depending on the solubility of the polymer material in question. Eventually the bead may increase in size to the extent where the polymer chains are totally solvated and only held together by the crosslinks, forming a gel structure. A non-crosslinked polymer particle would analogously dissolve if it was subjected to a good enough solvent.

2.1.4. Membranes

Another common physical form of chelating polymers is the membrane (or film) form. Membranes may be produced as flat sheets or tubes. The material thickness ranges in both cases from a few microns up to millimeters. Tubular material is made with inner diameters from tens of microns to millimeters. The diametrically smallest tubes are often called hollow-fibres, but no sharp line of distinction can be drawn, and the two denotations are often used interchangeably. Just as for the particulate materials, crosslinking affects membrane properties. Analogously with what is said about particles above, increase in crosslinking density makes the material more sturdy and decreases swelling tendencies.

2.2. Some Common Chelating Polymers used in Metal Separation, Enrichment and Recovery

Many different polymeric materials, of both natural and synthetic origin, are used in analytical chemistry, and analytical and preparative biochemistry for removing, separation and enrichment of metal ions. Among these materials are poly(acrylamide), poly(ethylene glycol), agarose, cellulose to mention just a few. The following discussion will, however, be concentrated on four of the most widely used synthetic polymeric materials that are most closely related to the work presented in this thesis, namely polystyrene, polyolefines, polymethacrylates and silica.

2.2.1. Styrene-divinylbenzene-based polymers

The first synthetic ion exchangers developed were made of sulfonated polystyrene, and polystyrene resins are still the most widely used base for organic reactive polymers. The structure of this material is depicted in Figure 2.3.

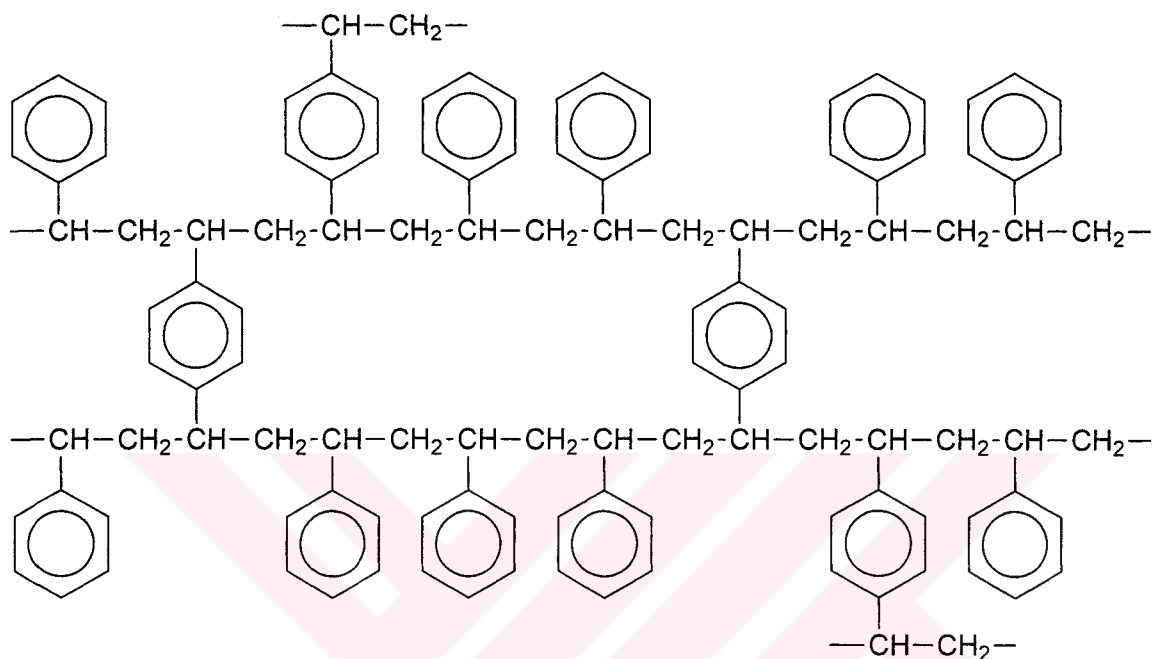


Figure 2.3. Structure of S-DVB polymer.

One reason for this popularity is undoubtedly that well characterized styrene-based materials are commercially available in a variety of physical forms and sizes, crosslinking densities, porosities, etc. Since chemical modification, in most cases, does not alter these physical properties of the preformed substrate, styrene-based polymers are convenient starting materials for the manufacturing of novel resins with a good control of the resulting properties.

Crosslinking of polystyrene matrices is readily made by co-polymerization of styrene with the difunctional monomer divinylbenzene (DVB) (Figure 2.4), and this affects the physical characteristics to a great extent. The resulting materials are often termed S-DVB.

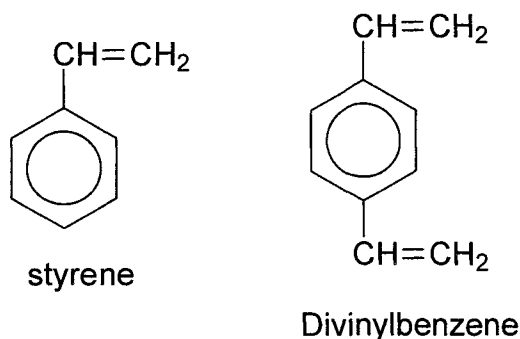


Figure 2.4. Structure of styrene and divinylbenzene.

Crosslinked polystyrene resins are, in their native form, characterized by a high hydrophobicity and insolubility in common solvents. The olefinic backbone and the lack of a hydrolyzible bond in the side chain provides for excellent hydrolytic stability. However, they exhibit a tendency to swell in aromatic solvents, the extent of which is controlled by the degree of crosslinking. They can also interact selectively with polarizable substances such as unsaturated and aromatic molecules by p-electron interaction, a property that can be both useful and troublesome (Glad, 1994).

A major reason for the popularity of styrene-based resins as base material for chelating polymers is the large number of easy modifications that can be carried out on the pendant phenyl groups in the material. The possibility of conversion of the aromatic side chains by electrophilic substitution has been thoroughly investigated and many such reactions have been described in the literature (Hodge ve Sherrington, 1988). An example is sulfonated S-DVB, the main type of strong cation exchanger which is manufactured by direct sulfonation of the pendant phenyl ring. Chloromethylation is another convenient and widely used route for preparing chelating S-DVB polymers that are suitable for further functionalization. The chloromethyl group is highly reactive towards nucleophiles, and a large number of functionalization schemes using this intermediate have been outlined (McKillop et al., 1983). There are two clear disadvantages with the chloromethylation procedure though. The first and most important is that the reagent, bis(chloromethyl) ether, which is the optimal reagent for the reaction, is highly carcinogenic. So are some of the possible reaction products in alternative reaction schemes designed to eliminate handling of bis(chloromethyl) ether

(Mckillop et al., 1983). The other problem with the method is that a certain amount of polymer crosslinking is inevitable in the chloromethylation step. The immobilized chloromethyl groups simply react with an aromatic group in another polymer chain and introduce methylene bridges in the material.

The thorough investigations performed on the functionalization of polystyrene and its derivatives have also made it interesting to attempt grafting of these monomers onto preformed polymeric substrates of different compositions. Radiation grafting of functional or reactive monomers onto films of polyolefines, as well as their substituted analogues, is a popular way of synthesizing ion exchange membranes. The use of polystyrene-based resins in chemistry is widespread, and areas where they are frequently utilized include adsorbents for organic constituents in preparative or analytical work-up from different matrices, as strong or weak cation or anion exchange resins, and as supports for the Merrifield type of solid-phase synthesis (Kesting, 1985; Merrifield, 1963).

2.2.2. Methacrylate Polymers

The methacrylate family of monomers comprises many members with different groups esterified or amidated to the common methacryloyl structure. These groups will, after polymerization, be pendant side chains to the polymer backbone, and as such influence the properties of the polymer in different ways. The most commonly used methacrylates share, however, some basic properties. The carbonylic link imparts a rather hydrophilic character, especially in comparison with polystyrene and polyolefines. There is a susceptibility for hydrolytic splitting of the ester or amide group, but this tendency is, to a certain degree, suppressed by the methyl group bound to the same carbon atom in the polymer backbone as the carbonyl group. This methyl group differentiates the methacrylates from the closely related acrylate family, and is important since it provides a sterical hindrance for attacks on the carbonyl group. The size and characteristics, i.e. length, branching, hydrophilicity etc., of the ester/amide-linked functionality also affect the hydrolytic stability, but the methacrylates are, generally, more stable than their acrylate counterparts.

Methacrylic polymers are inert towards most solvents used in analytical chemistry, and the stability can be further increased by crosslinking of the resin.

The methacrylate group of monomers is, as stated above, multifaceted, and there are a vast number of hydrophilic, hydrophobic, functional and reactive monomers commercially available. The reactive monomers can either be converted further prior to polymerization, or used directly in the synthesis of new materials whose functional groups can be utilized directly, or indirectly after a post-polymerization conversion into another functionality (Glad, 1994). Monomers especially suitable for such modification are, e.g., methacrylic acid, methacryloylchloride, hydroxyethyl methacrylate (HEMA), 2,3-epoxypropyl methacrylate (glycidyl methacrylate; GMA), DMA (Dodecyl methacrylate), Dimethyl amino ethyl methacrylate (DMAEMA) and others (Figure 2.5).

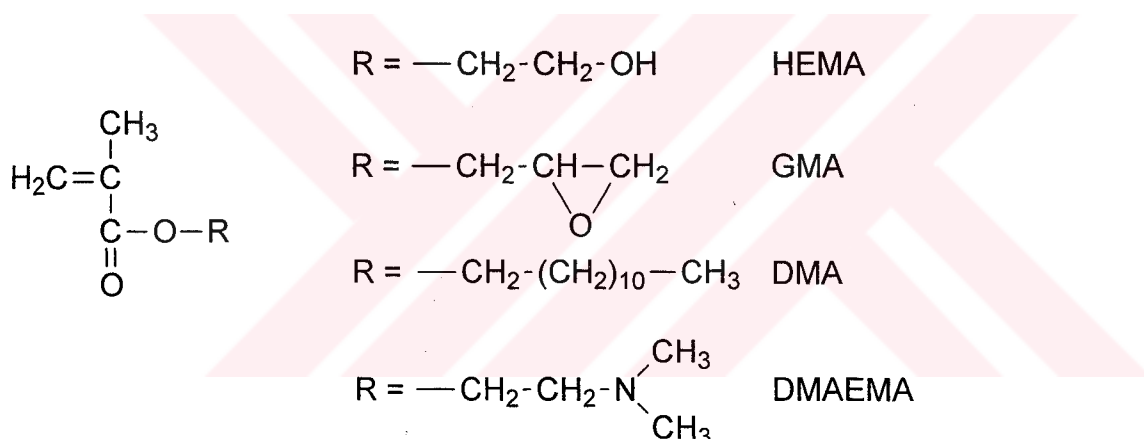


Figure 2.5. Structure of methacrylate monomers.

The modification of preformed polyHEMA particles has been thoroughly investigated by Coupek and co-workers (Kahovec and Coupek, 1988), and they have also used poly-HEMA resins epoxidized with epichlorohydrin as intermediates in the coupling of amines and other groups (Turkova et al., 1981; Kahovec and Coupek, 1988). Epoxy-group bearing methacrylate resins suitable for further functionalization can also be synthesized by the co-polymerization of GMA, and this has been extensively investigated by Svec and co-workers (Svec et al., 1975; Lukas et al., 1978; Horak et al., 1981) who have synthesized particulate materials with different properties as regards porosity, pore size, etc., from GMA

and the divinyllic crosslinker ethylene dimethacrylate. The same research group has also investigated the characteristics of a great number of resins, functionalized with different amines, with respect to their chelating, ion exchange and other properties (Hradil et al., 1982; Azanova et al., 1990; Svec et al., 1984). Such materials are widely utilized as adsorbents, ion exchangers, and chelaters in sample work-up, preconcentration and separation procedures.

The pendant epoxy group in GMA polymers offers a facile way of introducing a wide variety of novel functionalities into preformed supports. The epoxy group is characterized by a high reactivity and the ability to enter into a vast number of reactions (Lee and Newille, 1967). This reactivity is caused by the presence of the highly strained three-membered ring with deformed valency angles, and shortened bond between the carbon atoms. The epoxide reacts with nucleophiles (Figure 2.6) by a ring-opening reaction, and the order of reactivity has been found to be: $RS^- > RSH = R_1R_2NH > RO^- \gg ROH$.

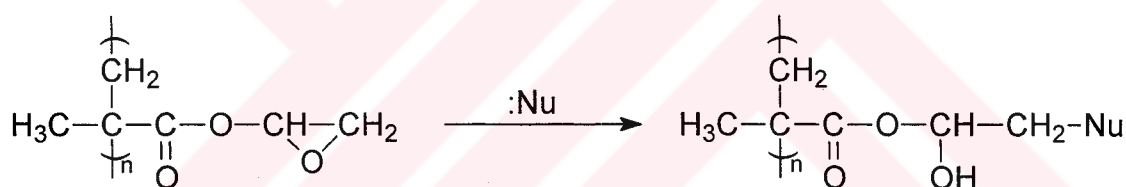


Figure 2.6. Schematic representation of nucleophilic substitution of a nucleophile onto a GMA polymer.

2.2.3. Olefines and Related Polymers

The polyolefine group of materials comprises polyethylene (PE), polypropylene (PP), etc. and their halogenated counterparts like poly(vinyl chloride) (PVC), the perfluorinated polytetrafluoroethylene (PTFE), polyvinylidenedifluoride (PVDF), polychlorotrifluoroethylene (PCTFE), and other chlorinated and fluorinated analogues. The structures of these polymers are shown in Figure 2.7.

These polymers are all very hydrophobic in nature and due to the lack of hydrolyzible groups, they are all very tolerant towards acids and bases. Because of their regular structure they tend to be highly crystalline and are therefore resistant to most solvents. The perfluorinated materials are, actually, the most inert polymers known today, and PTFE has no known solvent in spite of its total lack of crosslinking. The mechanical and thermal stabilities of the non-halogenated polyolefines are, however, not as good as those of polystyrene, polymethacrylates or silica. This, the high cost, and the problematic functionalization of the more highly inert halogenated polymers, impedes the use of spherical polyolefine particles in analytical applications.

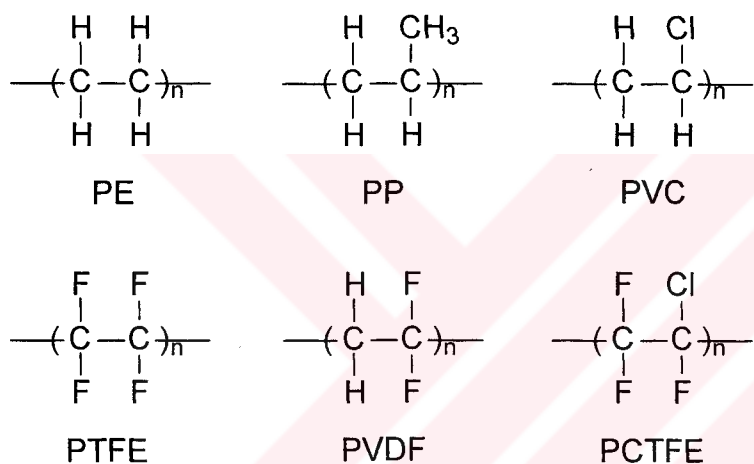


Figure 2.7. Structure of some polyolefines.

The modification of these materials is, as mentioned, difficult. Surface hydrophilization can be achieved by etching (Blais, 1974), gamma radiation and ion beam and plasma treatment. Selective hydroxylation and amidoximation can further be made. The most widely utilized modification of polyolefines is grafting of reactive or functional monomers to the original polymeric substrate, and this is currently used in the conversion of polypropene and polyethylene into chelating polymers (Saito and Sugo, 2000).

2.2.4. Silica

Silica (silicon dioxide) is still one of the most important polymers for use in analytical chemistry, and even though it is entirely inorganic, it is a widely used

polymeric material that must be treated in this connection. Silica materials are available in various physical forms, but are most commonly encountered as spherical beads of different sizes and porosities. Silica is mechanically very stable, and this, together with the good solvent inertness of the material, is the basis for its widespread use as a separation material in high performance chelation ion chromatography (HPCIC) applications (Jones and Nesterenko, 1997). Apart from commercially available flexible Empore membranes, consisting of silica microparticles entrapped in a PTFE web, silica based membranes are scarcely used, because of the inflexibility and fragility of the material.

The major problem with silica is that it is easily hydrolyzed, and it is therefore useful as a support in a pH-range from approximately 2 to 8.

Silica surfaces can be modified by several routes, the most common being the reaction of hydroxylated silica with alkoxy silane or chlorosilane reagents (Unger, 1979; Kirkland et al., 1989). These silanization reactions are easily carried out and a number of functional or reactive silanes are available. Silica materials suitable for ligand immobilization can be obtained by reaction with the epoxy- or amino-containing reagents (3-glycidyloxypropyl)trimethoxysilane or (3-aminopropyl)trimethoxysilane (Chang, 1976; Jervis et al., 1988). This yields epoxidized silica, which can be functionalized as outlined above for epoxy-carrying materials, or aminated silica, which is used with glutaraldehyde for, e.g., immobilization of enzymes.

2.3. Functional Groups of Chelating Polymers

The functional group atoms capable of forming chelate rings usually include oxygen, nitrogen and sulphur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether, phosphoryl and some other groups. Sulphur is in the form of thiol, thioether, thiocarbamate, disulphide groups etc.

These groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbents from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal ions or metal species under certain favorable conditions, to form chelate rings. The selective concentration and separation of elements from natural water systems depends both on elemental speciation and the chelating properties of the polymer.

2.3.1. Selection of chelating polymers

Synthetic chelating polymers have almost entirely displaced inorganic ion-exchange polymers, with a few exceptions such as metal phosphates (zirconium and stannic phosphates) and some oxides (MnO_2 , Al_2O_3 , SiO_2 gel, ect.). Conventionally, the resin materials can be classified into three main divisions: a) cation-exchangers, b) anion-exchangers, and c) chelating polymeric resins. These can further be subdivided into strong, weak, or intermediate types, depending of the functional group.

The choice of an effective chelating resin and its value in preparative and analytical method development is dictated by the physicochemical properties of the resin materials. These are the acid-base properties of the metal species and the resin materials, and the polarizability, selectivity, sorptive capacity, kinetic and stability characteristics of the resin. Chelating polymers usually contain polyfunctional groups. In the view of the complex nature of sea-water for instance, selection of the proper chelating polymeric material for a specific suite of trace elements is of most importance. One of the rules of selection is based on the concept of hard and soft acid and bases. Hard bases have localized charges and small ionic radii, whereas soft bases are large in size and have diffuse charges and high polarizabilities. A rule of thumb is that 'soft acid' tends to interact with 'soft bases' and conversely, 'hard acids' interact with 'hard bases'. A classification of selected ions and ligands by the hard and soft acid and base (HSAB) scale according to principle of Pearson is given in Table 2.1 (Hancock and Martell, 1989). The functional groups in the chelating polymer materials usually act as bases; oxygen-containing functional groups are hard and sulphur-containing group

soft. Functional groups with a basic nitrogen atom have an intermediate character. For example, uranium acts as a hard acid, chelating polymers having oxygen-containing functional groups can be used to extract uranium from sea-water or aqueous media. Also, it is reasonable to use sulphur-containing functional-group materials for soft acids such as the precious metals, Hg, Ag, etc. Although this rule is highly useful in practical selection and synthesis of chelating polymers, it should be borne in mind that there is a substantial difference in the stability of complexes formed by metal ions with macromolecular and low molecular-weight functional ligands. This is primarily caused by the polymeric structure for the resin material.

Table 2.1. Pearson classification of acids and bases (Pearson, 1963).

Acids	
Hard	Soft
H^+, Li^+, Na^+, K^+ $Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$ $Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}$ $Gd^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}$ $Si^{4+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, Th^{4+}, U^{4+}$ $Pu^{4+}, Ce^{4+}, WO^{4+}, Sn^{4+}$ $UO_2^{2+}, VO^{2+}, MoO^{3+}$	$Cu^+, Ag^+, Au^+, Tl^+, Hg^+$ $Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}$ $CH_3Hg^+, Co(CN)_5^{2-}, Pt^{4+}$ Te^{4+}, Br^+, I^+
Intermediate acids	
$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}$ $Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}$	
Bases	
Hard	Soft
$H_2O, OH^-, F^-, CH_3CO_2^-, PO_4^{3-}$ $SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-$ $ROH, RO^-, R_2O, NH_3, RNH_2, NH_2NH_2$	$R_2S, RSH, RS^-, I^-, SCN^-$ $S_2O_3^{2-}, R_3P, R_3As, (RO)_3P$ $CN^-, RNC, CO, C_2H_4, H^-, R^-$
Intermediate bases	
$C_6H_5NH_2, C_5H_5N, N_3^-, Br^-, NO_2^-, N_2, SO_3^{2-}$	

The kinetic characteristics of a chelating polymer are of considerable importance and depend on the nature and properties of the polymeric matrix and the degree of cross linkage. Whereas in the ordinary type of exchanger the exchange processes are more rapid and controlled mainly by diffusion, those in a chelating exchanger are slower and controlled either by a particle-diffusion mechanism or by a second-order chemical reaction. For complexation or sorption to occur, it is not sufficient

that surface functional groups are present; they must also be accessible for the chelation of the metal ion without steric hindrance. Thus within chelating resin particles, many surface functional groups may remain inactive in complexation because equilibrium can not be attained.

2.4. Comprehensive Approaches to Metal Ion Separation with Chelating Polymers

A comprehensive approach to a particular separation problem should account for: (i) the chemistry of a given ion under special conditions, including the interactions of the ion, M^{n+} , with all solution ligands, interactions of M^{n+} with other metallic ions, ligand exchange and redox reactions; (ii) the chemistry of the functional group in the polymer phase; (iii) the swelling behaviour of the polymeric network under the separation conditions and (iv) kinetic phenomena in the solution and polymer phases. A successful separation system must accommodate all these factors.

2.4.1. Selection of the inorganic coordinating ligand

Selecting a ligand for a defined separation task requires the following steps: (i) examination of the inorganic chemistry of the metal ion under the defined conditions; (ii) establishment of the predominant interactions between metal ion and ligand; (iii) selection of a separation strategy, such as host-guest interaction, chelate formation or ion pairing; (iv) considerations of co-ions and the effect on separation strategy (selectivity problem) and (v) consideration of whether the various elution pathways are efficient (elution problem).

2.4.2. The nature of the metal and of the reagent donor atoms

The nature of the reaction between metal ions and various organic ligands largely depends on the nature and charge of the metal ions, first and foremost on their electron structure. Ions in which the electron distribution is close to that of inert gases, are found to react more readily with the reagents in which the active atoms - the atoms directly participating in complex formation with metals - are oxygen atoms. This includes alkali and alkaline-earth metals, and the elements of titanium,

aluminium and scandium subgroups. Lanthanides and actinides also tend to react with oxygen, even though their electronic structure is different. The elements in this group give complexes with nitrogen, but not as a rule, with sulphur.

Metal ions with partly filled d-orbits form stable complexes with ligands containing polar groupings such as -N= , -NH_2 . these are transition metals which include, the elements of the iron subgroup, platinum metals, cupric copper, auric gold, etc. typically, these elements become bound to sulphur. It would appear that they may also be further stabilized by the formation of the donor pi-bond. These are typical complexing agents which yield stable complexes with different ligands. Palladium(II), for example, forms exceedingly stable compounds with numerous reagents, and the compounds are usually readily extractable with organic solvents (Warshawsky, 1983).

Cations with completely filled d-orbitals (Zn, Cd, Ga, In, Tl, etc.) also tend to react with readily polarizable ligands. They display different behaviour towards the donor atoms of the different reagents.

This classification should be considered as a rough approximation only. Sidgwick (Zolotov and Schmorak, 1970) estimated the relative tendencies of individual metals to react with oxygen and nitrogen. According to him, the following elements give more stable bonds with oxygen than with nitrogen: Mg, Ca, Sr, Ba, Ga, In, Tl, Zr, Th, Ge, Sn, V(IV), V(V), Nb, Ta, Mo(V), U(VI), Fe(III), and Co(II). This estimate is mainly based on the fact that the metal-oxygen bond is an ordinary covalent bond, while the metal-nitrogen bond is a coordinative bond. The elements in the second group (Be, Cr(III), Fe(II), Ru, Rh, Pd, Os, Ir, Pt) form oxygen bonds and nitrogen bonds which are approximately of equal strength. Finally, the elements Cu(I), Ag(I), Au(I), Cu(II), Hg, V(III), Co(III) and Ni are considered by Sidgwick to form stronger bonds with nitrogen than with oxygen. The first group includes ions with an electronic structure of the inert gas type and also ions with a small number of d-electrons. The third group includes ions with a large number of d-electrons or with a filled d-level.

More recently another classification was proposed by Ahrland et al. (Zolotov and Schmorak, 1970). Metal ions were subdivided into three groups in Figure 2.8:

- 1) Elements which form the most stable complexes with the first element of their group in the periodic system, i.e., N, O, F;
- 2) Elements which form the most stable complexes with atoms of the second or the following elements (P, S, Cl);
- 3) Elements which display an intermediate behaviour (different valency states may behave differently: Cu(I) belongs to the second group and Cu(II) to the third).

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Xe
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Kr
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Fm	Md	Md	(No)	(Lw)	

Figure 2.8. Distribution of metals in groups according to their tendency to react with different donor atoms. Elements within solid frame tend to react with P, S, Cl; elements within broken frame display an indeterminate behaviour; all other elements, except the inert gases and fluorine, tend to react with N, O, F.

2.5. Synthetic Chemical Modification Routes Leading to Chelating and Coordinating Polymers

The major synthetic chemical routes for the preparation of chelating and coordinating polymers are: (a) polymerization of functional monomers, (b) polymerization of non-functional monomers, followed by chemical modification, (c) functional monomers introduced into or grafted onto the prepared polymer, followed by polymerization and (d) immobilization of hydrophobic chelating extractants during polymerization or post-polymerization (solvent-impregnated polymers). These routes are shown in Figure 2.9.

Polymerization of functional monomers is a direct way to functional polymers, yet limitations with regard to the synthesis and ability of monomers, difficulties in the polymerization of several classes of monomers and difficulties in achieving bead-shaped particles of sufficient strength and porosity considerably reduce the attractiveness of this route. The second method of polymerization, using ion-templated monomers, is essentially a variation of the first, with very limited experience at the present time.

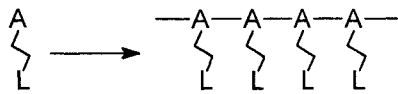
The ease of performing reactions on polymers with the advantage of commercial availability of polymers has prompted many researchers to perform multistep consequential modification reactions. The advantages outlined are offset by the fact that each step 'prints an error'. Thus the final polymer incorporate, in addition to the desired ligand, remnants of the functionalities of the intermediates. This diminishes the general usefulness of the multistep methodology.

The method of one-step functionalization attempts to overcome the above difficulties by preassembling the whole ligand and the following this with one-step attachment.

2.5.1. Polymerization of functional vinyl monomers

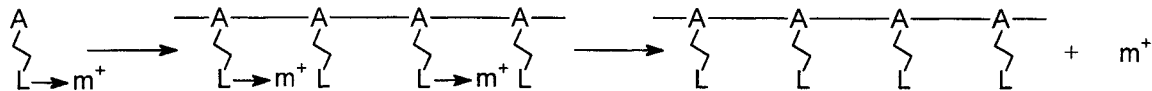
The commonly available vinyl monomers produced by companies engaged in bulk polymerization or in producing speciality polymers can be purchased and used as such. Styrenes, acrylates, vinylpyridines and vinylimidazoles are typical examples, and crosslinked copolymers can be readily obtained. Copolymerization of functional monomers with a divinyllic crosslinking agent appears to be the most direct approach to chelating and coordinating polymers. However, there is no guarantee that polymeric materials will be readily obtained. Because of this limitations, only small number of the functional monomers described in the general literature have become commercially significant in the synthesis of coordinating and chelating polymers. Consequently, only selected monomers will be presented here.

(a) Polymerization of monomer

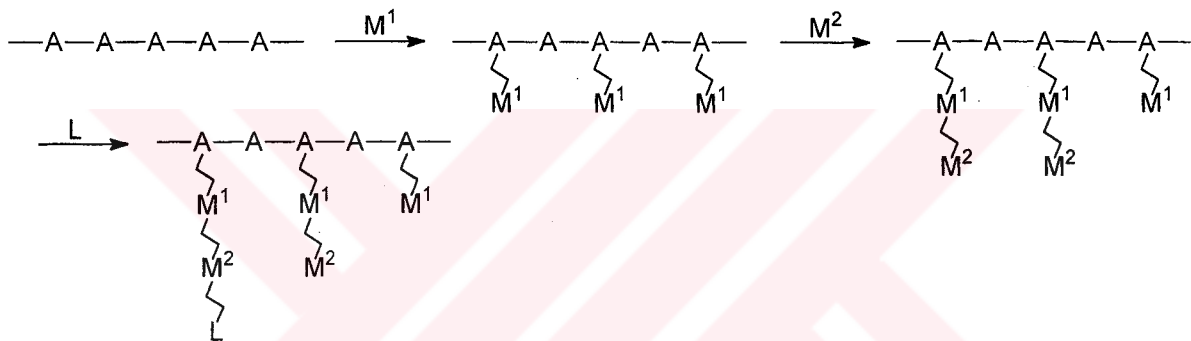


A=vinyl,etc. $\sim$ = bridging unit L= ligand

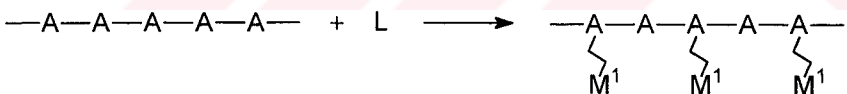
(b) Templated polymerization of monomer



(c) Multifunctionalization of polymers



One-step functionalization of polymers



M^1 and M^2 = modifying groups

(d) Physical impregnation

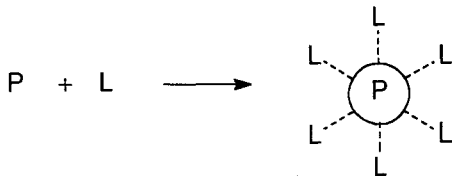


Figure 2.9. Synthetic routes to metal coordinating polymers: (a) polymerization of monomers, (b) templated polymerization of monomers, (c) grafting of second ligand, (d) physical impregnation of a hydrophobic ligand.

2.5.2. Polymerization of functional acrylate and methacrylate monomers

Acrylates, methacrylates and their corresponding acid chlorides are vinyl monomers which are readily converted to functional monomers. The reaction of methacryloyl chloride (**M-1**) with t-aminoalkylcarboxylic acids is followed by protection of the carboxylic terminal as its N-hydroxysuccinimide ester (**M-2**) and radical polymerization in benzene to polymer **P-1a**. Further reaction with methylhydroxylamine led to the N'-methylhydroxamic acid N-alkyl polyacrylamide (**P-1b**, crosslinked with N,N'-methylenebisacrylamide) (Figure 2.10). The polymer **P-1b** was found effective as an ion specific scavenger.

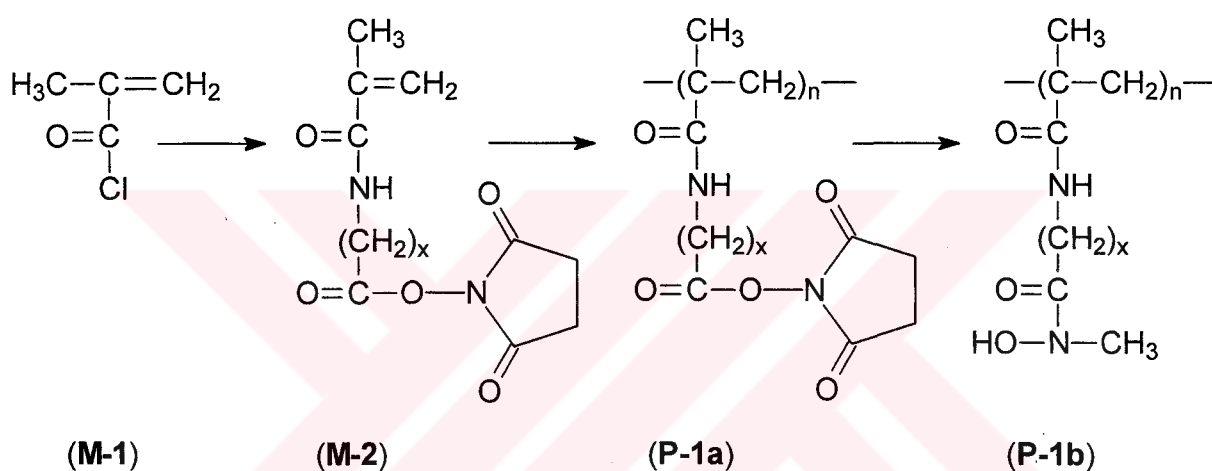


Figure 2.10. Synthesis of hydroxamic acid chelating polymers from acrylic monomers by polymerization.

In a similar sequence of reactions, poly(methacryloylglycylhistidine) (**PMGGHis**, **P-2b**), showing high affinity for Cu(II), and poly(N-hydroxyethylthioethyl)methacrylamide (**P-2a**) an efficient polymer scavenger for Hg(II) ions, were prepared (Figure 2.11)

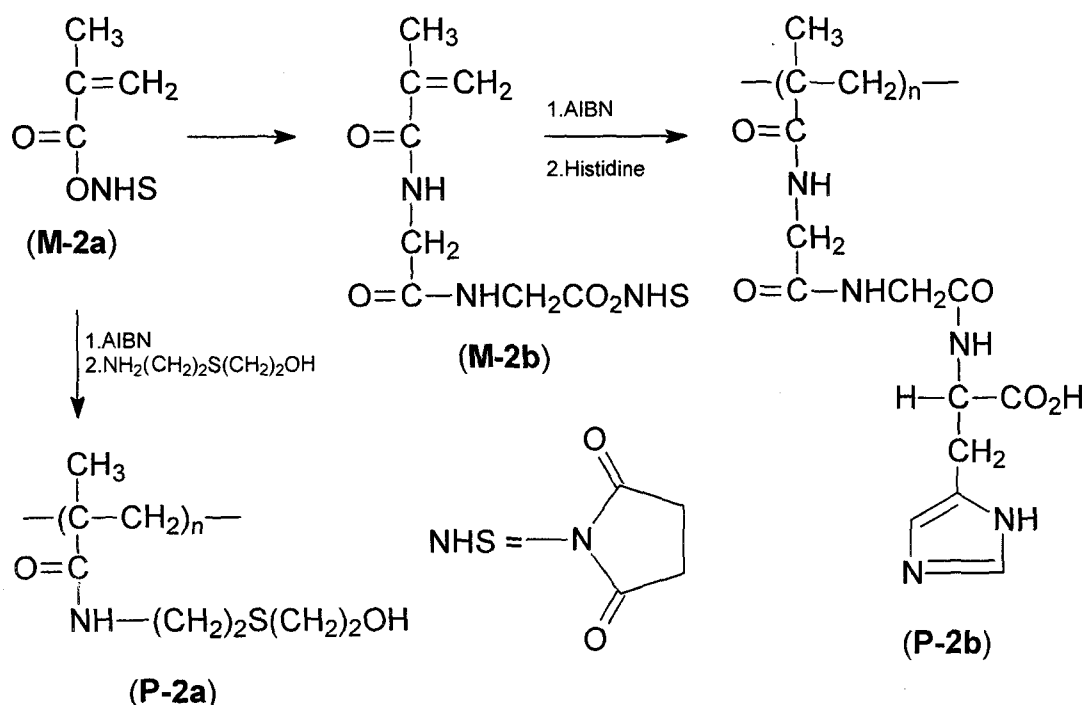


Figure 2.11. Polymerization of N-hydroxysuccinimide methacrylic esters followed by modification with amines and amino acids.

Polyacrylamide polymers, incorporating iminodiacetate groups, were made by aminomethylation of the N-methylolpolyacrylamide **P-3a** with iminodiacetic acid disodium salt. Polymer **P-3b** shows high stability constants with $\text{Ca}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Cu}(\text{II})$ ions (Figure 2.12).

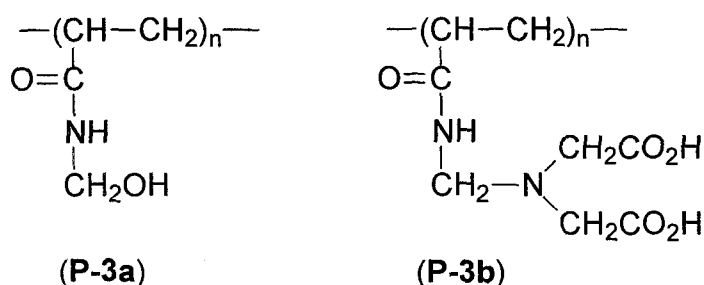


Figure 2.12. The structures of polyacrylamide polymers (P-3a) and iminodiacetate groups (P-3b).

2.5.3. Polymerization of vinyl aromatic monomers

1-Vinyl-4,5-dicarboxyimidazole (M-3) and 2-styryl-4,5-dicarboxylic acid imidazole (M-4) were polymerized in the presence of 5% divinylbenzene (DVB) to the corresponding polymers P-1 (from M-3) and P-2 (from M-4). The pH-dependent complexation of Cu(II), Ni(II), Cd(II), Zn(II) and Hg(II) in aqueous solutions were investigated (Figure 2.13).

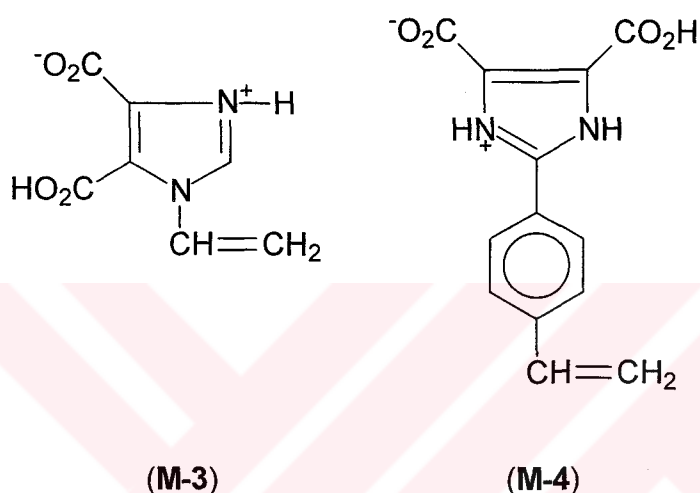


Figure 2.13. The structures of 1-Vinyl-4,5-dicarboxyimidazole (M-3) and 2-styryl-4,5-dicarboxylic acid imidazole (M-4).

3-Vinylpyrazoles (M-5), substituted in positions 4 and 5 with auxiliary chelating group (aldehyde, oxime, ester), were copolymerized in the presence of the diallylic species bis(3-vinyl-5-pyrazolyl) ketone (M-6) to yield, after saponification, poly(vinylpyrazolecarboxylic acid) chelating polymers (P-4) with very high binding capacity for Cu(II), Ni(II), Zn(II) and Mg(II) (Figure 2.14).

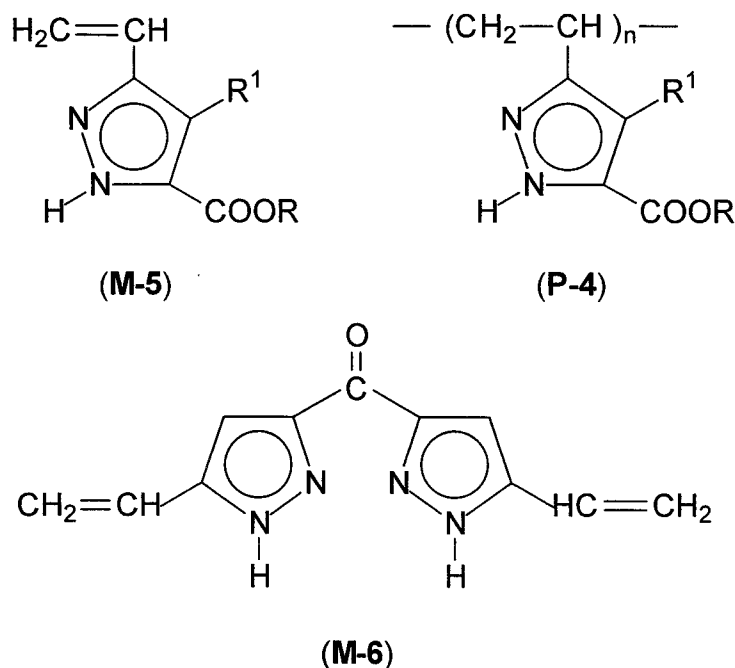


Figure 2.14. The structures of 3-Vinylpyrazoles (M-5), poly(vinylpyrazolecarboxylic acid) chelating polymers (P-4) and bis(3-vinyl-5-pyrazolyl) ketone (M-6).

2.6. Radiation-Induced Graft Polymerization Modification Routes Leading to Chelating and Coordinating Polymers

The radiation-induced graft polymerization (RIGP) is one of the techniques for modifying polymeric materials with new properties. The modification of polymeric materials by radiation-induced grafting was started over 30 years ago

Grafting proceeds in three different ways: (a) pre-irradiation (b) peroxidation and (c) mutual irradiation technique. In the pre-irradiation technique, the first polymer backbone is irradiated in vacuum or in the presence of an inert gas to form free radicals. The irradiated polymer substrate is then treated with the monomer, which is either liquid or vapour or as a solution in a suitable solvent. However, in the peroxidation grafting method, the trunk polymer is subjected to high-energy radiation in the presence of air or oxygen. The result is the formation of hydroperoxides or diperoxides depending on the nature of the polymeric backbone and the irradiation conditions. The peroxy products, which are stable, are then treated with the

monomer at higher temperature, hence the peroxides undergo decomposition to radicals, which then initiate grafting. The advantage of this technique is that the intermediate peroxy products can be stored for long periods before performing the grafting step. On the other hand, with the mutual irradiation technique the polymer and the monomers are irradiated simultaneously to form the radicals and thus addition takes place. Since the monomers are not exposed to radiation in the pre-irradiation technique, the obvious advantage of that method is that it is relatively free from the problem of homopolymer formation which occurs with the simultaneous technique. However, the decided disadvantage of pre-irradiation technique is the scission of the base polymer due to its direct irradiation, which brings forth predominantly the formation of block copolymers rather than graft copolymers. The different processes are represented through simple mechanisms provided below (Bhattacharya, 2000).

Irradiation with electron beams or gamma-rays onto a polymeric materials (trunk polymer) produced radicals (reaction sites) in the polymer. Using the radicals as starting sites for polymerization, vinyl monomers that come into contact are polymerized to form polymeric brushes (branch polymers). Although other excitation sources such as plasma and UV light can also produce radicals on the trunk polymer, RIGP is powerful in that it can introduce a high density of polymeric brushes bearing functional groups into the entire volume of the trunk polymer uniformly (Lee, 1997).

The advantage of RIGP include:

- (1) a selectivity of chemically and physically stable polymeric materials,
- (2) a wide application on various types and shapes of polymeric materials,
- (3) an unnecessary catalyst during reaction,
- (4) a wide range of applicable reaction temperature, and
- (5) an easiness of controlling the distribution of reaction sites in the trunk polymer.

This technique can be used to maintain the physical strength and chemical stability of the trunk polymer while appending various functionalities to the trunk polymer (Figure 2.15) (Sugo and Saito, 1989; Sugiyama et al., 1993).

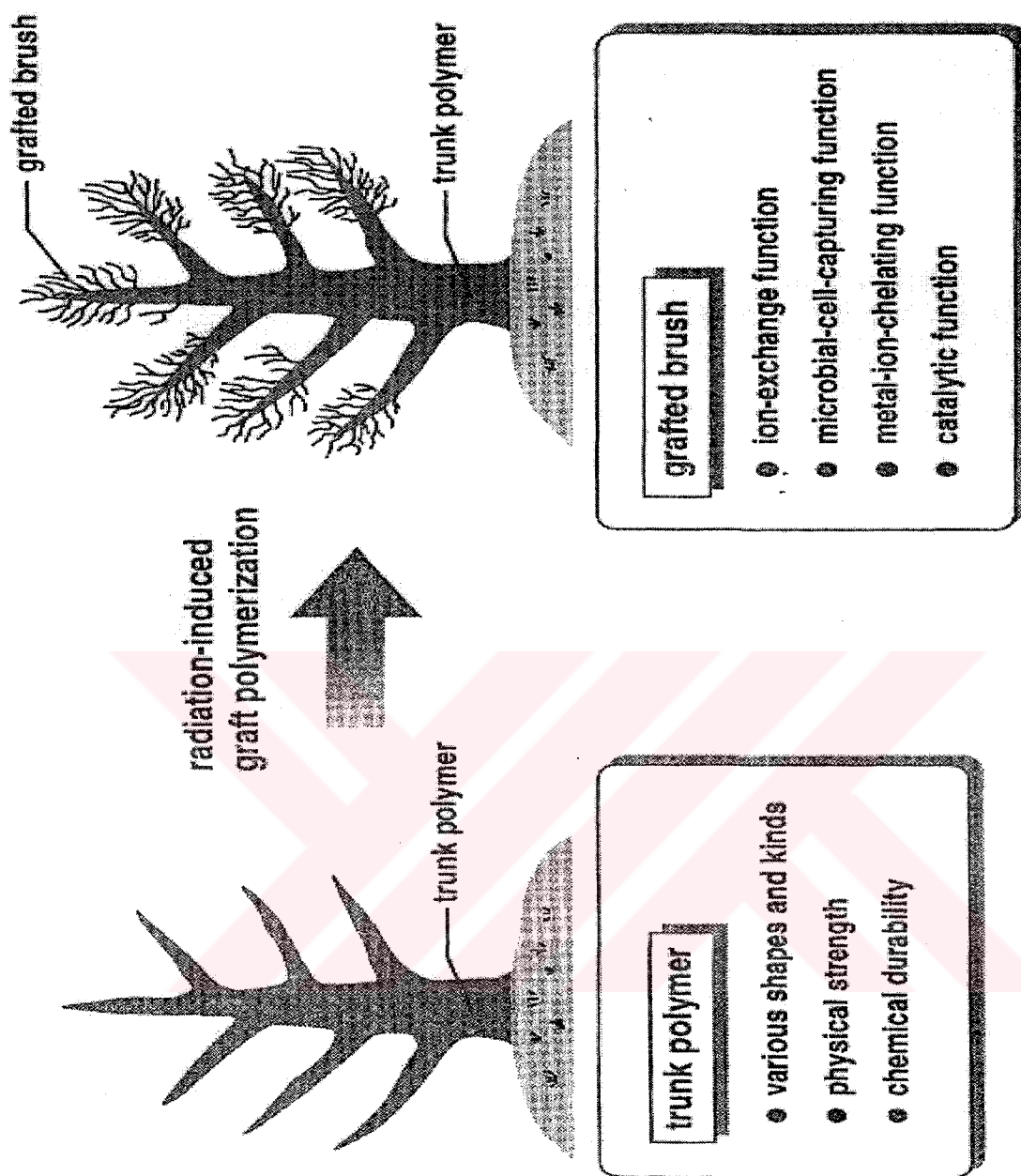


Figure 2.15. Schematic presentation and advantages of radiation-induced graft polymerization

When the simultaneous irradiation method is applied, homopolymer is easily produced in the monomer solution. Therefore, a process for the removal of homopolymer is necessary. On the other hand, for the preirradiation method, because the processes of irradiation and polymerization are separated, the whole process can be simplified. As a result, the pre-irradiation method is industrially more effective than simultaneous irradiation method.

By applying the above advantages of RIGP, ion exchange membranes, chelating resins and membranes, hemocompatible polymeric materials and affinity membranes have been developed (Lee, 1997).

2.7. Interpenetrating Polymer Networks (IPN)

An interpenetrating polymer network (IPN) is formed when one crosslinked polymer network is synthesized in the presence of another, preformed, crosslinked polymer network (Sperling, 1981). The two polymers can be of different or the same chemical composition, and the crosslinks can be physical or chemical in nature. The novel materials thus formed often exhibit a microscopic phase-separation providing unique properties, sometimes being a combination of the characteristics of the separate components (Barrett and Sperling, 1993).

Interpenetrating polymer networks have been used for a long time. They were in use even before the chainlike structure of the polymers, from which they were made, were elucidated in 1920 (Staudinger, 1920). Even though they were not aware of being IPN pioneers, chemists improved the properties of natural rubber by the formation of IPNs, early this century. Thomas Edisons chief chemist, Jonas Aylsworth, patented the first IPN material in 1914 (Aylsworth, 1914). It was a mixture of natural rubber and a phenol-formaldehyde resin, and the material was used in the Edison phonograph records. It was, however, not until 1960 that the term IPN was coined (Millar, 1960), when Millar used an IPN system of polystyrene in polystyrene as a model system for ion exchangers. Since that time, IPNs, in different physical forms and chemical compositions, have found numerous applications. They are today commercially used as energy-absorbing materials in, e.g., automotive bumpers, as dental filling materials, contact lenses, in medical applications, such as burn-dressing film and controlled release devices, and as noise- and vibration-damping materials (Barrett and Sperling, 1993).

2.8 Metal Ion Template Polymers

The principle applied involves the use of a polymer composition “memory” and

conformational arrangement of the molecules of a noncrosslinked polymer into a position suitable for complex formation with a metal and the subsequent fixing of the conformations formed by intermolecular crosslinking with removal of the template ions from the crosslinked system. Synthesis of metal ion template polymers proceeds in three steps: (1) a complex between a monomeric ligand and a metal ion is formed, (2) polymerization, (3) the metal ion is removed by treating with a dilute acid solution

Efendiev et al., prepared a crosslinked polymeric sorbents with macromolecular rearrangement favourable for sorption of copper ion. They found that increased the ion exchange capacity of the sorbent more than twice in comparison with the same copolymer crosslinked by conventional method without special arrangement of macromolecules (Kabanov et al., 1979). Akkaş and Güven prepared a poly(Acrylamide/Maleic acid) hydrogel in a prestructured manner to increase their capacities for removal of uranyl ions. They showed that such a prestructuring, by using uranyl ion as a template ion, improved the uranyl ion uptake capacity of similar hydrogels by 15-20 % (Akkaş and Güven, 2000).

2.9. Selective polymer-supported chelating reagents

The selectivity of chelating resins for targeted metal ions is of great importance in the separation of the metals from complex solutions. Selectivity can be increased with ligands that can coordinate or chelate with the target metal ion. For example, crown ethers have been covalently bound to a polymer matrix and can selectively remove a target metal ion from a solution containing several other ions in equal concentration (Hayashita et al., 1996).

The following recent literature describes the selectivities of a variety of polymer-supported ligands used in metal ion separations (Beauvais and Alexandratos, 1998).

2.9.1 Amine ligands

A large body of literature exists describing the use of the amine-containing

polymers for selective separations. The reaction of poly(ethyleneimine) with poly(vinyl benzaldehyde) produces the resin shown in the Figure 2.16 which has a high selectivity for Fe(III) over Cu(II), Ni(II), Co(II), Fe(II), Mn(II), and Zn(II) in a competitive study (Chanda and Rempel, 1993a). The resin was selective for Cu(II) over the other metal ions listed in the absence of Fe(III).

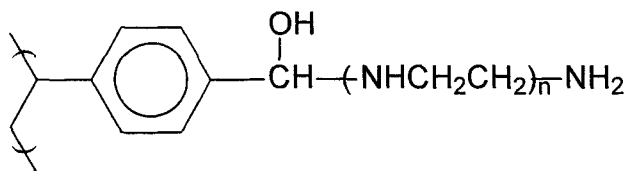


Figure 2.16. Polystyrene-supported poly(ethyleneimine).

2.9.2. Heterocyclic amine ligands

A wide variety of heterocyclic amines are utilised in metal ion separations. A copolymer of 1-(acrylamidoethyl)-3-hydroxy-2-methyl-4(1H)-pyridinone and N,N-dimethylacrylamide (Figure 2.17) was able to chelate Fe(III) from poisoned blood plasma (Feng et al., 1994). An 1-(2-aminoethyl)piperazine resin (Figure 2.18) was synthesized from the reaction of 1-(2-aminoethyl)piperazine with poly(vinylbenzyl chloride) (Yi-Yong and Xing-Zhong, 1994). The resin was then examined for its affinity with precious metal ions. The resin had good sorption capacities for Au(III), Pt(IV), Ir(IV), and Os(IV) in 0.1 M HCl, as well as Pd(II) and Ru(III) in 0.5 M HCl. The resin also separated Au(III) and Pd(II) from a 0.1 M HCl solution containing those ions with Cu(II), Ni(II), and Fe(III).

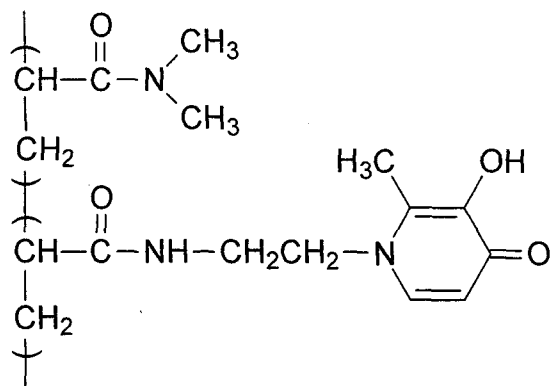


Figure 2.17. Copolymer of 1-(β-acrylamidoethyl)-3-hydroxy-2-methyl-4(1H) pyridinone and N,N-dimethylacrylamide.

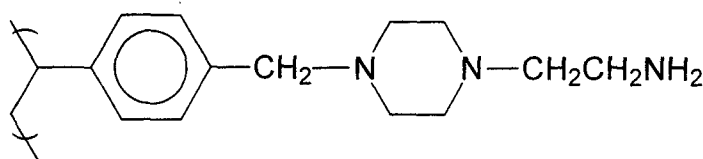


Figure 2.18. Polystyrene-supported 1-(2-aminoethyl)piperazine.

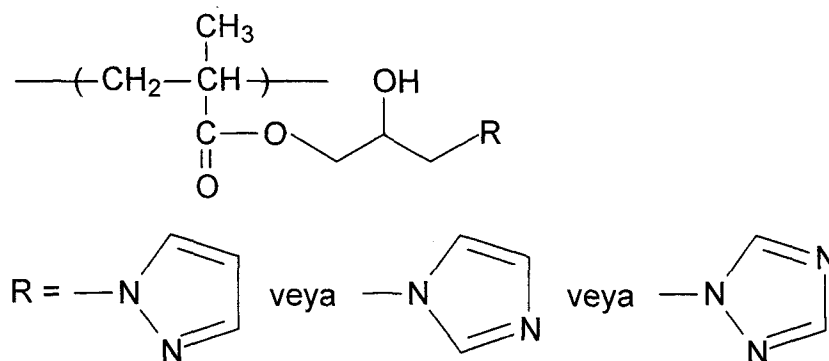


Figure 2.19. Poly(glycidyl methacrylate)-supported pyrazol, imidazole and 1,2,4- triazole.

Poly(glycidyl methacrylate) resin was modified with pyrazole, imidazole, and 1,2,4-triazole (Figure 2.19). All three resins selectively removed Cu(II) from a solution also containing Cd(II), Co(II), Ni(II), and Zn(II) at pH >2.5. The sulfur analog of poly(glycidyl methacrylate), which containing a thiirane ring, was modified with pyrazole, imidazole, 1,2,4-triazole, and tetrazole (Figure 2.20) (van Berkel et al., 1995a). The imidazole, triazole, and tetrazole resins selectively removed Cu(II) from a solution which contained Cu(II), Cd(II), Co(II), Ni(II), and Zn(II) at pH > 2.5. Poly(glycidyl methacrylate) and its sulfur analog were modified with 1,3-bis(benzamidazol-2-yl)propylamine (Figure 2.21) (van Berkel et al., 1995b). Both resins demonstrated selectivity for Cu(II) from a solution containing Cu(II), Cd(II), Co(II), Ni(II), and Zn(II) at pH > 2.5. At a pH > 4.5, The poly(glycidyl methacrylate) resin also removed Zn(II) from the same solution, while the sulfur analog removed Cd(II) and Zn(II). Reillex HPQ (Reilly Industries), which is quaternized poly(4-vinylpyridine) resin (Figure 2.22), selectively removed chromate from solutions with a pH range of 2-8 containing sulfate and chloride ions in a several hundred-fold excess (Chanda and Rempel, 1993b).

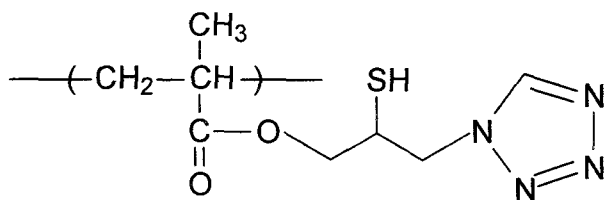


Figure 2.20. Poly(thioglycidyl methacrylate)-supported tetrazole.

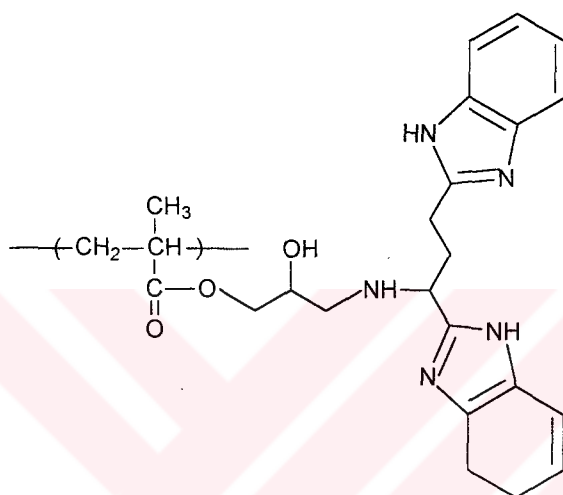


Figure 2.21. Poly(glycidylmethacrylate)-supported 1,3-bis(benzimidazol-2-yl)propylamine.

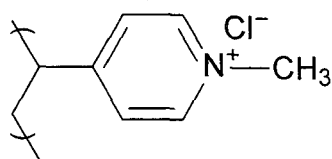


Figure 2.22. Quaternized poly(4-vinylpyridine).

2.9.3. Amidoxime ligands

Polymer fibers prepared from the grafting of acrylonitrile to polypropylene through irradiation were modified with hydroxylamine to give amidoxime ligands (Figure 2.23) (Kabay et al., 1993). The polymer complexed Cu(II) from solution at pH 6 as well as U(VI) from sea water. Poly(acrylonitrile) was also grafted on to poly(vinyl alcohol) fibers and modified with hydroxylamine (Weimping et al., 1993).

The modified fibers selectively removed Au(III) from solutions containing Au(III)/Cu(II)/Zn(II), Au(III)/Cr(III), and Au(III)/Ni(II) at pH 2.8. A starch- acrylonitrile copolymer was modified to produce an amidoxime polymer which displayed a selectivity order from pH 5 solutions of Hg(II) > Cu(II) > Pb(II) > Zn > Ni(II) > Cr(III) (Zhang et al., 1993).

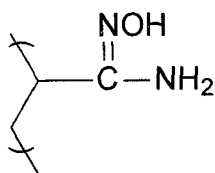


Figure 2.23. Polymeric amidoxime.

Duolite ES 346 (Rohm and Haas Co.), which contains amidoxime groups was used to recover gallate from 1 M NaOH solutions with one hundred-fold excess of aluminate, which simulates Bayer leachates (Schilde et al., 1995).

A number of chelating polymers containing amidoxime group synthesized by Güven et al. by using radiation induced polymerization and adsorption capacity of amidoxime groups for the uptake of uranyl ions from aqueous solutions was shown (Şahiner et al., 2000; Pekel et al., 2000).

2.9.4. Dithizone ligands

Poly(4-vinylpyridine) was modified with dithizone ligands (Figure 2.24) and found to have a good affinity for Hg(II). The polymer selectively removed Hg(II) from a solution containing Cd(II) and Zn(II) buffered at pH 3 with 0.2 M acetate. In a solution buffered at pH 3 with 0.3 M acetate containing Hg(II) and Pd(II), the polymer complexed both metal ions. The metal ions were selectively eluted with 0.5 M nitric acid / 2% ammonium nitrate and 0.2 M hydrochloric acid / 1% thiourea for palladium and mercury, respectively. Hg(II) and Pd(II) were also separated from Cd(II) at pH 3 with a 0.2 M acetate buffer (Shah and Devi, 1996).

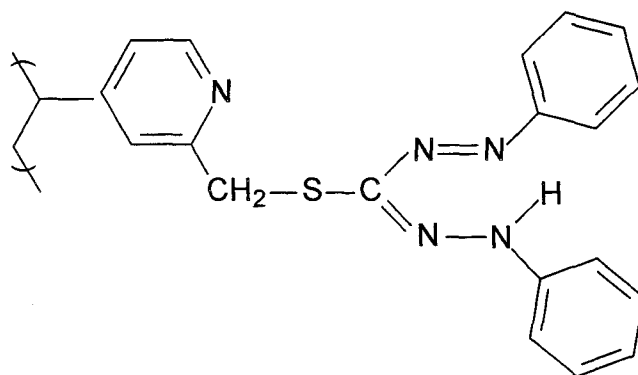


Figure 2.24. Poly(4-vinylpyridine)-supported dithizone.

2.9.5. Carboxylic acid and hydroxamic acid ligands

Copolymerization of N acryloyl diethyl iminodiacetate with acrylic acid was carried out (Figure 2.25) (Montembault et al., 1994) and the resulting copolymer complexed over 97 % $^{152}\text{Eu(III)}$ from solution at pH 4. Polystyrene was modified with phthalic anhydride via a Friedel-Crafts reaction to give a poly(4-vinyl-2'-carboxybenzophenone) resin (Figure 2.26) (Kamble and Patkar, 1994). The resin maintained a high affinity for Cu(II) in the presence of Cd(II), Ni(II), and Zn(II). In addition, the resin was selective for Fe(III) over Cu(II) and Ni(II) at pH < 3. Styrene was copolymerized with lead(II) vinylbenzoate to form a template resin (Figure 2.27) which was then stripped of the Pb(II) ions (Zeng, Murray, 1996). The resin was selective for Pb(II) over Cd(II) and Cu(II) in competitive studies and pH 2.6-2.8. The selectivity was increased by a factor of 1.7 over Cd(II) and three over Cu(II) compared to the untemplated resin. The capacities are all, however, extremely low (measurable in terms of micromoles per gram).

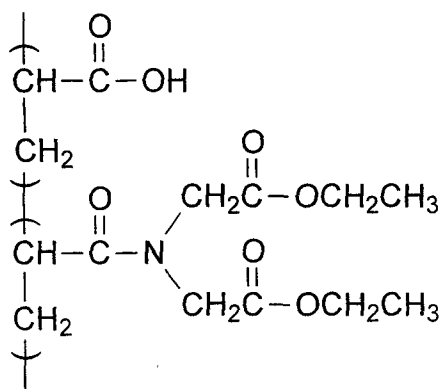


Figure 2.25. Poly(N-acryloyl diethyliminodiacetate)-co-acrylic acid.

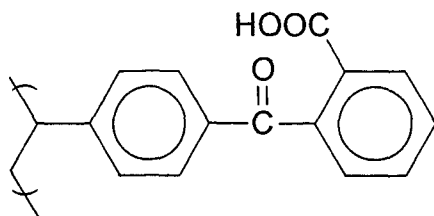


Figure 2.26. Poly(4-vinyl-2'-carboxybenzophenone).

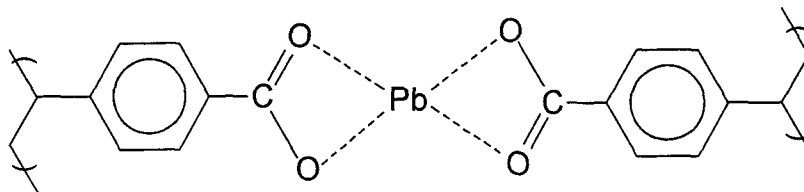


Figure 2.27. Pb(II) templated polyvinylbenzoate.

A poly(hydroxamic acid) resin was prepared from the reaction of poly(4-vinyl-2'-carboxybenzophenone) with hydroxylamine (Figure 2.28) (Kamble and Patkar, 1994). Although the resin had a high loading capacity for Cu(II), it selectively removed Fe(II) over Cu(II) and Ni(II) at pH < 4. Poly(methacrylohydroxamic acids) (Figure 2.29) were prepared from the reaction of poly(methacryloyl chloride) with several N-arylhydroxylamines (Agrawal and Rao, 1996). Each of the polymers had an affinity for selected metal ions in the order of Cu(II) > Zn(II) > Ni(II) > Co(II) > Pb(II) > Fe(II) at optimal pH (between 3.5 and 5 for various metal ions). Poly(hydroxamic acid) beads synthesized from polymethacrylate strongly complexed Cu(II), Fe(II), and Pb(II) at pH 5 (Haron et al., 1994). In addition, Co(II), Cu(II), and Fe(III) were selectively eluted from the resin with pH 4 acetate buffer, 0.1 M oxalic acid / 1 M HCl, respectively. Pb(II) and Ni(II) could be selectively eluted with 4 M HNO₃ and pH 3.5 acetate buffer, respectively.

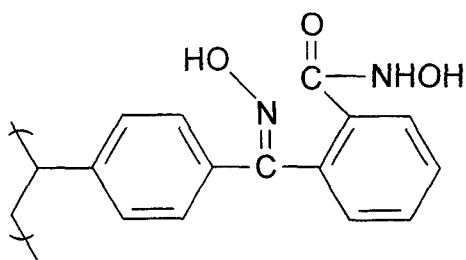


Figure 2.28. Poly(hydroxamic acid) resin.

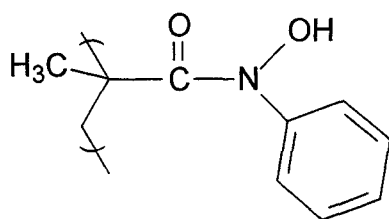


Figure 2.29. Poly(methacrylohydroxamic acid).

2.9.6. Crown Ether Ligands

Crown ethers have been immobilized within polymer supports and used in metal ion separations. Resins formed from the condensation polymerization of dibenzo-18-crown-6 and formaldehyde were modified with phosphonate monoethyl ester and phosphonic acid groups (Figure 2.30) (Zhao and Bartsch, 1995). The phosphonate monoethyl ester resin demonstrated selectivity for K(I) over Cs(I), Li(I), Na(I), and Rb(I) at pH < 8, and selectivity for Li(I) from the same solution at pH > 8. The phosphonic acid crown resin was selective for Li(I) at pH > 8. A resin prepared from the condensation polymerization of N,N-dibutyl sym-(propyl)dibenzo-16-crown-5-oxyacetamide with formaldehyde (Figure 2.31) was selective for Na(I) over Cs(I), K(I), and Rb(I) in 80% aqueous methanol by Yamashita et al. Thiacycrown ether polymers were prepared from the copolymerization of 6-(4'-vinylbenzoxo) - 1,4,8,11- tetrathiacyclotetradecane with styrene or N-vinylpyrrolidone (Figure 2.32) (Yamashita et al., 1996). The thiacycrown ether/ styrene copolymer was selective for Ag(I) and Hg(II) over Cd(II), Cu(II), and Ni(II) in a 50/50 dichloromethane /water solution. The thiacycrown ether/N-vinylpyrrolidone copolymer was selective for Ag(I) over Cu(II) in water.

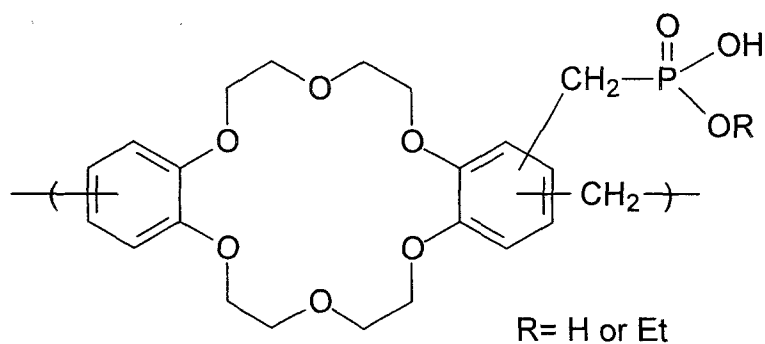


Figure 2.30. Polymeric dibenzo-18-crown-6 modified with phosphonate monoester or phosphonic acid ligands.

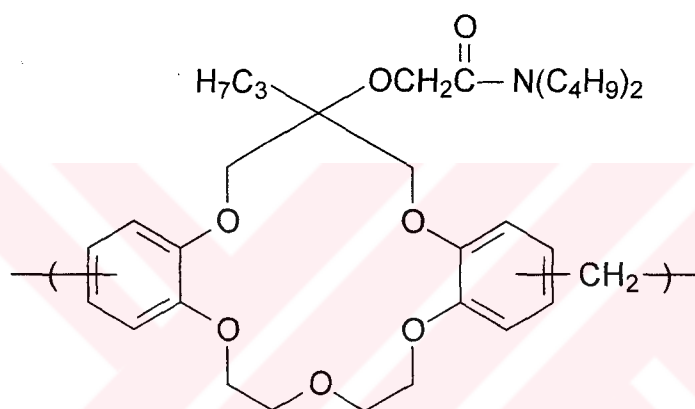


Figure 2.31. N,N-dibutyl sym-(propyl)dibenzo-16-crown-5-oxyacetamid polymer.

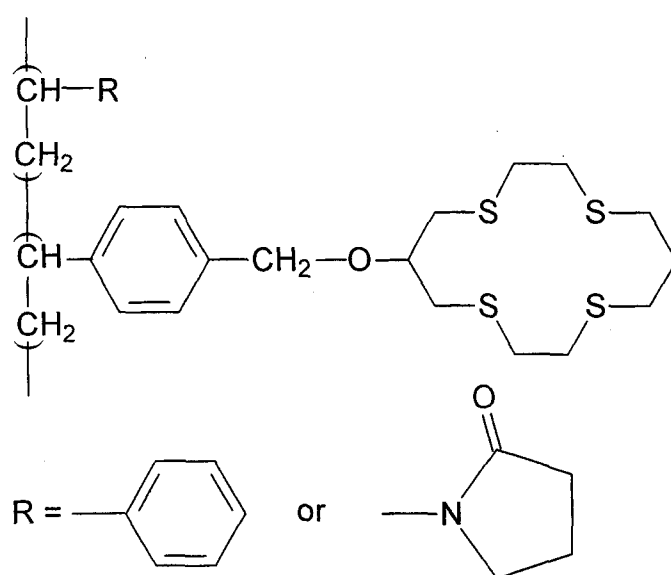


Figure 2.32. Thiacycrown ether copolymers.

2.9.7. Phenol-based ligands

Catechol, phenol and resorcinol were polymerized with formaldehyde in a condensation polymerization (Figure 2.33) (Dumont et al., 1996). The catechol resin was selective for Li(I) over Cs(I), K(I), Na(I) and Rb(I) in an alkaline solution. The phenol and resorsinol resins were selective for Cs(I) in the same solution. A quinol-crotonaldehyde resin (Figure 2.34) was selective for metal ions in the order $\text{Co(II)} > \text{Cd(II)} > \text{Cu(II)} > \text{Fe(II)} > \text{Mg(II)}$ in a solution containing 1 M NaNO_3 at pH 10 (Sahoo et al., 1994). Condensation polymerization was also utilized to prepare a polymer from 2-hydroxy-4-ethoxypropiophenone and ethylene glycol (Figure 2.35) that would chelate metal ions in the order $\text{U(VI)} > \text{Fe(III)} > \text{Cu(II)} > \text{Ni(II)}$ at pH 2.5 by Patel et al. The polymerization of 2,4-dihydroxypropiophenone with 1,4-butanediol (Figure 2.36) also showed an affinity for metal ions in order $\text{U(VI)} > \text{Fe(III)} > \text{Cu(II)} > \text{Ni(II)}$ at pH 2.5 (Patel et al., 1995).

Another resin prepared from 2-hydroxyacetophenone oxime, 4-hydroxybenzoic acid and formaldehyde (Figure 2.37) demonstrated an affinity for metal ions in the order $\text{Mg(II)} > \text{Zn(II)} > \text{Mn(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Co(II)}$ at pH 3 (Samal et al., 1993). A selectivity order of $\text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Mg(II)} > \text{Mn(II)} > \text{Co(II)}$ at pH 8 was found with a resin prepared from the 2,4-dinitrophenylhydrazone derivative of 2-hydroxyacetophenone, 2-hydroxy-benzoic acid and formaldehyde (Rath et al., 1994). Resins prepared with the 2,4-dinitrophenylhydrazone derivative of quinacetophenone (Figure 2.38) demonstrated an affinity for metal ions in the order $\text{Mg(II)} > \text{Mn(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Co(II)} \approx \text{Ni(II)}$ at pH 8 (Parija et al., 1993). Chelating resins containing phenolic Schiff bases (Figure 2.38) complexed Cu(II) and Ni(II) over at pH range of 3-8 (Samal et al., 1996).

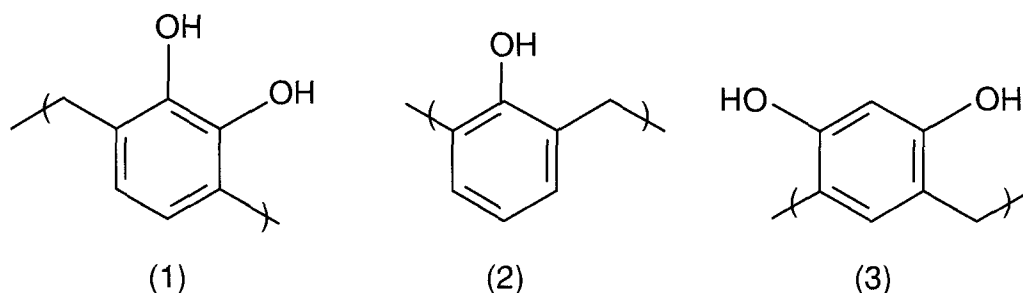


Figure 2.33. Condensation polymers of catechol (1), phenol (2), and resorcinol (3) with formaldehyde.

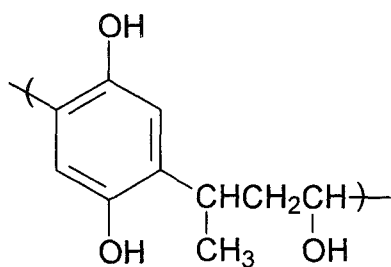


Figure 2.34. Quinol-crotonaldehyde condensation resin.

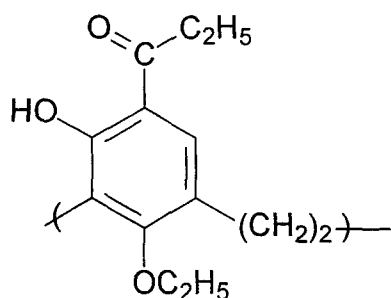


Figure 2.35. Condensation polymer of 2-hydroxy-4-ethoxypropiophenone with ethylene glycol.

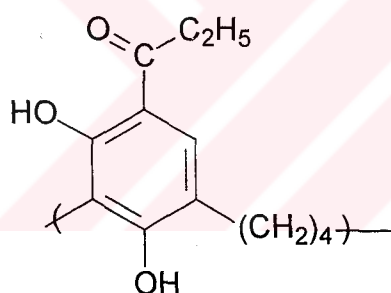


Figure 2.36. Condensation polymer of 2,4-dihydroxypropiophenone with 1,4-butanediol.

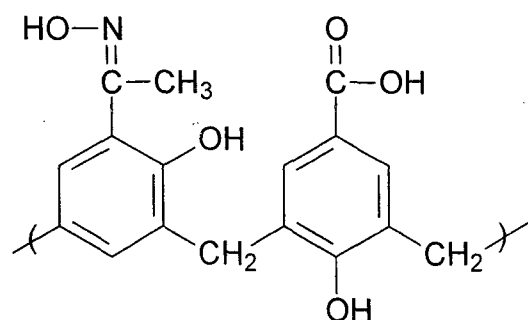


Figure 2.37. Condensation polymer of 2-hydroxyacetophenone oxime and 4-hydroxybenzoic acid with formaldehyde.

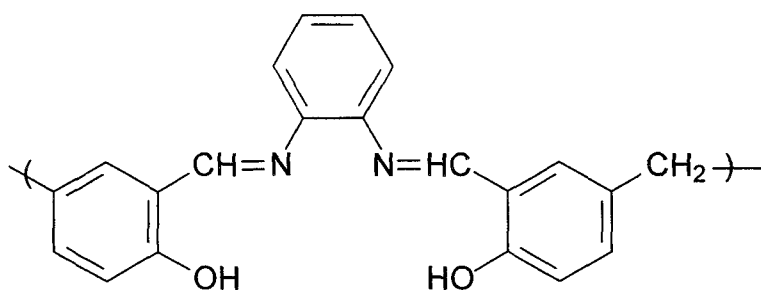


Figure 2.38. Phenolic Schiff base.

2.9.8. Phosphorus-based ligands

Phosphorus-based ligands are receiving an increased emphasis in both synthesis and separation studies. Selectivity for noble metal ions has been achieved with quaternary phosphonium chloride supported on poly(vinylbenzylchloride) (Figure 2.39) (Fujiwara et al., 1993). Mo(VI) was complexed from solution at a pH range of 1-3 with a phosphonic acid resin (Figure 2.40) (Jyo et al., 1996). Resins modified with α -aminopyridylphosphonic acid (Figure 2.41) complexed Ca(II) and Co(II) at pH 9.5, while α -aminopyridylphosphonic acid resins complexed only Ca(II) (Menard et al., 1994). The aluminium form of an aminobenzylphosphonic acid resin (Figure 2.42) were used to complex Eu(III) from a 1 M HNO₃ solution (Alexandratos and Hussain, 1995). A bifunctional sulfonic acid/diphosphonic acid resin (Figure 2.43) was synthesized and found to rapidly complex very high level of lanthanide and actinide ions (Alexandratos et al., 1996; Horwitz et al., 1993). This resin was prepared by the copolymerization of tetraethyl vinylidenediphosphonate. The diphosphonic acid ligand has also been covalently bound to a poly(vinylbenzylchloride) support (Alexandratos et al., 1995).

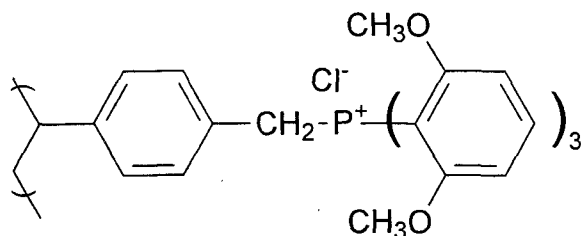


Figure 2.39. Polystyrene-supported quaternary phosphonium chloride.

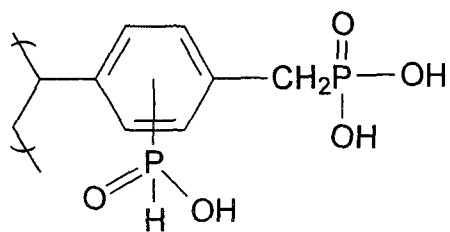
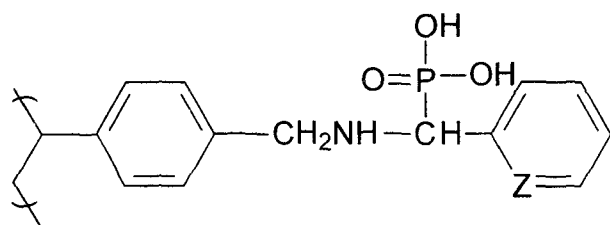


Figure 2.40. Polystyrene-supported phosphonic acid resin.



Z= N or CH

Figure 2.41. Polystyrene-supported α -aminoalkylphosphonic acid resin.

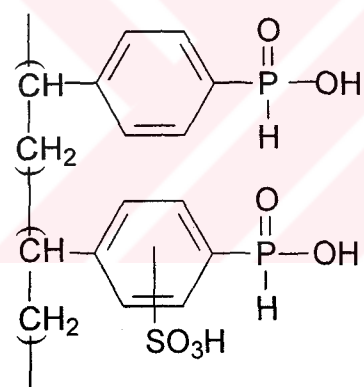


Figure 2.42. Sulfonated phosphonic acid supported on polystyrene.

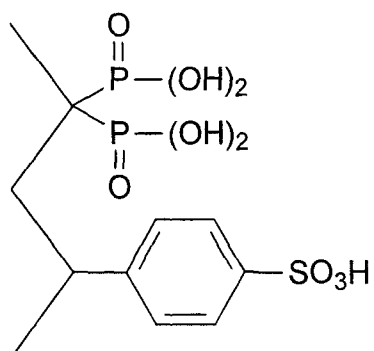


Figure 2.43. Sulfonic acid/diphosphonic acid resin.

2.10. Applications of Chelating and Coordinating Polymers

So far, this thesis has dealt with the preparation of chelating polymers and their general properties. The variety of monomers, polymerization methods and modification techniques, coupled with the researchers' ingenuity, provides an inexhaustible number of chelating materials. Let us now examine the required properties for a metal-binding polymer in aqueous solutions.

A successful polymeric ligand should stand out for its performance, not necessarily for its method of synthesis. Yet achieving that goal will be difficult without knowing the synthetic limitations. The criteria sought are: (i) distinctly characterized metal-binding groups; (ii) a well-characterized polymer with good swelling in polar solvents; (iii) good chemical stability of metal-binding groups and matrix against hydrolytic, oxidative, and radioactive conditions; (iv) matrix stability against thermal, osmotic shocks or both; (v) good reversible, complexation/elution steps and (vi) good rates of metal binding and release.

Most polymeric materials only partially fulfill these demands; for example, organic and inorganic matrices differ remarkably on points (iii) and (iv). Chemical stability depends much on polymerization method, polymer tacticity, chelating group distribution and mode of attachment of the ligand to the polymer. Higher chemical stability is shown by aromatic polymers and chemical modifications are also of importance. Multi-step modifications lead to structurally ill-defined polymers, while single-step modifications generally lead to more defined polymer structures.

Chelating polymers that are specific materials for metal ions, have been especially used in many application areas in aquatic chemistry. The main application of chelating polymers consist of extraction of metal ions from sea water, recovery of noble metal ions and separation and pre-concentration of trace metal ions.

2.10.1. Extraction of metal ions from seawater

Uranium is one of the most valuable metals in seawater. The concentration of the insoluble uranium tricarbonates in the sea is 3 $\mu\text{g/L}$ and the total calculated

reserves are 5×10^9 tonnes. Various inorganic and organic adsorbents for the recovery of uranium in seawater have so far been synthesized. Since an early effort to recover uranium from sea water by adsorption on hydrated titania proved uneconomical, (Vernon and Shah, 1983; Sugasaga et al., 1981), due to physical weakness of the adsorbent, the search for polymers of improved structure has been in progress in many countries. Vernon and Shah have developed resins and fibers by amidoximation of crosslinked acrylonitrile-ethylacrylate copolymers and demonstrated the application of polyamidoxime (PAO)/polyhydroxamic acid (PHA) in continuous extraction of uranium from sea water.

Poly(acrylamidoxime) resin have been used for the separation and simultaneous concentration of Fe^{3+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} from sea water and pond water. Sequestered metals were at least 90 % recovered with a standard deviation of $\leq 5\%$. However, this resin was shown to have no affinity for Na^+ , K^+ , Ca^{2+} , or Mg^{2+} ions tested over the pH range 2-8. Egawa and Harada used a similar resin with amidoxime functional group for recovery of uranium from sea water. The elution of uranium adsorbed on this resin was accomplished by passing 1 N H_2SO_4 solution through it and a recovery of 80 % uranium in sea water was achieved (Egawa and Harada, 1979).

Uranium specific polymers and processes of extraction from sea water have been extensively applied by JAERI (Japan Atomic Energy Research Institute). JAERI has developed more suitable sorbent materials for the recovery of uranium from seawater on the basis of chelating resins which meet the criteria of high physical and chemical stability against seawater, fast and selective uptake of uranium, and a sufficient loading capacity. Most of the work is centralized on uranium extraction from sea water by poly(amidoxime) resins. The project of rare metals collection from seawater is in progress as an application of the adsorbents in a pilot plant in Japan. JAERI has already investigated a separative elution of uranium and vanadium from an amidoxime sorbent which had been immersed in seawater, and proposed the selective elution of uranium and vanadium from an amidoxime polymer with 0.5 and 1 M hydrochloric acid.

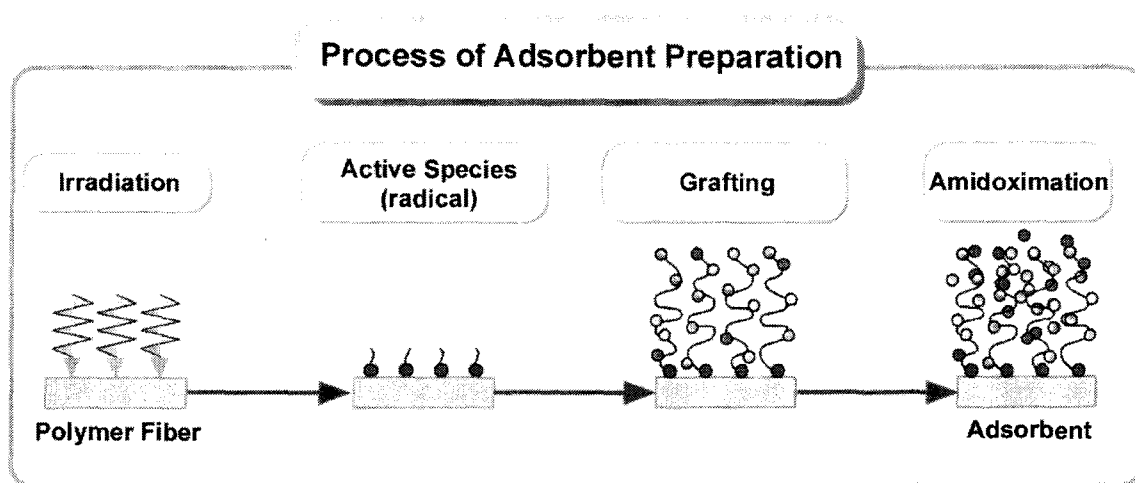


Figure 2.44. General process of preparation of amidoxime adsorbents.

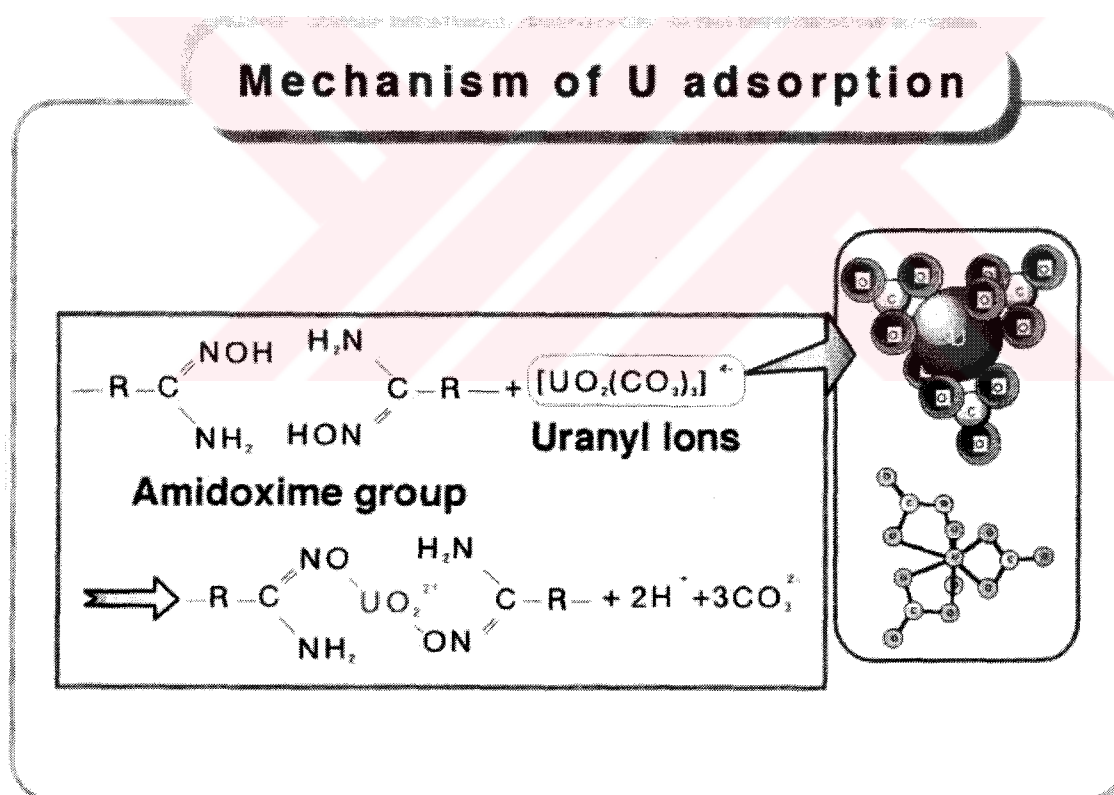


Figure 2.45. Mechanism of U adsorption from seawater.

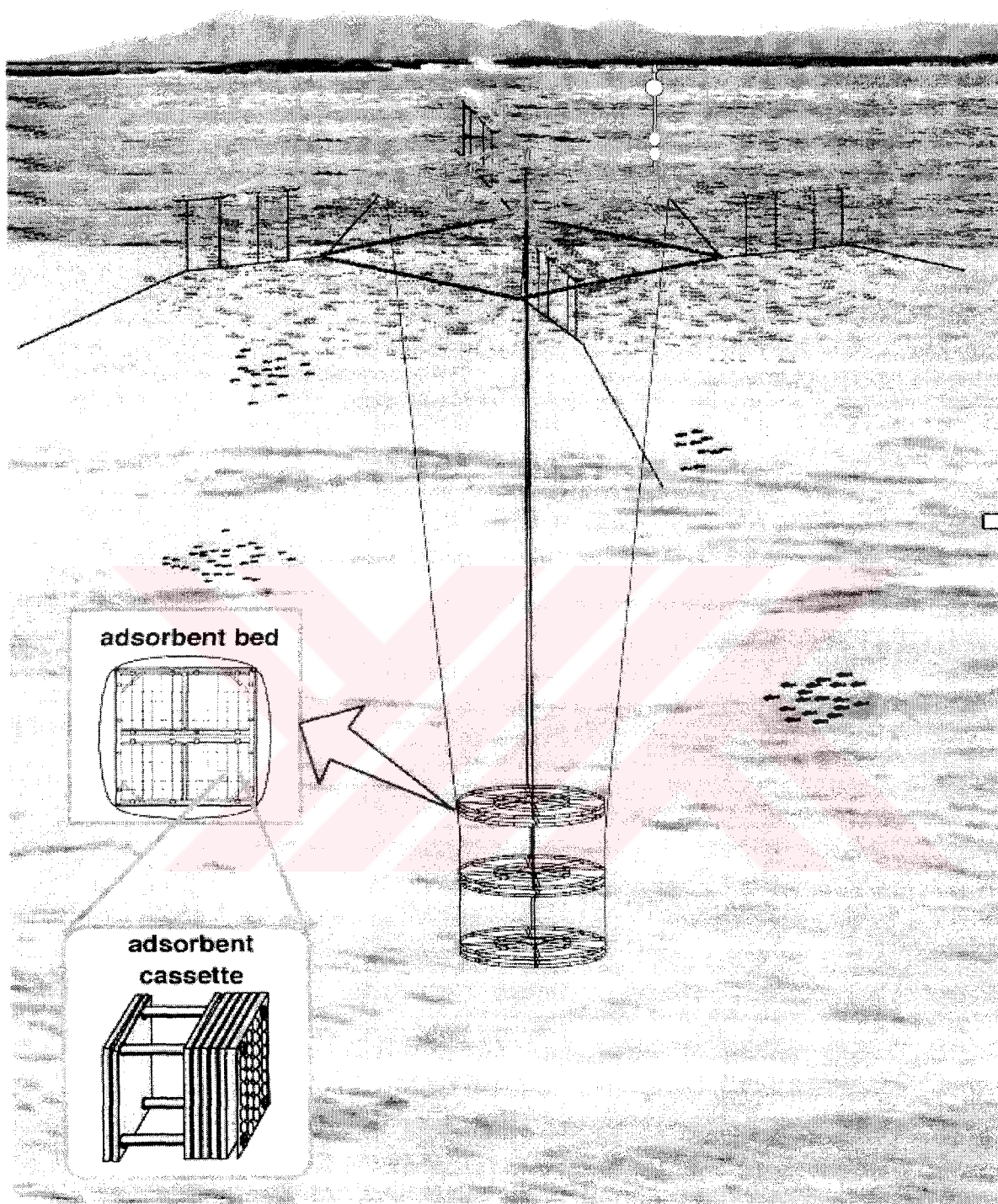
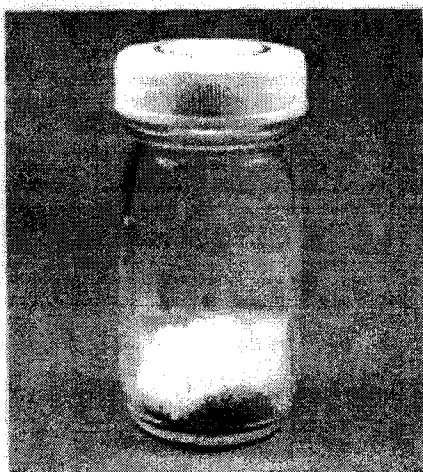
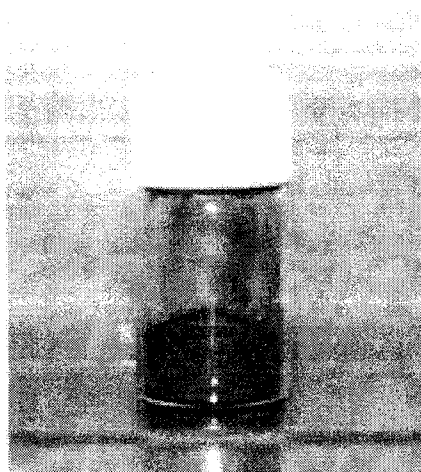


Figure 2.46. System for hanging of adsorbent in seawater, pilot plant for rare metal collection from seawater.



**Yellow cake
(ADU)**



**Vanadium
(V₂O₅)**

Figure 2.47. Uranium and Vanadium obtained from seawater in JAERI.

As can be seen in Figure 2.44, firstly, the base polymer is irradiated by high energy radiation (γ -radiation or e-beam) to produce radicals. After formation of radicals on the adsorbent, grafting can be done with any specific monomer containing CN group. The cyano group of grafted chains are converted into the amidoxime group by reaction with hydroxylamine. Finally, a new adsorbent containing specific amidoxime functional groups can be obtained. Amidoxime containing polymeric materials which are specific for uranium and vanadium is being produced with this process in material development department in JAERI. It was found that two of the amidoxime groups on the polymer formed chelate with one uranyl ion in sea water which is given in Figure 2.45. System for hanging of polymeric adsorbents in seawater and pilot plant for rare metal collection from seawater by JAERI in Japan is given in Figure 2.46. Uranium and vanadium metal ions are being collected by this pilot plant rare metal collection system and after collection process, metal ions are being eluted (recovered) fractionally by a reagent and then are obtained as pure compounds. The collected and purified uranium and vanadium compounds are shown in Figure 2.47.

In other studies, to improve the adsorption rate of uranium from seawater, hydrophilic amidoxime fibers were prepared by cograftering of methacrylic acid with

acrylonitrile onto polypropylene fibers by Kawai et al. and highest amount of uranium adsorbed (0.2 mg U ion/g adsorbent per day) onto the amidoxime fiber from seawater (Kawai et al., 2000).

Fractional elution and determination of uranium and vanadium adsorbed on amidoxime fiber from seawater were also investigated by Suzuki et al. They have obtained further information about the characteristics of the amidoxime polymer, and explored a method to elute iron and copper adsorbed on the amidoxime fiber from seawater prior to the release of uranium. Furthermore, they also found that vanadium adsorbed strongly on amidoxime fiber, and established a procedure to recover vanadium quantitatively from it (Suzuki et al., 2000).

2.10.2. Noble metal recovery

In many applications for recovery of valuable metals from hydrometallurgical liquids, there is a constant demand for more selective chelating resins. In this respect, the chelating polymers containing sulphur donor atoms are receiving a great deal of attention since they display high selectivity towards noble metal cations.

An epoxy group containing monomer, glycidyl methacrylate (GMA), was grafted onto three nonwoven fabric made of polyethylene (PE), polypropylene (PP) and a hybrids of PP and PE (PP/PE) by Kim et al. The resultant epoxy groups converted to sulfonic acid (SO_3H) groups. The SO_3H groups were introduced onto the PP/PE nonwoven fabric at a density of 2.0 mmol/g while maintaining the necessary physical strength of the fabric. The SO_3H groups captured the silver ion with a molar ratio of unity (Kim and Saito, 1999).

Recently, new chelating polymers bearing a functional group based on triisobutylphosphine sulphide (TIBPS) have been synthesized. It has been shown that these polymers are highly selective towards gold and palladium chlorocomplexes in hydrochloric acid media and do not adsorb other noble metals (Pt, Rh and Ir) nor alloy associated base metals (Fe, Cu, Ni, and Zn) (Sanchez et al., 2000).

In one study, the high nitrogen content of chitosan is the main reason for its ability to sorb metal ions through several mechanisms including ion-exchange or chelation, depending on the metal and the pH of the solution. Glutaraldehyde was used to crosslink chitosan through imine linkage between amine groups of chitosan and aldehyde groups of the crosslinking agent by Ruiz et al. This modified biosorbent was studied for palladium recovery in acidic medium (around pH = 2). Palladium sorption capacity was found as 180 mg/g at pH 2 (Ruiz et al., 2000).

In another study regarding noble metals, the adsorption of Pd(II) and Au(III) on the Duolite GT-73 had been investigated by Iglesias et al. The results obtained in chloride media showed a higher adsorption for Au(III) (0.58 ± 0.03 mmol/g resin) than for Pd(II) (0.262 ± 0.015 mmol/g resin); however, the adsorption for Pd(II) is faster. (Iglesias et al., 1999)

2.10.3. Separation and pre-concentration of trace metal ions

Accurate analysis of metal ions especially at trace level is one of the most difficult and complicated analytical tasks since it requires the rigorous requirements of versatility, specificity, accuracy, and sensitivity in the analysis. In the analysis of trace metal ions present in various samples like natural and waste water, biological, and alloy samples, the direct determination with various instrumental methods is not possible owing to matrix effect and low concentration of metal ions in the sample. Thus the need of separation and pre-concentration of metal ions arises to enhance the concentration of the solution to be determined. In addition to permitting the analysis of lower concentration samples than would otherwise be possible, the application of pre-concentration results in the reduction and simplification of the sample matrix and the immobilization of the analyte in a more stable chemical form. To obtain the reliable data, the best course is to separate the analytes of interest from the matrix constituent and determine them in the isolated state. This results in greater sensitivity but calls for elegant separation and concentration technique. Various methods used for this purpose are liquid-liquid extraction, precipitation technique, freezing-based concentration methods, carbon adsorption, distillation, sublimation, evaporation, and the use of ion exchange

polymers. Among all of these, ion-exchange resins are the most suited for trace analysis. These are of several types, such as cation exchangers, anion exchangers, and chelating resins. In recent years, the use of chelating resins has increased extensively (Kantipuly and Katragadda, 1990). In general, chelating resins are a group of materials having complexing or chelating groups on their surface, e.g., Chelex 100, which is based on the chemical modification of a resin surface with iminodiacetic acid groups (Schmuckler, 1965). Extractions of metal ions using chelating resins have several advantages over conventional methods:

- (a) Selective determination of metal ions will be possible by using a chelating resin having a ligand possessing high selectivity to the targeted metal ion.
- (b) It is free from difficult phase separation, which is caused by the mutual solubility between water and organic solvent layers.
- (c) The chelating resin method is an economical method since it uses only a small amount of ligand and extraction solvent and this also increases the sensitivity of the system.
- (d) Trace metal ions at as low as ppb can be determined because the targeted ion is enriched on the solid phase.
- (e) The concentration of metal ion can be visibly estimated from the color intensity of the solid phase if the metal complex formed possesses adsorption in the visible wavelength region.
- (f) Use of carcinogenic organic solvents is avoided and thus the technique is ecofriendly to nature.

Chelating agents anchored to polymeric support have various types of functional groups. These chelating agents form complexes with metal ions only in certain pH ranges. So when a sample containing metal ion is passed over a chelating resin at certain pH values, metal ion forms chelate with the chelating agent on the polymeric support and thus are retained by the resin; thus impurities are not retained and they pass through. During elution, the eluent chosen is such that it helps in knocking out the metal ion from the chelate site on the resin. This is generally achieved by changing the pH, i.e., by making use of acids. This also helps in regeneration of the resin and thus chelating resin can be reused. Such types of separation avoid use of carcinogenic organic solvents and are ecofriendly to nature.

Various polymeric chelating resins used for the pre-concentration, separation, and determination of trace metal ions.

Amidoxime is extensively used in analytical chemistry as a photometric agent or extracting reagent for metal ions. Amidoxime is a selective reagent for the transition metal ions (Cu, Ni, Co, Zn, V) and lanthanides such as uranium has attracted great interest as a chelator for these metal ions. Separation of transition metal ions UO_2^{2+} , V(V), Cu(II), Ni(II), Co(II) and Zn(II) on various amidoxime chelating polymers was reported by many researchers.

In one study, fibrous adsorbents containing amidoxime groups were synthesized by radiation-induced grafting of acrylonitrile onto fibers and adsorption of heavy metal ions such as copper ions were attempted and the results, amidoximes are supposed to be bidentate, two amidoximes may be used for chelate formation with a copper ion which makes a square planar chelate (Okamoto et al., 1985).

Methacrylic acid/acrylonitrile grafted polypropylene was prepared with radiation-induced grafting technique by Shiraishi and Tamada et al. and then nitrile groups were converted the amidoxime groups. The resultant grafted polymer adsorbent was used for removal of Cd from scallop waste, it was showed that, the amidoxime adsorbent recovered 96.1 % of Cd in the waste solutions at pH 6 (Shirashi et al., 2002).

The polyethylene adsorbents were prepared by radiation-induced grafting of acrylonitrile and acrylic acid co-monomer onto PE film, and subsequent amidoximation of poly-AN. The amidoxime, carboxyl and amidoxime/carboxyl groups onto PE acted as a chelating site for selected UO_2^{2+} , the uranyl ion uptake increased almost in proportion to the amount of functional groups in PE adsorbents (Choi and Nho, 2000).

Three kinds of functional groups, iminodiacetate (IDA), amidoxime (AO), and phosphoric acid (PA) were introduced into a microfiltration hollow fiber membrane, by radiation-induced grafting by Tsuneda et al. The IDA chelating hollow fiber was superior to the AO chelating hollow fiber with regard to the collection of cobalt ion

(Tsuneda et al., 1991).

The other study about amidoxime, N-vinyl-2-pyrrolidone (VP)/Acrylonitrile (AN) copolymeric hydrogels were synthesized by using γ -radiation and amidoximated for the purpose of uranyl ion adsorption. The adsorption capacity was found as 0.54 g UO_2^{2+} /g dry amidoximated copolymeric hydrogels. From the stoichiometric calculations, it was found that the bonding between UO_2^{2+} ions and amidoxime groups is 1 to 4 (Pekel et al., 2000).

Analytical and physicochemical properties of a crosslinked poly (vinyl pyridine) based resin containing dithizone were examined by Shah and Devi. The resin was further used for the preconcentration of copper, nickel and zinc at batch and column level. The loading capacities of the resin for copper, nickel and zinc were observed to be 0.51, 0.59 and 0.65 mmol/g of dry resin respectively (Shah and Devi, 1998).

Acrylamide-maleic acid (AAm/MA) hydrogels were prepared by gamma irradiation of their aqueous solution by Akkaş and Güven. UO_2^{2+} ion uptake on Poly (AAm/MA) hydrogels was investigated using two types of gel system prepared by a simple irradiation method and a prestructured reaction. It was observed that gels prestructured with UO_2^{2+} ions adsorbed approximately 15-20 % more UO_2^{2+} ions than gels prepared in pure water (the usual method). It was also found that the uranyl ion adsorption capacity of hydrogels increased with an increasing amount of maleic acid in the gel system (Akkaş and Güven, 2000).

A ring opening reaction with either cyclohexene oxide or cyclohexene sulphide was used in the modification of two types of polymeric resins. Both resins contained amino groups, one being obtained by reacting the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer with ethylenediamine, the second by reacting the VBC/DVB copolymer with diethyl malonate followed by aminolysis with ethylenediamine. Modification resulted in a set of novel chelating resins, which was characterized and used in metal ion uptake experiments. These resins are highly selective towards copper(II) in acetate buffered solutions. The selectivity of the modified resins decreases in the order, $\text{Cu(II)} > \text{Cd(II)} > \text{Zn(II)} > \text{Ni(II)}$,

which is different from the Irving-Williams series. The highest affinity towards Cu(II) ions has been found for the resin modified with cyclohexene oxide, for which $\log K_d$ was 4.91 at pH 5.6 (Trochimezuk et al., 2001).

Water-soluble copolymers containing sulfonic acid and tertiary amine groups were synthesized by radical copolymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid and N-acryloyl-N-methyl piperazine. The sulfonic acid units dominated in the copolymer composition. The metal ion binding affinity strongly depended on the copolymer composition and the pH. With increasing content of sulfonic acid moieties the affinity for metal ion binding increased. The copolymer with the highest content of sulfonic acid showed the highest affinity to Ag(I), comparable to both homopolymers. The copolymer with the highest content of N-acryloyl-N-methyl piperazine units showed a high selectivity for Ni(II) and did not retain Co(II), Zn(II), and Cd(II), when compared with the other copolymers and the homopolymers (Rivas et al., 2001).

A new polystyrene-divinylbenzene resin containing 1-2-thiazolylazo-2-naphthol functional group was synthesized and its sorption behaviour for 19 metal ions including Zr(IV), Hf(IV) and U(VI) was investigated by batch and column experiments. The chelating resin showed a high sorption affinity for Zr(IV) and Hf(IV) at pH 2. The elution order of metal ions at pH 4 was evaluated as: Zr(IV) > Hf(IV) > Th(IV) > V(V) > Nb(V) > Cu(II) > U(VI) > Ta(V) > Mo(VI) > Cr(III) > Sn(IV) > W(VI) (Lee, W., et al., 2001).

Phosphonate-derivatized polystyrene-divinylbenzene-based (PS-DVB) resins were prepared from chloromethylpolystyrene-divinylbenzene (Cl-CH₂-PS-DVB) by the *Arbuzov*-reaction using lithium or sodium alkyl chlorophosphites. Base-promoted hydrolysis of the diethyl phosphite-derivatized resin in refluxing 1,4-dioxane resulted in phosphonic acid-derivatized PS-DVB resins with an average capacity of 0.8–2.2 mmol phosphonate, depending on the alkyl chlorophosphate used. Both the free phosphonic acid as well as the diethyl, dibutyl- and bis(2-ethylhexyl)-phosphonate-derivatized sorbents were investigated in terms of their extraction characteristics for U(VI), Th(VI) as well as for other transition metal ions such as Fe(III), Zn(II), Co(II), Cd(II), Ni(II) and Cu(II) from

acidic aqueous solutions. In contrast to phosphonate resins, the phosphonic acid-derivatized resins exhibited a high sorption capacity and selectivity for U(VI) (Merdivan et al., 1999).



3. EXPERIMENTAL PART

3.1. Materials and Methods

The 3,3'-iminodipropionitrile and acryloyl chloride used in the first part of this study were supplied by Aldrich Company and distilled under vacuum before use. Azobisisobutyronitrile (AIBN) was obtained from Merck (Germany) and recrystallized from methanol before use. Triethylamine and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) were obtained from Merck and used as received. Nonwoven fabric polypropylene coated by polyethylene fabric was supplied by Kurashiki Sen-I Kako Co. Okayama, Japan. Methacrylic acid glycidyl ester was purchased from Tokyo Kasei Co., Japan. 3,3'-iminidipropionitrile used in the second part of this study was purchased from Kanto Chemical, Tokyo, Japan and used without purification. Other reagents were of analytical or higher grade. A 6 (w/v) % solution of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was prepared using 50/50 (v/v) % water/ methanol as the solvent, and its pH was adjusted to 7 with solid KOH.

1000 ppm standard solutions for chemical analyses from Cica-reagent Kanto Chemical-Co Inc. company were used for the adsorption studies for low concentration of V(V), Pb(II), Cu(II) and Co(II) metal ions. In uranyl ion uptake studies standard solution containing 10 ppm of above mentioned metal ions were used by diluting to required concentrations.

Metal salts used in the adsorption experiments $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were obtained from Merck (Germany) and $\text{Pb}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were supplied by BDH (England).

3.2. Preparation of Amidoximated Poly(N,N'-dipropionitrile acrylamide)

3.2.1. Synthesis of N,N'-dipropionitrile acrylamide and Its polymer

3,3'-iminodipropionitrile (3mL), triethylamine (4.2mL) and acetone (30mL) were placed in a three-necked flask equipped with magnetic stirrer, reflux condenser

and dropping funnel, and the contents were cooled to approximately 0 °C in an ice bath as shown in Figure 3.1.

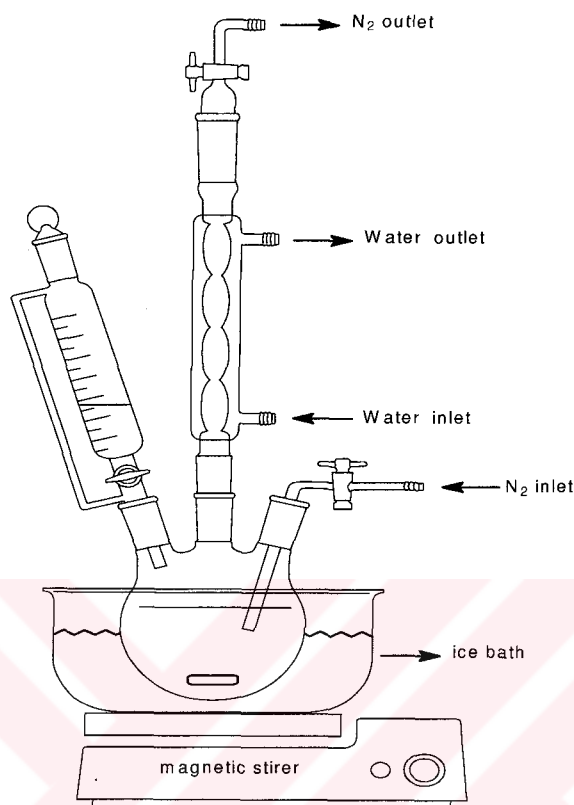


Figure 3.1. Schematic illustration of synthesis of monomer.

Acryloyl chloride (2.4 mL) was added dropwise from dropping funnel with constant stirring and purged with nitrogen gas for half an hour and the system was closed. This mixture was stirred for 3 hours at approximately 0 °C in an ice bath. The product formed was washed with distilled water to remove the quaternary ammonium salt of triethylamine and extracted with chloroform, dried over anhydrous sodium sulphate and the solvent was evaporated in vacuum. The resultant monomer was dissolved in ethanol and polymer was synthesized by solution polymerization using azobisisobutyronitrile as polymerization initiator in ethanol at 70 °C for 12 h with constant stirring. The polymer was precipitated with n-hexane and then washed with distilled water. Poly (N,N'-dipropionitrile acrylamide) (poly(DPAAm)) thus obtained was dried at 30 °C in a vacuum oven, for further test and analyses.

3.2.2. Amidoximation of pendant nitrile groups

The polymer obtained, poly(N,N'-dipropionitrile acrylamide) was reacted with the methanol solution of hydroxylamine (1:1 in $\text{NH}_2\text{OH}\cdot\text{HCl}\cdot\text{NaOH}$) at 80 °C. During the amidoximation reaction, samples were taken from the reaction vessel at certain time intervals and the conversion to amidoxime structure was followed by determining the changes in CN triple bonds of polymer from respective FT-IR spectra. After amidoximation reaction was completed, the amidoximated polymer taken from reaction vessel was washed with distilled water and then dried at 30 °C in a vacuum oven.

3.3. Preparation of Nonwoven Fabric Containing Graft Chains with Two Amidoxime Groups per Repeating Unit

The preparation of nonwoven fabric grafted with side chains containing two amidoxime groups per monomeric unit consisted of three steps; (1) grafting of an epoxy-group containing monomer, glycidyl methacrylate (GMA) by preirradiation grafting technique, (2) modification of epoxy group with 3,3'-iminodipropionitrile, and (3) amidoximation reaction of CN groups on the grafted chains.

Firstly, GMA was grafted onto PE coated PP non-woven fabrics by pre-irradiation technique: irradiation by electron beam was performed in nitrogen atmosphere at ambient temperature using a cascade electron accelerator (Dynamitron, IEA-3000-25-2, Radiation Dynamics) which was operated at a voltage of 2 MeV and current of 1 mA at Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute (JAERI). The concentration of GMA solution was set at 10 (w/w) % in methanol as the solvent. The degree of grafting, defined below, was calculated from the weight gain.

$$\text{Degree of grafting (\%)} = 100[(W_1 - W_0) / W_0] \quad (\text{Eq. 3.1})$$

where W_0 and W_1 are the weight of the trunk and GMA grafted nonwoven fabrics in dry state, respectively.

Secondly, the GMA grafted nonwoven fabric was immersed in 0.425 M 3,3'-iminodipropionitrile in ethanol solution. The reaction was performed at 80 °C for different time periods to construct the conversion curve. After binding of iminodipropionitrile groups onto the epoxy group of grafted polymer branches, the remaining unreacted epoxide groups were hydrolyzed with acid solution for 2 hours at 80 °C. Subsequently nonwoven fabric was washed with methanol and firstly dried at room temperature and then in a vacuum oven at 40 °C. The percent replacement of the epoxide groups with the iminodipropionitrile group was calculated as follows:

$$\text{Conversion (\%)} = \text{mmol iminodipropionitrile} / \text{mmol GMA} \quad (\text{Eq. 3.2})$$

Finally, 6 (w/v) % solution of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) was prepared using 50/50 (v/v) % water/ methanol as the solvent, and its pH was adjusted to 7 with KOH. The 3,3'-iminodipropionitrile (IDPN) grafted nonwoven fabrics were immersed in the hydroxylamine solution at 80 °C to convert the cyano groups into amidoxime (AO) groups for reaction times ranging from 0.5 to 2 h. AO group density was evaluated as follows;

$$\text{AO density (mmol/g)} = 1000 (W_3 - W_2) / 33 / W_2 \quad (\text{Eq. 3.3})$$

where W_3 and W_2 are the weights of the amidoximated nonwoven fabric and IDPN non-woven fabric, respectively. The value of 33 is the molecular weight of the hydroxylamine. After the completion of amidoximation reaction, amidoximated graft polymer was treated with 2.5 % KOH solution at 80 °C for 2 hours, and followed by washing with pure water until the washing was alkali-free.

3.4. Characterization of Monomer, Polymers and Amidoximated Polymers

3.4.1. FTIR analysis

In order to characterize N,N'-dipropionitrile acrylamide, its polymer and amidoximated form; and the structure of trunk PP/PE nonwoven fabric, fabric

grafted with GMA and, modified with 3,3'-iminodipropionitrile and amidoximated detailed FTIR analyses were made. Spectra were taken on KBr discs by using Nicolet 520 FT-IR Spectrophotometer.

3.4.2. Thermogravimetric analysis (TGA)

The thermogravimetric analyses were performed by utilizing Du Pont Instruments-Thermal Analyser, Model 951. Thermogravimetric studies were carried out under dry nitrogen atmosphere and 10 °C / min heating rate. Dynamic weight loss curves and their derivatives were obtained.

3.4.3. Differential Scanning Calorimetry (DSC)

Du Pont Instruments-Thermal Analyser, equipped with DSC module 910 was used to investigate DSC behaviour of samples under the conditions mentioned above.

3.4.4. GC-MS

The Gas Chromatography (GC 5890, Hewlett-Packard, Palo Alto, CA, USA) coupled with mass detector (MS 572, Hewlett-Packard, Palo Alto, CA, USA) was used to check the purity of monomer (N,N'-dipropionitrile acrylamide). The operational conditions of GC-MS system were as follows: HP-1 column (25mx 0.2 mm and 0.02µm of film thickness) was used and the flow rate of mobile phase was 1.0 mL/min. The sample was first held for 1 min at 50 °C, then the temperature increased to 180 °C with 20 °C/min heating ramp and then temperature was kept at 180 °C for 5 min. Finally temperature was increased to 250 °C with 25 °C/min heating ramp and kept at 250 °C for 10 min.

3.4.5 Elemental Analysis

Elemental analysis was performed on Perkin Elmer Series II, 2400 CHNS/O analyser to determine the elemental composition (C, H, N) of poly(DPAAm) and amidoximated poly(DPAAm).

3.4.6. Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) pictures were taken for pristine and grafted and modified samples coated with gold layer by using Hitachi Scanning Electron Microscope for the second part of this study.

3.5. Adsorption Experiments

3.5.1. Adsorption experiments at low metal ion concentration

A particular amount (around 0.015g) of amidoximated poly(DPAAm) was treated with metal ion solutions (30 mL) in order to get information on the relative performance of the amidoximated poly(DPAAm) adsorbent. The adsorption kinetics of uranium, vanadium, copper, cobalt and nickel ions from 100 ppb standard solutions were followed at pH 5 acetate buffer solution and 25 °C. For this purpose, the amount of metal ions adsorbed was checked at 30 min, 1 h, 3 h, 6h, 12 h and 24 h time intervals. After the adsorption equilibrium time was determined, the samples were contacted with five different concentration of metal ion solutions (3.3, 10, 100, 500 and 1000 ppb) at pH 5 acetate buffer with continuous stirring at 25 °C for those predetermined time periods. Metal ion concentrations remaining in the solution after every adsorption stage were determined by using Hewlett Packard 4500 series Inductively Coupled Plasma analyser (ICP).

The metal ion adsorption selectivity of amidoximated poly(DPAAm) was performed by using a mixture of aqueous solution of 100 ppb of each five metal ions following the procedure given above.

Amidoximated nonwoven fabric adsorbent was subjected to a pre-treatment by contacting for 2 h with a 2.5 % KOH solution at 80 °C as described in the literature (Kawai et al., 2000). A known amount (around 0.025 g dry weight, 1x1 cm²) of wet nonwoven fabric sample was then contacted with metal ion solutions (40 mL). To obtain information on the relative performance of the amidoximated nonwoven adsorbent in kinetic terms, the adsorption of uranium, vanadium, lead, copper, and

cobalt ions from 100 ppb standard solutions at pH 5 and 25 °C were followed as a function of time, samples being taken for evaluation at 15, 30, 60 and 120 min intervals. Once the adsorption equilibrium time was determined, the known weights of adsorbent samples were contacted with solutions containing different concentrations (3.3, 10, 100, 500 and 1000 ppb) of metal ions at pH 5 with continuous stirring at 25 °C for those predetermined time periods.

Selective metal ion adsorption tests were performed by using a mixture of aqueous solution of 100 ppb and 500 ppb of each five metal ions by following the procedure given above.

Metal ion concentrations remaining in the solution after every adsorption stage were determined by using Hewlett Packard 4500 series Inductively Coupled Plasma analyser (ICP).

3.5.2. Adsorption experiments at high metal ion concentration

Adsorption capacity of amidoximated poly(DPAAM) and amidoximated nonwoven fabric was determined for four different metal ions ($\text{UO}_2(\text{VI})$, $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Co}(\text{II})$) from different concentration (100 ppm - 1500 ppm) of aqueous metal ion solutions by a batch process. Approximately 0.05 g dry amidoximated poly(DPAAM) was placed into 40 mL metal ion ($\text{UO}_2(\text{VI})$, $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Co}(\text{II})$) solutions at pH 5 buffer in the bottle agitated magnetically at moderate rpm for sufficient time. In order to determine the amount of metal ions adsorbed onto amidoximated poly(DPAAM), $\text{Co}(\text{II})$, $\text{UO}_2(\text{VI})$, and $\text{Cu}(\text{II})$ ions concentrations remaining in the solutions were determined by using Philips 8710 UV-Vis spectrophotometer by using sodium salicylate and ammonia as complexing agents for $\text{UO}_2(\text{VI})$ and $\text{Cu}(\text{II})$ ions, respectively. The concentration of $\text{Pb}(\text{II})$ ions was determined with an Shimadzu model AAS. Adsorption studies as mentioned above were also carried out for amidoximated nonwoven fabric (0.015 g).

The amounts of metal ion adsorbed per unit mass of the amidoximated poly(DPAAM) and nonwoven fabric were evaluated by using the following expression,

$$q_e = \frac{(C_0 - C_e).V}{W} \quad (\text{Eq. 3.4})$$

where, q_e is the amount of metal ions adsorbed onto unit dry mass of amidoximated poly(DPAAm) or nonwoven fabric (mg/g), C_0 and C_e , are the concentrations of metal ion solutions initially and after treatment for a certain period of time (mg/L), respectively, V , is the volume of aqueous phase (L) and W is the amount of dry amidoximated poly(DPAAm) or nonwoven fabric used (g).

3.6. Seawater Treatment

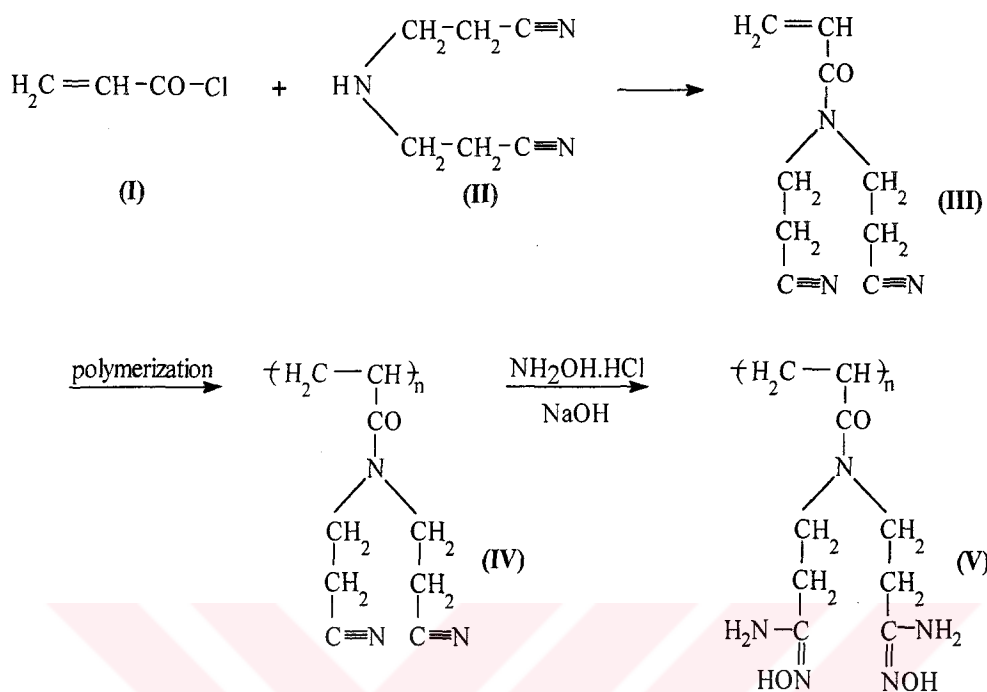
The adsorptions of uranium and vanadium ions from seawater were evaluated in flow-through mode. The amidoximated poly(DPAAm) was packed into a column with an inner diameter of 0.7 cm and height of 5 cm. Seawater was circulated upward through the amidoximated poly(DPAAm) loaded column at a flow rate of 6 mL/min at 25 °C. After 1 hour, 1 day and 1 week contact time, the adsorbent was taken out from the column and immersed in 1 M HCl to elute the adsorbed uranium and vanadium. Amounts of adsorbed uranium and vanadium ions from eluted solutions were determined by ICP.

4. RESULTS AND DISCUSSION

The design, synthesis and application of chelating polymers that can selectively complex metal ions from multi-component solutions have been an important area of research during the last decades (Collega et al., 1980; Lutfor et al., 2000; Trochimczuk et al., 2001; Maria et al., 2001; Zhanhai, et al., 2002). Chelating polymers are effective adsorbents used to enrich and separate various metal ions from seawater and aqueous media. Uranium is one of the most valuable metals in seawater. Many types of adsorbents have been developed and tested for the recovery of uranium from sea water and aqueous media (Karadağ et al., 1995; Saraydın et al., 1995; Akkaş and Güven, 2000, Rivas et al., 2001). Conventionally, most of the uranium adsorption papers in literature involve the incorporation of a nitrile group into a polymer matrix, followed by the conversion of the nitrile group into an amidoxime group by using the alkaline solution of hydroxylamine (Şahiner et al., 2000; Pekel et al., 2000; Riqueza et al., 2002). Most of the studies centralized on the uranium adsorption from seawater by poly(amidoxime) polymer which is mostly originated from an acrylonitrile polymer. Amidoxime chelate adsorbents typically contain functional amidoxime $[-C=NOH(NH_2)]$ groups that can chelate with some metal ions and create stable chelating systems, so that very pure metal ions can be obtained by elution. The currently available systems generally contain one amidoxime unit per repeating unit of the base polymer. This study has been planned for the synthesis of a new monomer carrying double pendant nitrile groups, whose polymer was later converted into amidoxime groups with the idea of obtaining a novel polymeric adsorbent.

4.1. Synthesis of Amidoximated Poly(DPAAM)

The synthesis of an acrylic polymer containing two amidoxime groups per repeating unit essentially involves three steps. As indicated in the experimental section, the synthesis of monomer, N,N'-dipropionitrile acrylamide, its conversion into polymer and further modification into amidoxime structures follow the order given in Scheme 4.1.



Scheme 4.1. Reaction scheme showing the synthesis of amidoximated poly(N,N'-dipropionitrile acrylamide).

The first step is the synthesis of monomer by an organic substitution reaction. The reaction of acryloyl chloride (I) with 3,3'-iminodipropionitrile (II) results in the formation of N,N'-dipropionitrile acrylamide (III), an acrylic monomer with two pendant cyano groups. The second step is the polymerization of N,N'-dipropionitrile acrylamide by free radical mechanism using a thermal initiator. The polymer thus obtained (IV) with a maximum conversion of 77 % is a white powder and soluble in several polar solvents such as DMF, DMSO, THF, acetone, ethanol and chloroform. The final step is the amidoximation (V) of cyano groups of poly(N,N'-dipropionitrile acrylamide). The cyano groups were converted to amidoxime groups by reacting with hydroxylamine hydrochloride in methanol solution.

4.2. FTIR Characterization

4.2.1. Characterization of N,N'-dipropionitrile acrylamide (DPAAm) and poly(DPAAm)

The FT-IR spectra of starting materials acryloyl chloride, 3,3'-iminodipropionitrile, and newly synthesized monomer DPAAm, and poly(DPAAm) are shown in Fig.4.1. In the FT-IR spectrum of 3,3'-iminodipropionitrile a sharp band at 2249 cm^{-1} characterizing $\text{C}\equiv\text{N}$ group is clearly seen. In the FT-IR spectrum of acryloyl chloride, there is a strong band due to the stretching vibration of halide attached to $\text{C}=\text{O}$ groups at 1794 cm^{-1} . The observed $\text{C}=\text{C}$ bands at 1616 cm^{-1} and 900 cm^{-1} , $\text{C}=\text{O}$ band at 1652 cm^{-1} and $\text{C}\equiv\text{N}$ band at 2249 cm^{-1} in the FT-IR spectrum of monomer are also present in the spectra of acryloyl chloride and 3,3'-iminodipropionitrile. All specific bands mentioned above for the monomer are also seen in the FT-IR spectrum of polymer with the exception of the bands at 1616 cm^{-1} and 900 cm^{-1} due to $\text{C}=\text{C}$ double bond which disappeared upon polymerization.

In GC-MS analysis of N,N'-dipropionitrile acrylamide, retention time of the monomer was observed at 9.56 minutes and the purity of the monomer was found to be more than 99 % as given in Figure 4.2. Mass spectrometric peak intensities corresponding to characteristic fragment ions for this chromatographic peak at 9.56 min are given in Table 4.1. The molecular ion peak (M^+) intensity of the monomer was observed to be smaller with respect to other fragment ion peaks in the mass spectrum. This is a typical behavior observed in GC-MS spectra resulting mainly from highly energetic ionization (70 eV) in the electron impact ionization source and the nature of the molecule. As can be seen from this table, the molecular ion and fragment ions comply with the theoretical molecular weight (177g/mole) of the monomer molecule (N,N'-dipropionitrile acrylamide).

Elemental analysis of poly(DPAAm) and amidoximated poly(DPAAm) are given in Table 4.2. Experimental results obtained are generally in good accordance with the theoretical values, though nitrogen content of amidoximated poly(DPAAm) is found to be smaller than expected.

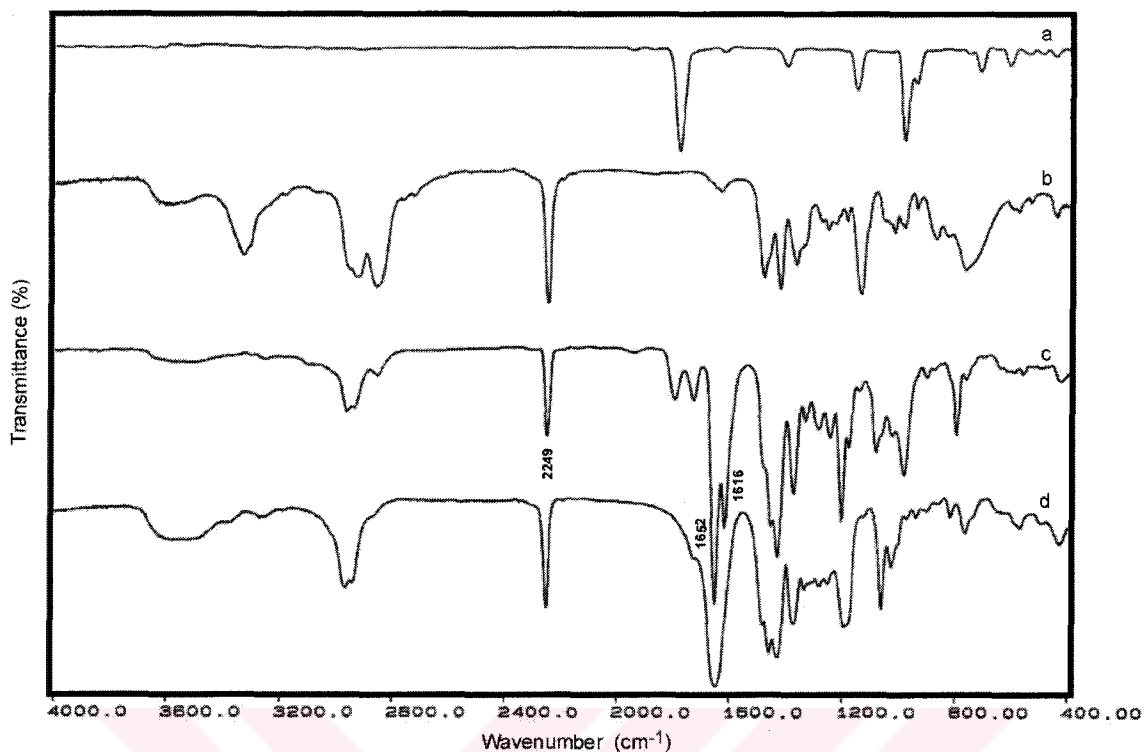


Figure 4.1. The FT-IR spectra of (a) Acryloyl chloride, (b) 3,3'-iminodipropionitrile, (c) N,N'-dipropionitrile acrylamide (d) poly(N,N'-dipropionitrile acrylamide).

Table 4.1. GC-MS data of N,N'-dipropionitrile acrylamide.

m/z	Peak intensity(%)	Observed ions	Possible fragmented groups
177	5,2	$[\text{CH}_2\text{CHCON}(\text{CH}_2\text{CH}_2\text{CN})_2]^+$ (M^+)	
150	1	$[\text{CH}_2\text{CHCON}(\text{CH}_2\text{CH}_2\text{CN})\text{CH}_2\text{CH}]^+$	HCN
137	35	$[\text{CH}_2\text{CHCONCH}_2\text{CH}_2\text{CH}_2\text{CN}]^+$	$\bullet\text{CH}_2\text{-CN}$
55	100	$[\text{CH}_2=\text{CH-CO}]^+$	$\bullet\text{N}(\text{CH}_2\text{-CH}_2\text{-CN})_2$
27	43,3	$[\text{CH}_2=\text{CH}]^+$	$\bullet\text{CON}(\text{CH}_2\text{-CH}_2\text{-CN})_2$

Table 4.2. Elemental analysis data of poly(DPAAm) and amidoximated poly(DPAAm).

	Calculated			Experimental		
	C%	H%	N%	C%	H%	N%
Poly(DPAAm)	61.00	6.21	23.73	59.34	6.46	21.94
Amidoximated poly(DPAAm)	44.44	7.00	28.80	41.06	7.53	21.06

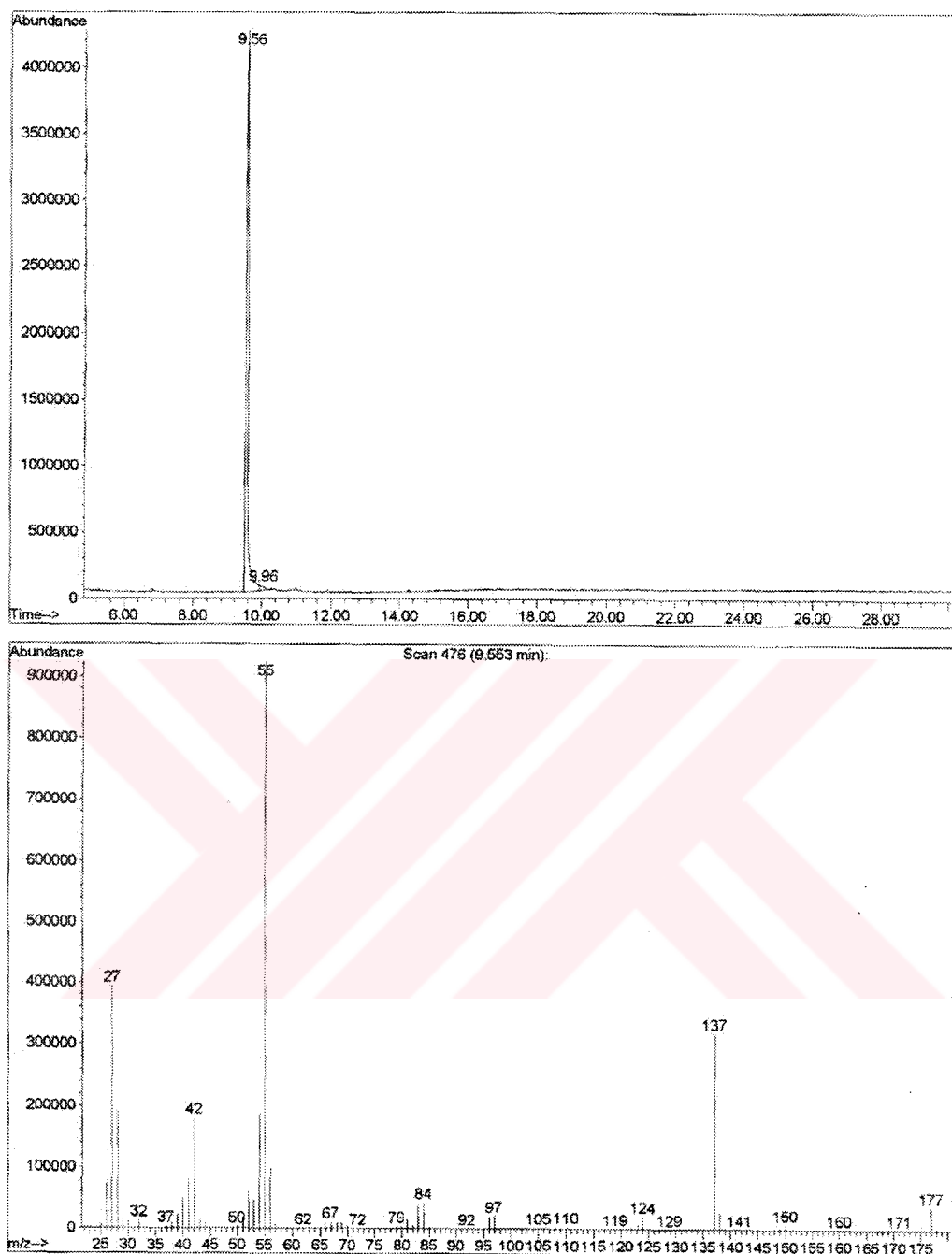


Figure 4.2. GC-MS spectra of N,N'-dipropionitrile acrylamide.

4.2.2. Characterization of amidoximated poly(DPAAm)

In order to follow the course of the reaction scheme, FT-IR analysis was used. The samples taken from the reaction medium at certain intervals during the

amidoximation reaction process were dried, and their FT-IR spectra were taken. As can be seen from Figure 4.3, the intensities of CN triple band at 2249 cm^{-1} of the polymer decrease proportionally with the reaction time. The relative decrease in the intensity of characteristic CN triple band in the polymer as a function of reaction time is shown in Figure 4.4. Practically the conversion is 97 % complete in 3 hours and 99 % of CN groups in the polymer were transformed into amidoxime groups in 10 hours. After the completion of amidoximation reaction, the finger print region of spectrum changed significantly. According to Scheme 1, $\text{C}\equiv\text{N}$ groups are expected to be replaced with $\text{H}_2\text{N}-\text{C}=\text{NOH}$ groups at the end of the reaction. As a result of amidoximation, a newly formed band belonging to N-O stretching vibration appeared at around 903 cm^{-1} . The bands at 3219 and 3346 cm^{-1} are assigned to antisymmetric and symmetric stretching modes of NH_2 groups, respectively (Figure 4.3f). These results clearly show the disappearance of original nitrile groups and formation of amidoxime groups through the treatment with hydroxylamine under specified reaction conditions.

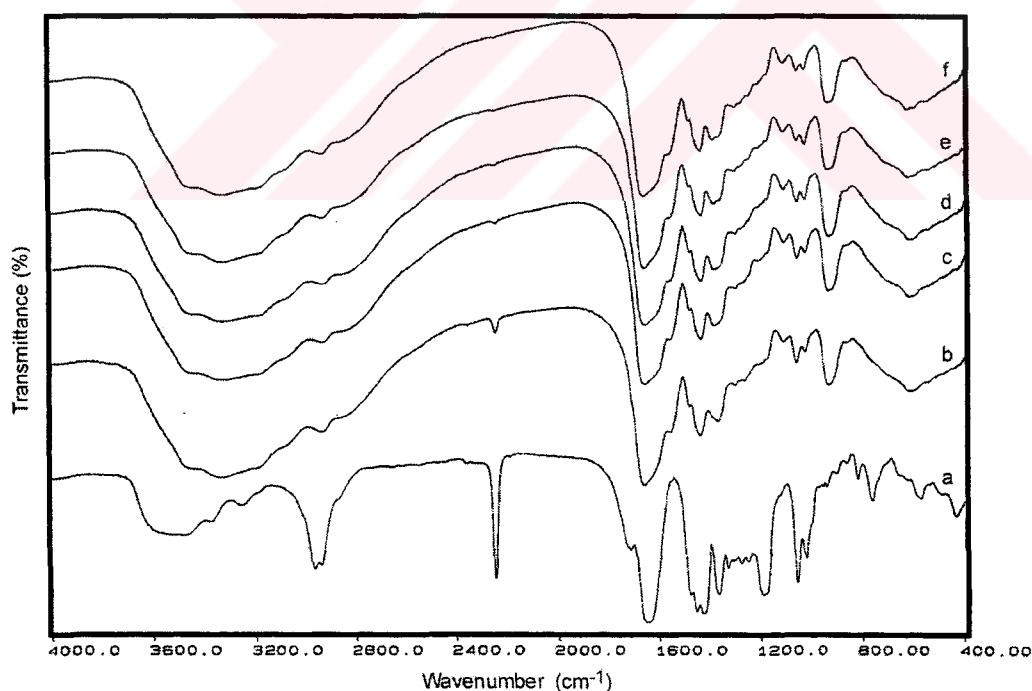


Figure 4.3. The FT-IR spectra showing the course of amidoximation with reaction time a) 0 h, b) 1 h, c) 2 h, d) 4 h, e) 8 h, f) 10 h.

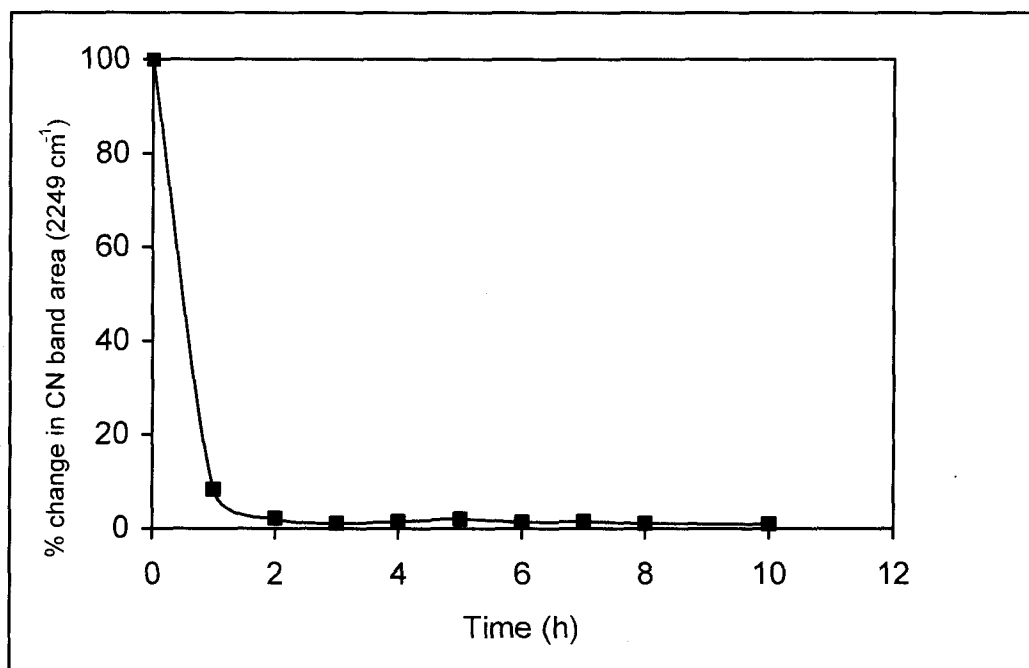


Figure 4.4. The % change in the relative intensity of $C \equiv N$ band of poly(DPAAm) with reaction time.

4.3. Thermal Characterization

4.3.1. Thermal characterization of poly(DPAAm) and amidoximated poly(DPAAm)

The analyses of poly(DPAAm) before and after amidoximation reaction were also carried out by thermal analysis methods. In order to understand the thermal behavior of poly(DPAAm), the thermogravimetric analysis (TGA) was performed in N_2 atmosphere at a heating rate of $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$. The dynamic thermogram of poly(DPAAm) and its derivative are given in Figure 4.5.

There are three peaks in the derivative curves at $327\text{ }^{\circ}\text{C}$, $343\text{ }^{\circ}\text{C}$ and $383\text{ }^{\circ}\text{C}$. As can be seen from this thermogram, polymer can keep its thermal stability until approximately $250\text{ }^{\circ}\text{C}$. The first stage of degradation starts at $305\text{ }^{\circ}\text{C}$ and ends approximately at $340\text{ }^{\circ}\text{C}$ giving a peak maximum at $327\text{ }^{\circ}\text{C}$. At the end of the first degradation stage, 45 % weight loss of poly(DPAAm) was observed. The second degradation step overlapped with the first at around $340\text{ }^{\circ}\text{C}$ and ended at $365\text{ }^{\circ}\text{C}$.

giving a peak maximum at 342 °C and almost 70 % weight loss was observed. The final degradation step started at 365 °C and ended at 450 °C giving a peak maximum at 383 °C and 1.3 % residue at 700 °C.

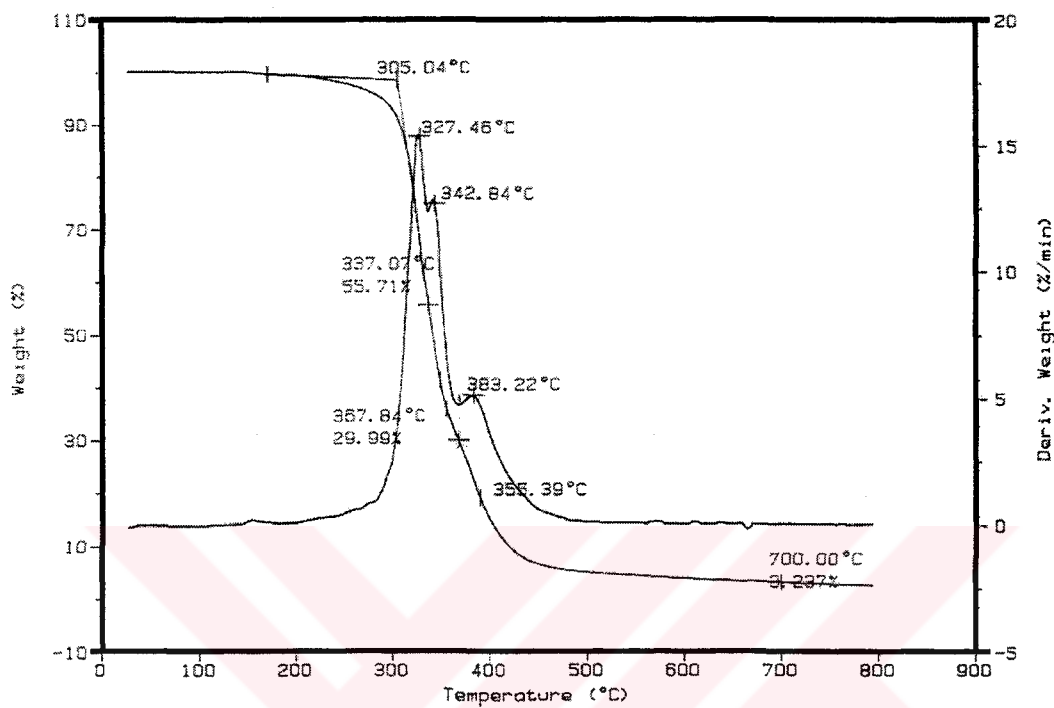


Figure 4.5. The dynamic and derivative thermograms of poly(DPAAm).

Various stages of thermal degradation were also followed by FTIR analyses. The FTIR spectra belonging to original poly(DPAAm) and 20 %, 50 % and 70 % degraded poly(DPAAm) at different degradation temperatures are given in Figure 4.6. After 20 % degradation, the intensity of $C\equiv N$ band at 2249 cm^{-1} decreased and this band almost disappeared at 50 % weight loss and a new band appeared at 1539 cm^{-1} which was assigned to $C=C$ stretching. It is assumed that, the first and the second step degradations involved the ring formation between the adjacent CN groups (Coleman et al., 1978) and the structure of polymer thus changed. Moreover the theoretical considerations show that, the poly(DPAAm) is composed of 70 % imino groups attached to the backbone consisting of 30 % acryoyl groups. It is therefore assumed that, stepwise degradation of polymer follows weight losses corresponding to degradation of these parts.

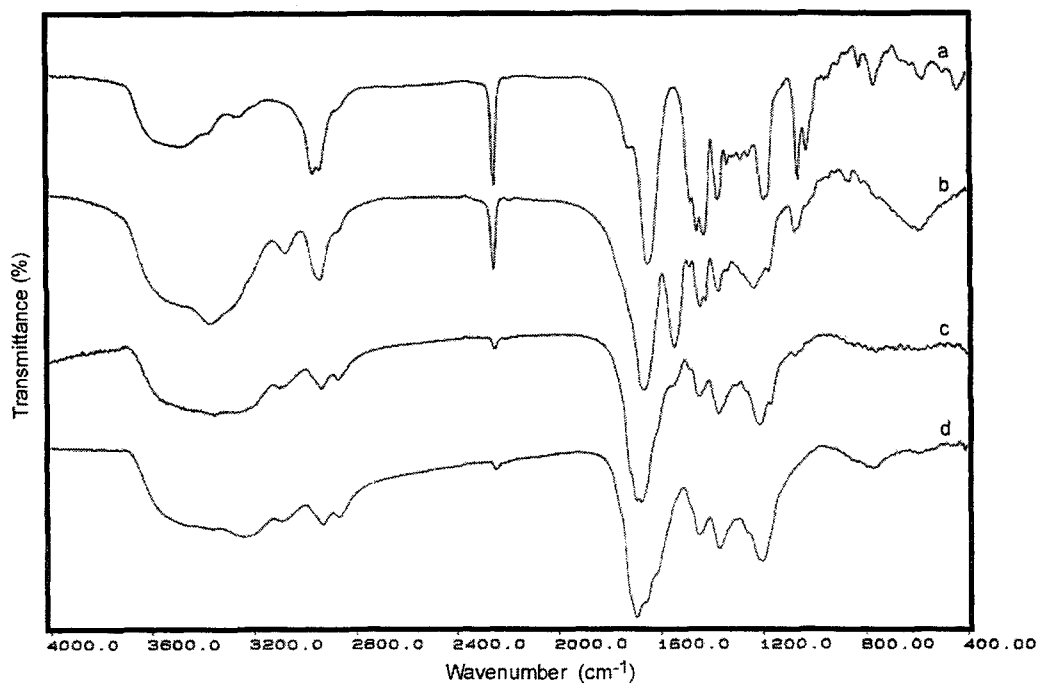


Figure 4.6. The FTIR spectra of thermally degraded poly(DPAAm); Spectra corresponding to a) 0 %, b) 20 %, c) 50%, d) 70 % weight losses.

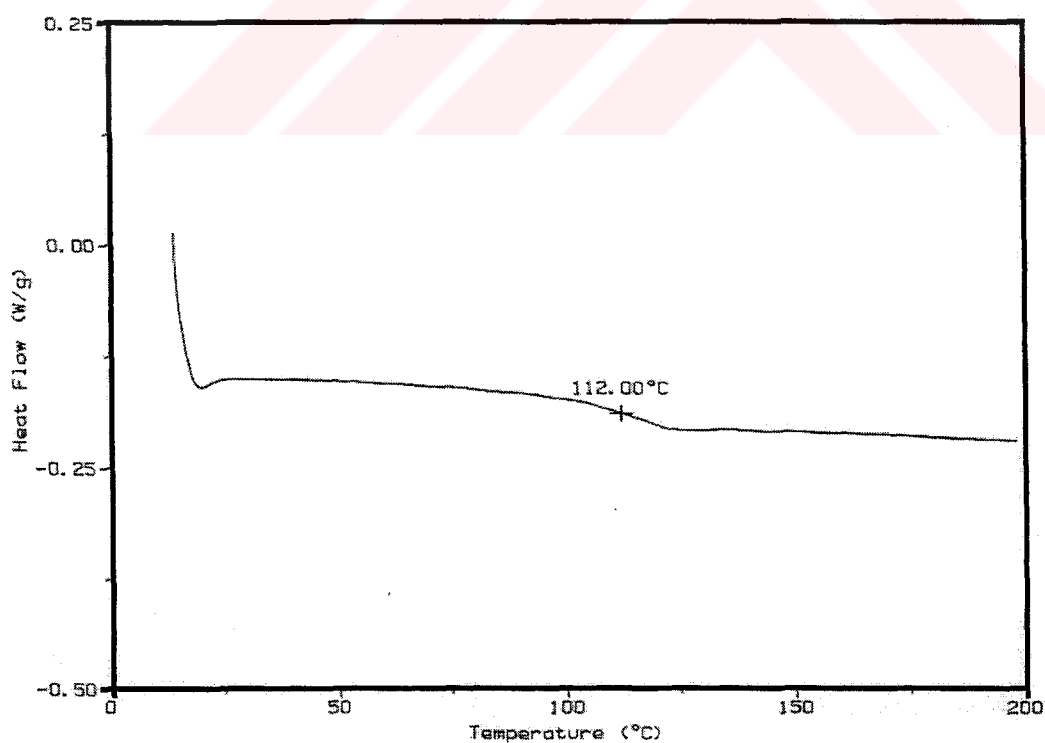


Figure 4.7. The DSC thermogram of poly(DPAAm).

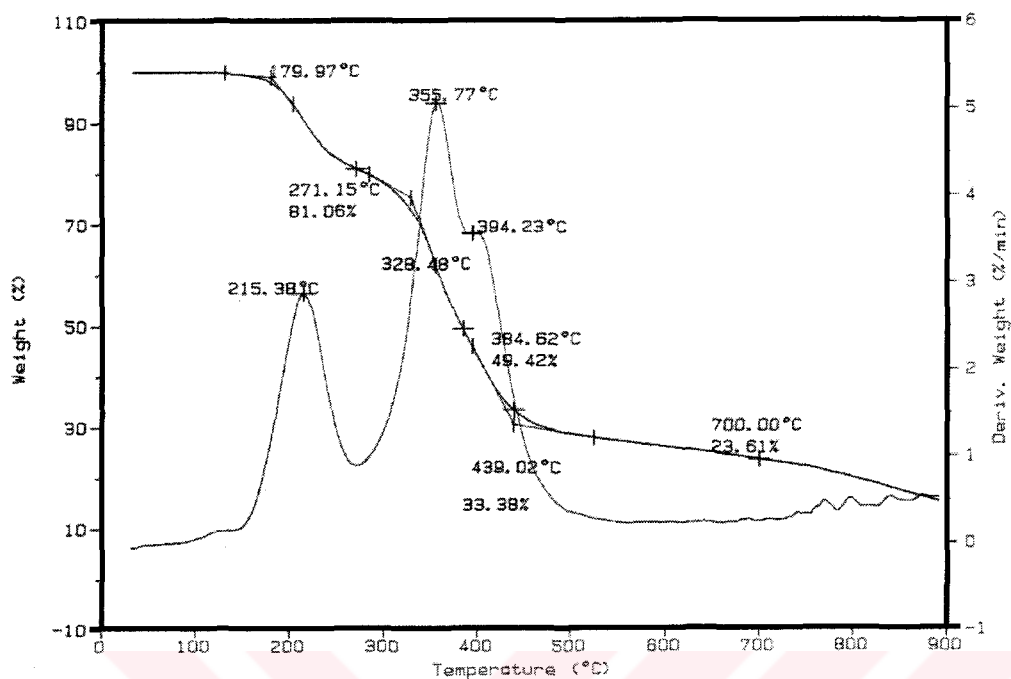


Figure 4.8. The dynamic and derivative thermograms of amidoximated poly(DPAAm).

The T_g value of the poly(N,N'- dipropionitrile acrylamide) was determined to be 112 °C by DSC and is given in Fig. 4.7. To complete the thermal characterization of final product, i. e. amidoximated poly(DPAAm), its dynamic thermogram was taken and shown in Figure 4.8. The main differences observed in this thermogram as compared to that given in Figure 4.5 is that upon amidoximation the poly(DPAAm) becomes thermally less stable and degradation starts at around 180 °C and with the exception of first derivative peak, the most of the thermogram is very similar to that of poly(DPAAm).

4.4. Adsorption Studies for Amidoximated Poly(DPAAm) at Low Metal Ion Concentrations

In order to investigate the adsorption kinetics of five different metal ions (U(VI), V(V), Cu(II), Co(II) and Ni(II)) onto amidoximated poly(DPAAm), approximately 0.015 g of adsorbent was treated with 100 ppb metal ion solutions at pH 5 buffer

solution at 25 °C. Figure 4.9 shows the adsorption curves of U(VI), V(V), Cu(II), Co(II) and Ni(II) ions onto amidoximated poly (DPAAm) from 100 µg/L (ppb) aqueous solution at constant pH 5. The adsorption values are given as the percentage of metal ions initially present.

High adsorption rates are observed within 30 min for vanadium ion and 1 hour for uranium ion and the plateau values (i.e., adsorption equilibrium) were reached approximately at 98 % (210 µg/g) removal of vanadium ion within 1 hour and 98 % (200 µg/g) removal of uranium ion within 3 hours.

The adsorption equilibria of Cu(II) and Ni(II) ions have been attained in about 30 min with 40 % (105 µg/g) for Cu(II) and in 3 hours with 15.5 % uptake (31.06 µg/g) for Ni(II) ions. The adsorption rate of Co(II) ion gradually increased and not reaching equilibrium even 24 hours. The adsorption value of 61 % (123 µg/g) was reached for cobalt ions at the end of 24 hours.

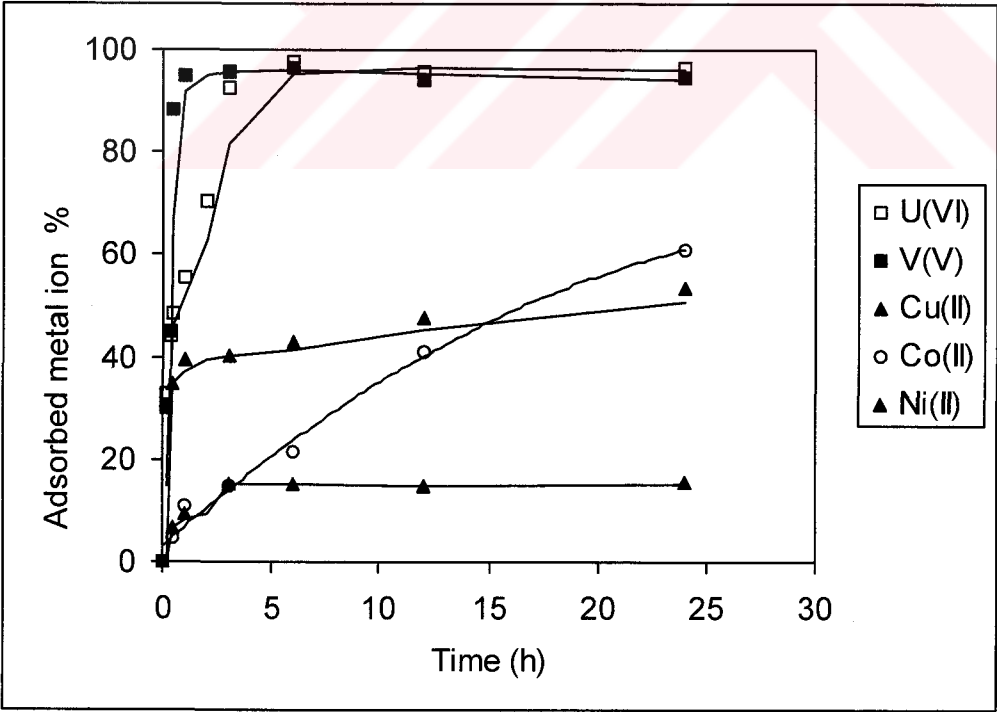


Figure 4.9. Adsorption kinetics of various metal ions from the same (100 ppb) initial concentrations.

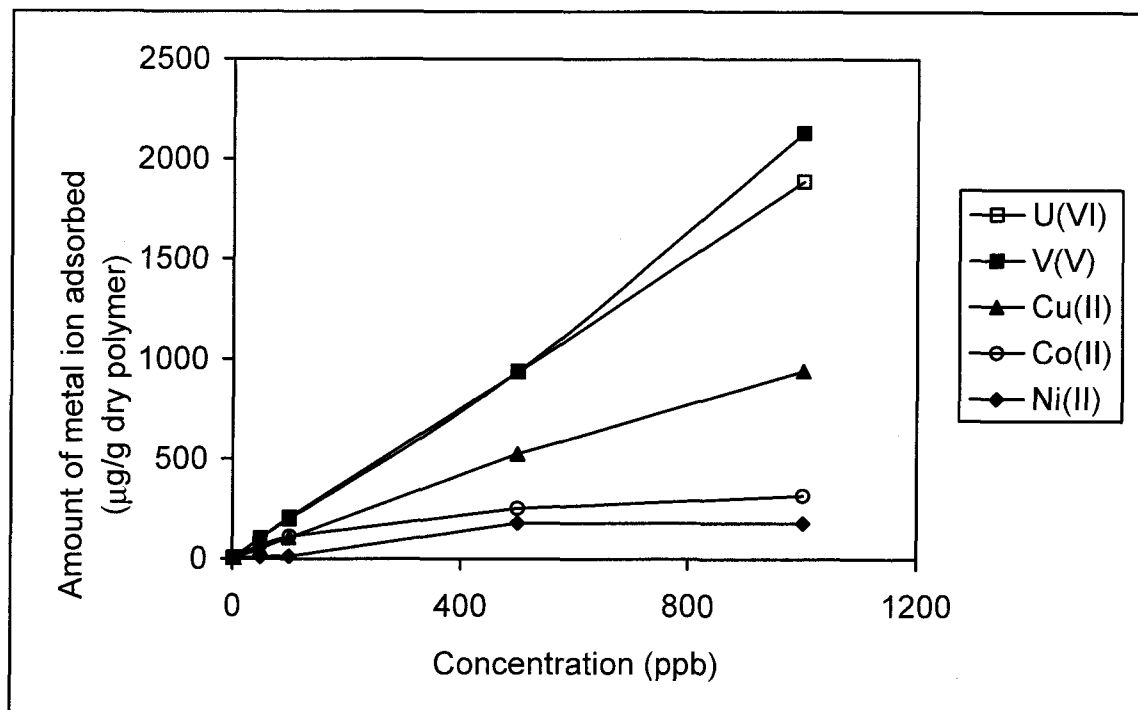


Figure 4.10. Dependence of metal ion uptake on the initial concentrations of metal ions.

The effect of initial concentration of metal ions on the adsorption behavior of amidoximated poly(DPAAm) (0.015 g) was determined in 6 hour contact times for U(VI), V(V), Cu(II), Ni(II) and 24 hour for Co(II) ion for five different metal ion concentrations (3.3, 50, 100, 500 and 1000 ppb) and given in Figure 4.10. Figure 4.10 shows that adsorption of uranium, vanadium and copper ions increased almost linearly with increasing initial metal ion concentration. Adsorption of cobalt and nickel ions reached equilibrium after 500 ppb initial concentration.

The new adsorbent exhibited higher affinity for V(V) and U(VI) ions, the highest values were found to be 1887 µg/g (93 %) and 2132 µg/g (98 %) from 1000 ppb metal ions solution, respectively. Almost complete removal (100 % adsorption) of vanadium and uranium ions have been reached easily for all concentrations studied. These values are 941 µg/g, 318 µg/g and 178 µg/g for Cu(II), Co(II) and Ni(II) ions corresponding to 54 %, 64 %, 15 % adsorption of initial amounts, respectively. The adsorption capacity for uranyl ion by a new adsorbent containing two amidoxime groups per repeating unit prepared by this method is better than

that of the chelating resins prepared by the method of Park et al. and Kise et al. (Park et al., 1996; Kise et al., 1985). The unique advantage of this polymer is that it contains double amidoxime groups per repeating unit, an additional diethylene spacer unit between neighbouring amidoxime groups in each monomeric unit. This polymer is known to be the first acrylic bidentate amidoxime polymer in the amidoxime polymer family reported in the literature. These properties make this new adsorbent more accessible for the adsorption of metal ions in aqueous systems than the conventional adsorbents having only one amidoxime group per repeating unit.

4.4.1. Competitive adsorption

The selectivity of amidoximated poly(DPAAm) is checked for 100 ppb mixture solution of U(VI), V(V), Cu(II), Co(II) and Ni(II) metal ions. Figure 4.11 shows the result of the selectivity experiment for amidoximated poly (DPAAm). The selectivity for a very dilute solution of a metal ion is expressed as the distribution coefficient (D) which is a useful measure of capacity of an adsorbent (Sahni and Reedijk, 1984).

$$D = (\text{mg } M^{n+}/\text{g of dry polymer}) / (\text{mg } M^{n+}/\text{mL of solution})$$

The distribution coefficients D of each metal ion in the mixture solution under competitive conditions were determined by using the above equation. The results are given in Figure 4.11. It can be seen from this Figure that the new adsorbent selectively adsorbed uranium ion compared to the other metal ions. The distribution coefficient of uranium is 3 times higher than that for vanadium ion and approximately 150 times higher than those of Cu(II) and Co(II) ions. There was a very big difference between nickel and other metal ions. Nickel ion was not adsorbed effectively. The selectivity order was found to be U(VI) > V(V) >> Co(II) = Cu(II) >> Ni(II) for 100 ppb mixture metal ion solution. This can be explained as follows: the amidoximes exist predominantly in the syn-hydroxyamino form that is stabilized by an intramolecular hydrogen bond. They generally undergo a metal-assisted hydroxyl proton dissociation upon coordination and a rule of thumb is that 'soft acid' tends to interact with 'soft bases' and conversely, 'hard acids' interact

with 'hard bases'. A classification of selected ions and ligands as hard and soft acid and bases (HSAB) according to the scale of Pearson was given earlier in this thesis (Hancock and Martell, 1989). The functional groups in the chelating polymer materials usually act as bases; oxygen and -NH_2 containing functional groups being hard and uranium and vanadium act as hard acids hence the selectivity towards these ions. The chelating polymers containing excess amidoxime groups having oxygen and -NH_2 containing functional groups synthesized in this work can be used to extract selectively uranium and vanadium. Ni(II) , Cu(II) and Co(II) act as intermediate acids, -NH_2 and oxygen containing functional group however act as hard bases thus explaining the low affinity for these ions.

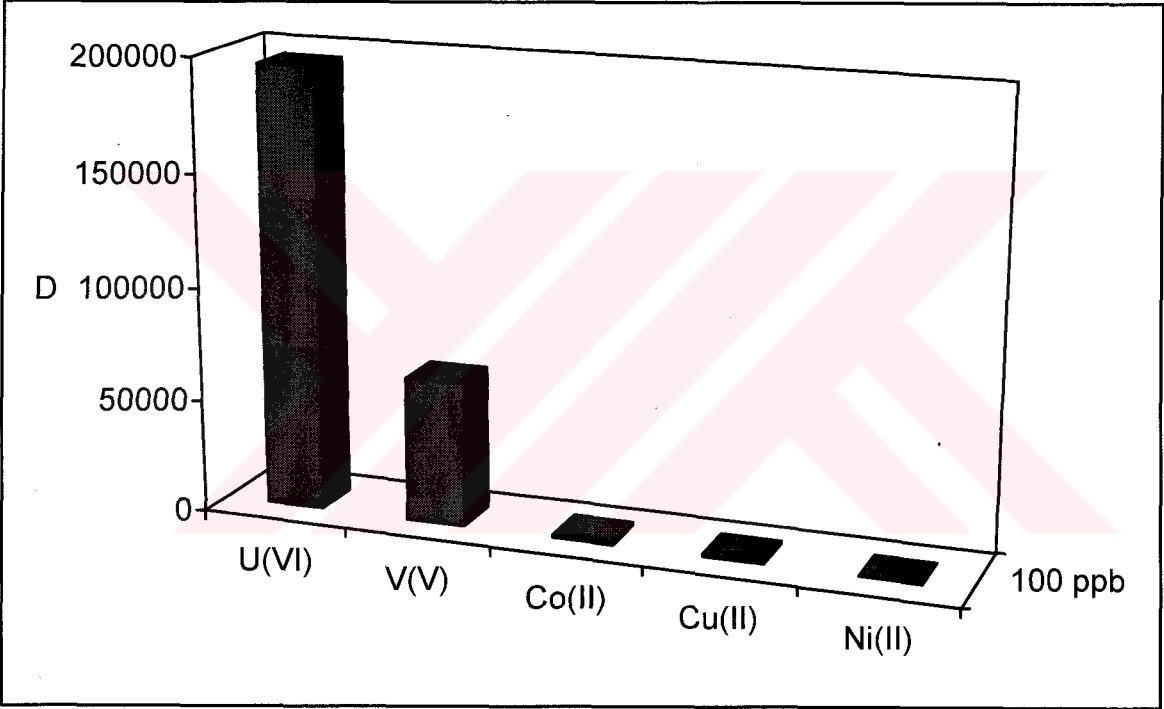


Figure 4.11. Adsorption selectivity of amidoximated poly(DPAAm) for the indicated metal ions.

4.4.2. Seawater treatment

Uranium and vanadium ions adsorption from seawater were also evaluated in flow-through mode as shown in Figure 4.12. After 1 hour, 1 day and 1 week contact time, adsorption capacity of amidoximated poly(DPAAm) were found to be 13.08, 28.1, 27.13 $\mu\text{g U ion/g}$ of adsorbent and 30.36, 31.16, 33.27 $\mu\text{g V ion/g}$ of adsorbent, respectively. These results show that, after 1 day of contact time no

appreciable increase in adsorption of V(V) and U(VI) were observed and equilibrium degree of adsorption values were already reached. As can be seen from the Figure 4.11, amidoximated poly(DPAAm) has almost reached the adsorption equilibrium in 1 h for vanadium and 1-3 h was sufficient for uranium ion. In terms of kinetic evaluation (rate of adsorption), batchwise adsorption of U(VI) and V(V) onto amidoximated poly (DPAAm) were nearly the same as with the sea water treatment process. This new polymer has a higher vanadium and uranium ion adsorption capacity and adsorption rate from seawater than those that were developed by various groups. The detailed comparison of uranium ion adsorption from seawater treatment is given on page 101 of this thesis.

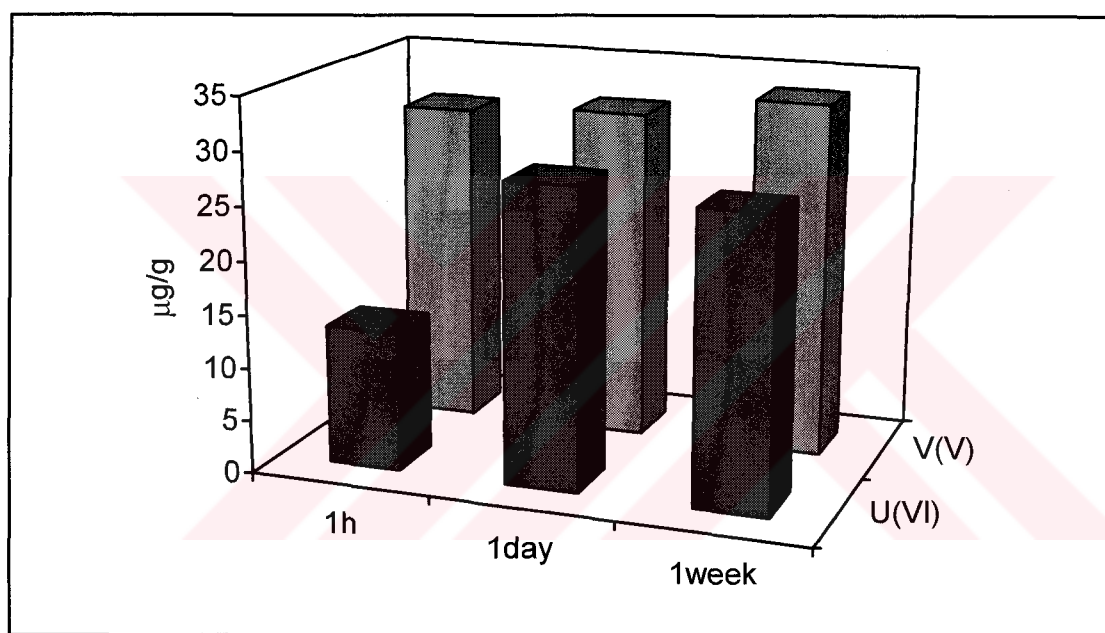
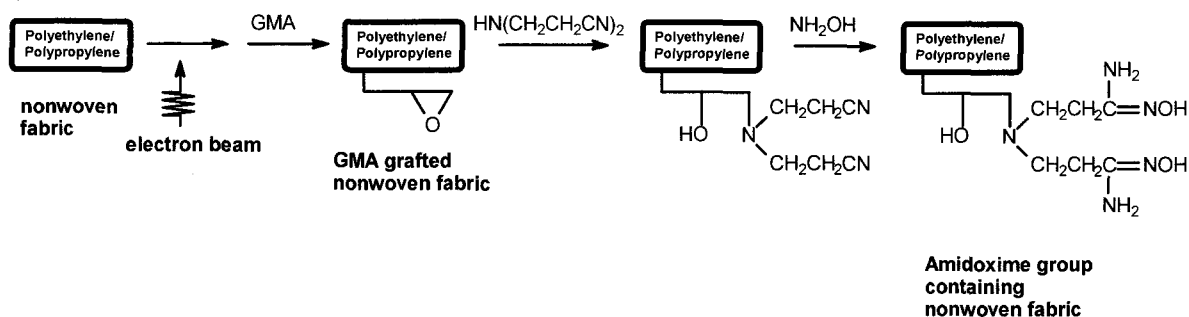


Figure 4.12. Adsorption of uranium and vanadium ions from seawater at different contact times.

4.5. Grafting of GMA onto Trunk Nonwoven Fabric

The preparation of nonwoven fabric containing surface grafted chains with two amidoxime groups per one monomeric unit requires the three steps as illustrated in Scheme 4.2: (1) grafting of an epoxy-group containing monomer, glycidyl methacrylate GMA, by pre-irradiation grafting technique, (2) functionalization of epoxy ring with 3,3'-iminodipropionitrile, and (3) amidoximation reaction of CN groups on the grafted chains.



Scheme 4.2. Schematic preparation of polymeric fabric adsorbent containing two amidoxime groups per repeating unit of grafted chains.

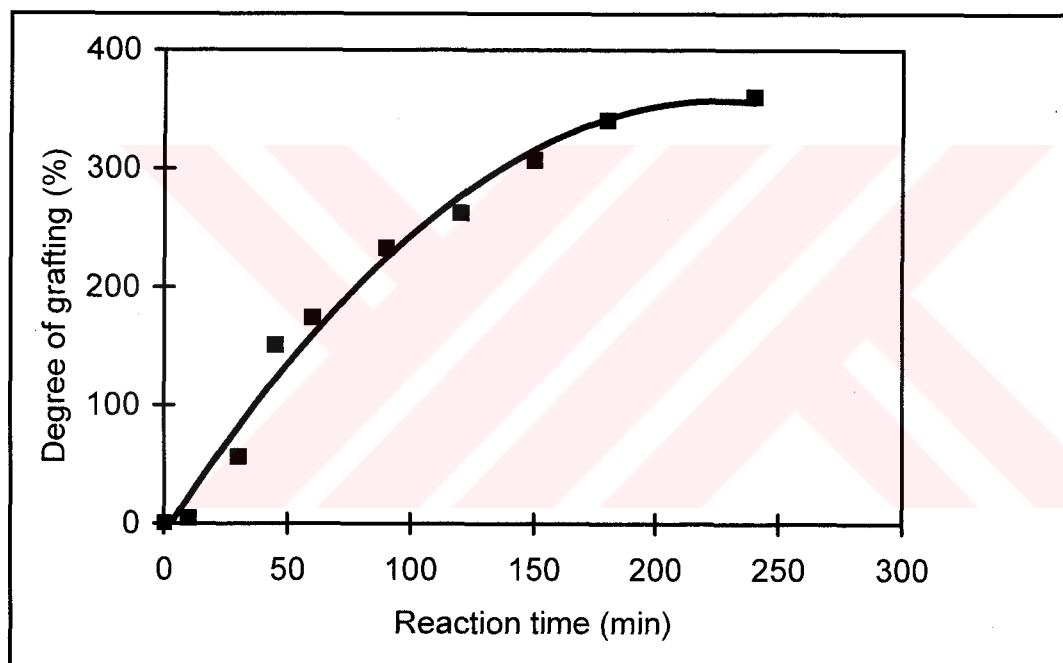


Figure 4.13. Grafting of GMA onto trunk PP/PE fabric, pre-irradiated to 200 kGy by accelerated electrons.

The degree of GMA grafting (dg) on nonwoven fabric (polypropylene fabric coated with polyethylene) previously irradiated to a total dose of 200 kGy by an electron accelerator is shown in Figure 4.13 as a function of reaction time (contact time with monomer solution). The optimum GMA grafting conditions were previously determined to be 10 w/w % GMA/methanol at 40 °C (Kim et al., 1998). As can be seen from Figure 4.13, degree of grafting increases almost linearly with increasing reaction time up to 100 min. The degree of grafting reached about 350 % (w/w)

upon contacting the e-beam activated trunk polymer with the GMA solution for 3 hours. After 3h reaction time no appreciable increase in grafting of GMA was observed and equilibrium degree of grafting value was reached.

The FTIR spectra of trunk polymer and 58 %, 150 %, 175 %, 200 % and 300 % GMA grafted polymers are presented in Figure 4. 14. The characteristic absorption bands of $-\text{CH}_3$ anti-symmetric stretching (at 2966 cm^{-1}), $-\text{CH}_2$ anti-symmetric stretching (at 2917 cm^{-1}), and $-\text{CH}_2$ symmetric stretching (at 2847 cm^{-1}) groups were observed in the FTIR spectrum of trunk polymer. Upon grafting of GMA onto the trunk polymer, the additional bands, which are characteristic of GMA structure, appeared. The $-\text{CH}$ stretching vibrations of epoxy rings occur in $3065\text{--}3008\text{ cm}^{-1}$. $-\text{C}=\text{O}$ stretching vibration band belonging to GMA at 1736 cm^{-1} and symmetrical stretching or ring breathing frequency of the epoxy ring, all ring band stretching and contracting in phase occurring at 1265 cm^{-1} are clearly seen (Silverstein et al., 1991).

4.5.1. Functionalization of GMA grafted polymer with IDPN

As has been explained in detail in the experimental part, the epoxy rings of GMA grafts were tried to be opened by attaching iminodipropionitrile groups. Figure 4.15 shows the percent replacement of the epoxide groups by IDPN groups for fabrics with different degree of GMA grafts as a function of reaction time. The extent of conversion value was calculated by using Eq.3.2 given in the experimental part.

Figure 4.15 shows that the conversion of epoxy groups has not been fully completed and a maximum of 70 % conversion has been achieved for all systems. This may be due to inactivation of some epoxy groups during the grafting process.

Depending upon the degree of grafting and replacement by IDPN, the nonwoven cloth became increasingly less flexible and it was observed that at higher degrees of grafting ($>150\%$), the cloth became even brittle. Considering these limitations 150 % of GMA grafting and 80 h of IDPN reaction time were selected as optimum conditions for the preparation GMA grafted fabrics containing iminodipropionitrile

pendant groups. The graft fabrics synthesized under these conditions were later used in all experimental studies for characterization and further metal ion uptake studies.

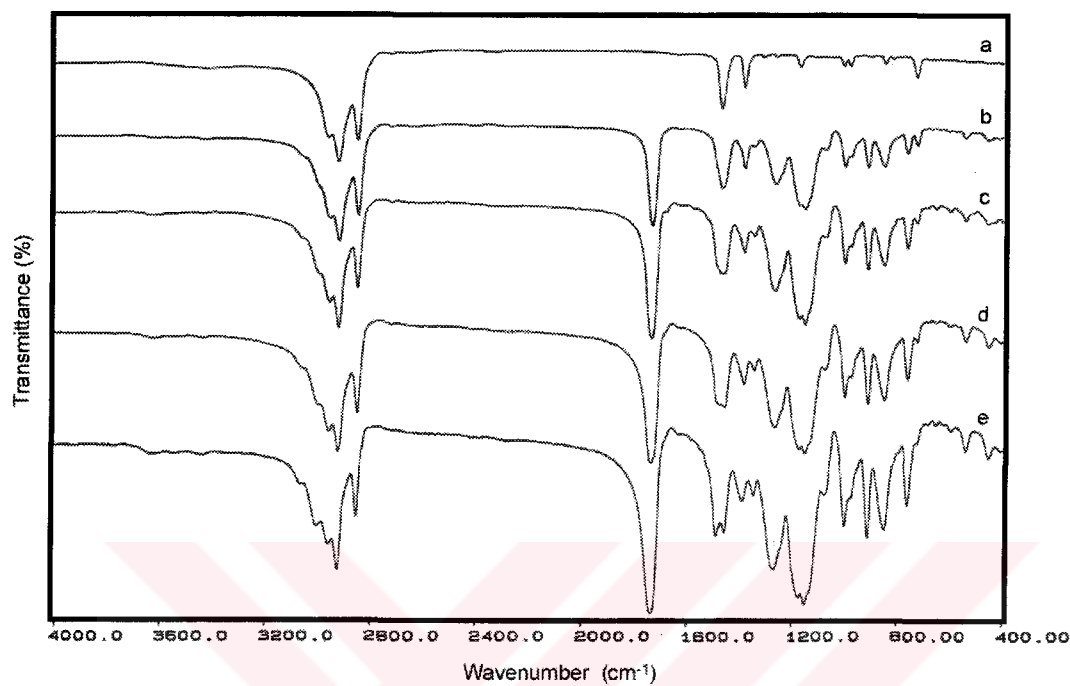


Figure 4.14. The FTIR spectra of a) trunk polymer and, b) 58%, c) 150%, d) 175%, e) 200 % GMA grafted polymer.

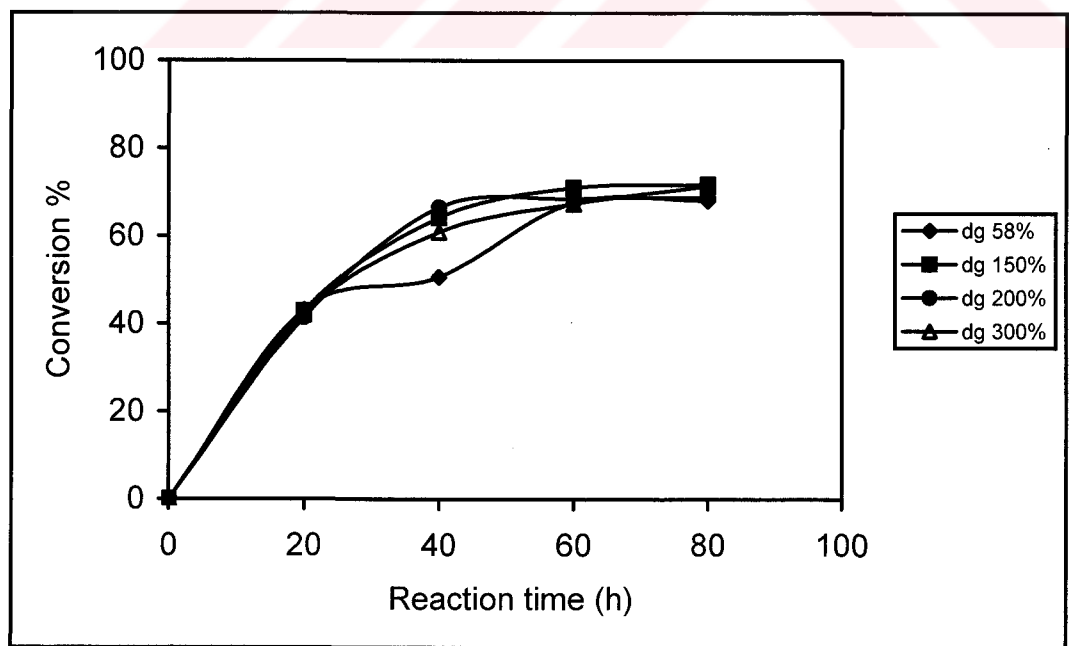


Figure 4.15. Conversion of epoxide groups of GMA graft chains with various degree of grafting into 3,3'-iminodipropionitrile.

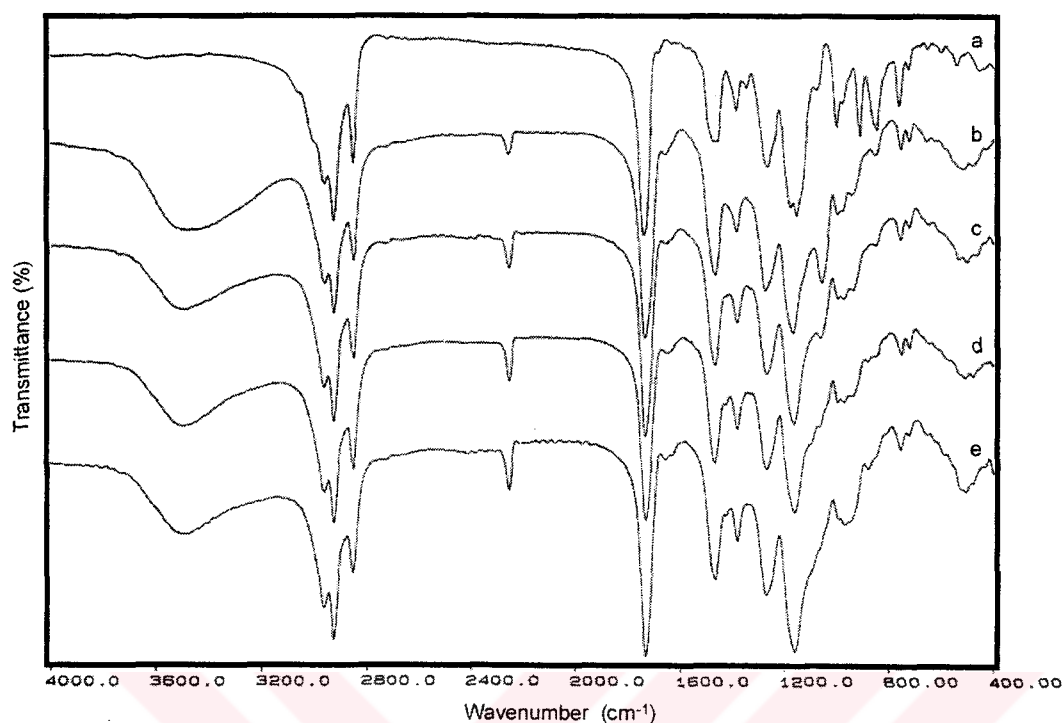


Figure 4.16. FTIR spectra of 150 % grafted polymer modified with 3,3'-iminodipropionitrile at different reaction times, a) 0 h, b) 20 h, c) 40 h, d) 60 h, and e) 80 h.

The FTIR spectra of 150 % GMA grafted polymer and its 3,3'-iminodipropionitrile modified form prepared at different reaction times is given in Figure 4.16. A sharp band at 2249 cm^{-1} very characteristic of $\text{C}\equiv\text{N}$ band and new absorption bands between $1000\text{--}1100\text{ cm}^{-1}$ region for $\text{C}\equiv\text{N}$ stretching vibration which come from 3,3'-iminodipropionitrile structure are clearly seen in Figure 4.16 b, c, d and e. The broad hydroxyl band, which originates from ring opening of epoxy group, was observed in the $3400\text{--}3800\text{ cm}^{-1}$ region.

4.5.2. Amidoximation of functionalized GMA grafts

The final aim of this study was to prepare a new fibrous adsorbent containing surface grafted chains carrying excess amidoxime groups. This has been tried to be reached by converting the double nitrile groups attached to epoxy units of GMA chains into amidoxime (AO) groups. The nitrile groups were converted into AO

groups by reacting them with NH_2OH . The AO group density was calculated by using Eq.3.3. The density of AO groups reached a maximum at 1.5 hour of contact time as given in Figure 4.17. The density of AO groups slightly decreases at longer reaction times. This is assumed to be due to degradation of the GMA groups after 1.5 hour of reaction time. For the 58 % GMA grafted fabric, density of amidoxime groups showed lower values (0.85 mmol/g product), the other grafts however showed similar behaviour, yielding an AO density of 2 mmol/g fabric at around 1.5 h of reaction time.

In order to follow the amidoximation reaction spectroscopically, FTIR analyses were also performed. The samples taken from the reaction medium at certain time intervals during the amidoximation process were dried, and their spectra were recorded as given in Figure 4.18. The sharp band observed in the spectra of amidoximated samples at 1650 cm^{-1} belongs to $\text{C}=\text{N}$ stretching vibration of the amidoxime groups. The broad band observed at $3219\text{--}3346\text{ cm}^{-1}$ is due to anti-symmetric and symmetric vibration modes of NH_2 groups. After 1.5 h of amidoximation time, the band at 2249 cm^{-1} was observed to disappear due to depletion of CN groups of original samples.

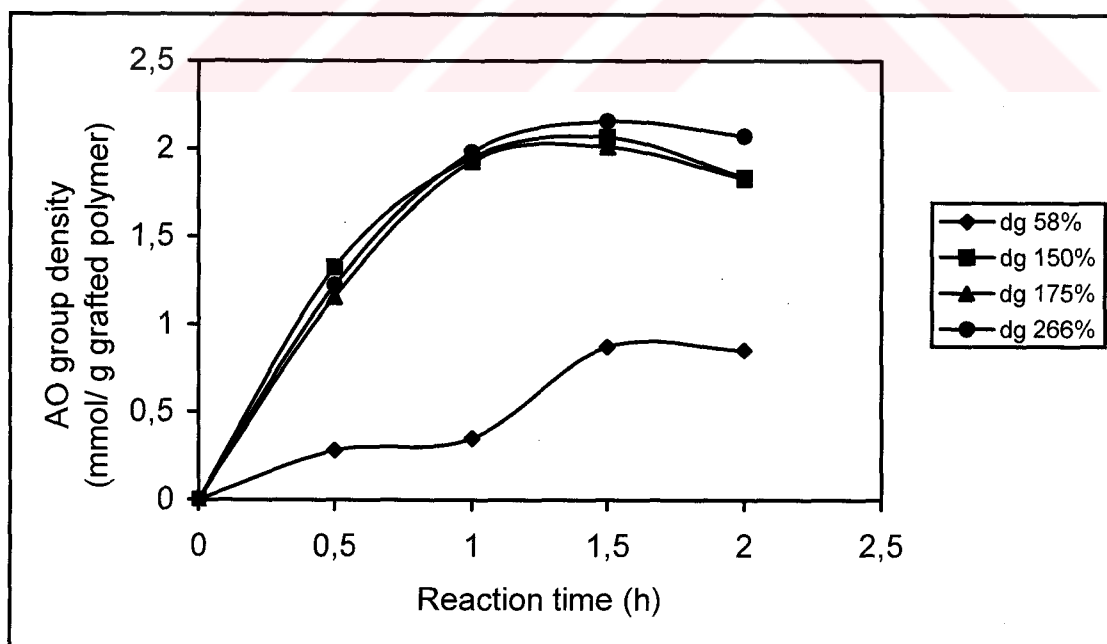


Figure 4.17. Amidoxime group density vs. amidoximation time for various degree of grafts.

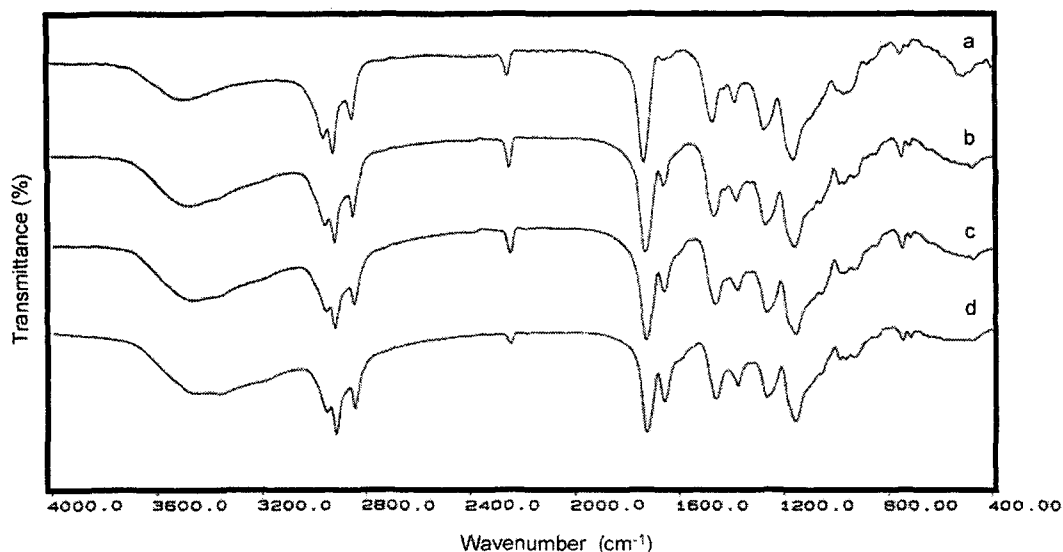
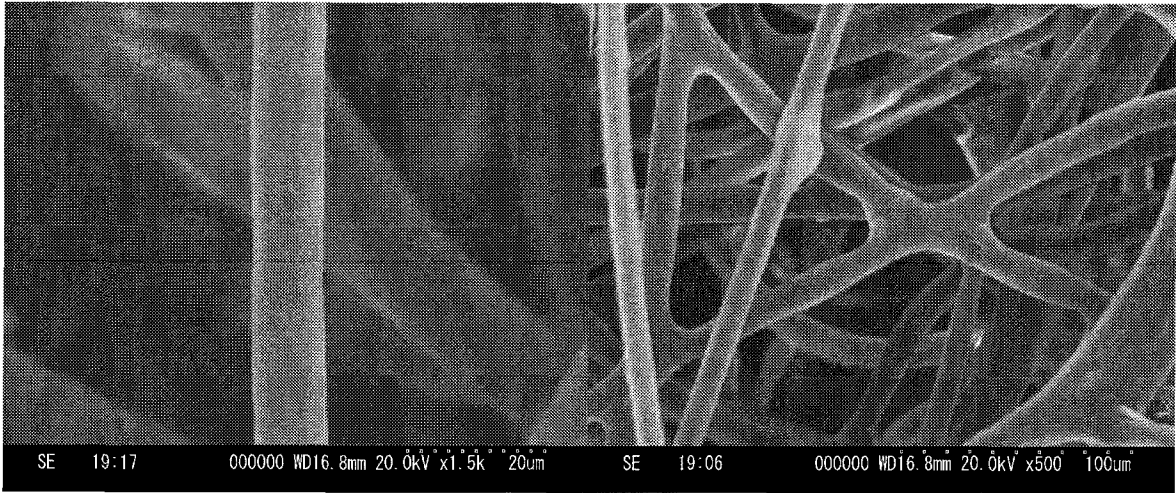


Figure 4.18. FTIR spectra showing the progress of amidoximation reaction at different reaction times, a) 0, b) 30 min, c) 1 h, and d) 1.5 h.

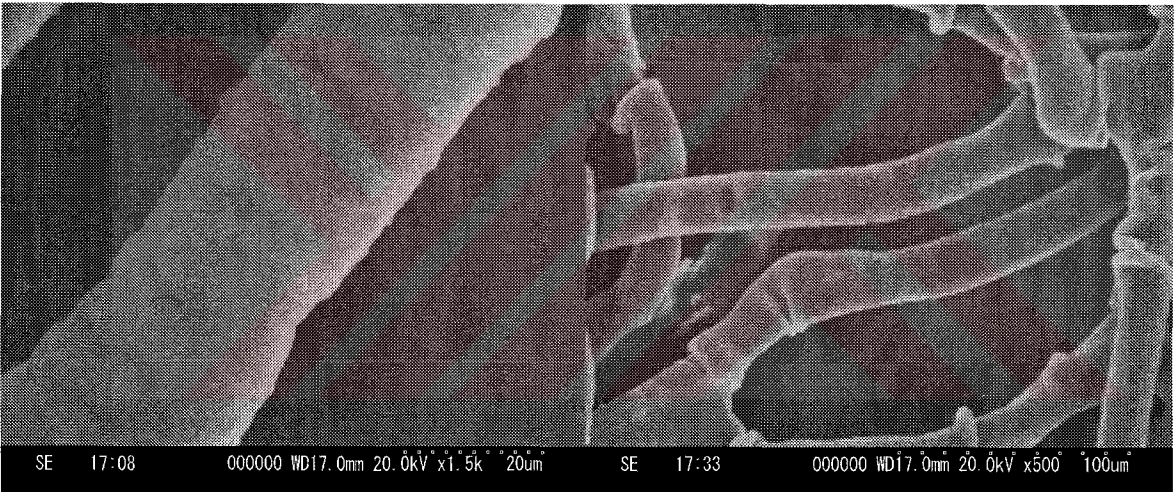
4.5.3. Characterization by SEM

Characterization of the nonwoven fabrics by SEM was made to compare the difference in the physical appearance of grafted and original samples, functionalized and amidoximated samples, and to see if there were any observable physical changes on the fabrics which might have occurred during the conversion process and subsequent treatment with 3,3'-iminodipropionitrile or after amidoximation reaction.

SEM photographs of trunk polymer, and 150 % GMA grafted non-woven fabric, and iminodipropionitrile modified and, amidoximated fabrics are given in Figure 4.19 and Figure 4.20, respectively. The average diameters of the fabrics of trunk polymer and 150 %, GMA grafted fabrics are determined to be 11.6 and 27.4 μm respectively. The iminodipropionitrile modified and amidoximated fabrics have average diameter of 27.6 and 27.6 μm respectively. The increase in the diameter of fabrics after grafting with GMA and change in their physical appearance are the additional physical evidences for the grafting process. No physical changes have been observed upon amidoximation reaction which has been expected.

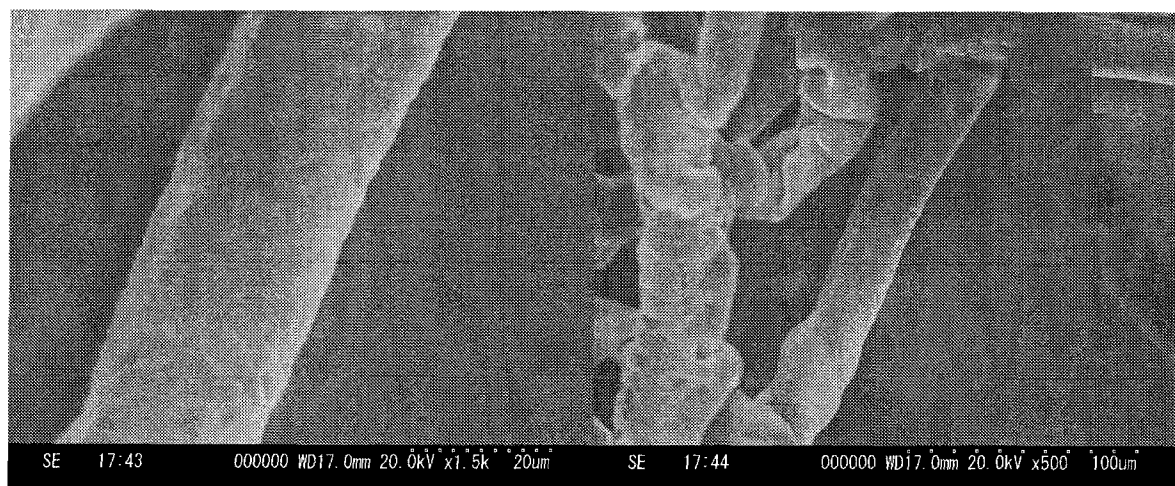


a

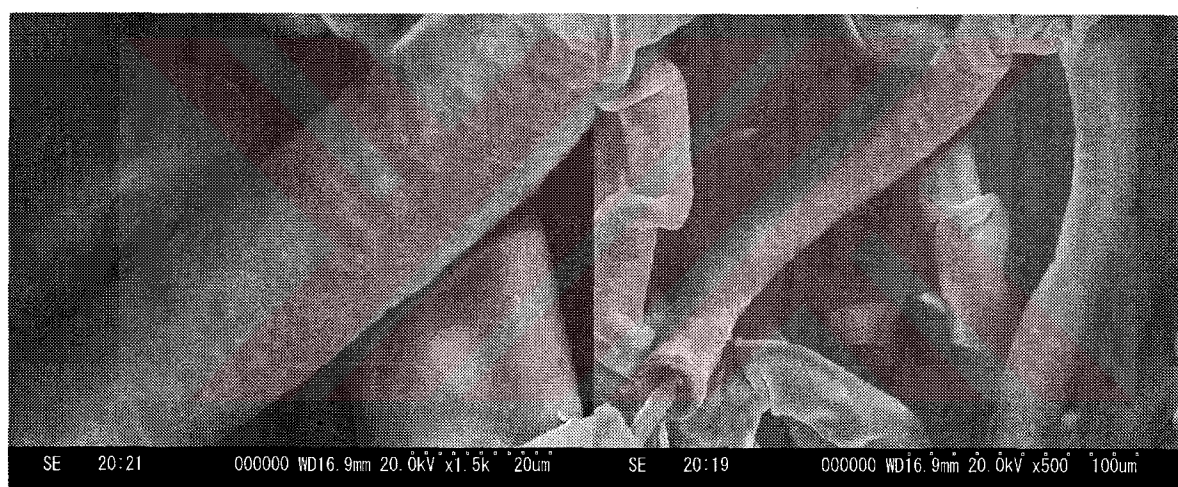


b

Figure 4.19. SEM photographs of a) trunk non-woven fabric, b) 150 % GMA grafted non-woven fabric, at two different magnifications (500X and 1500X).



a



b

Figure 4.20. SEM photographs of samples a) modified with iminodipropionitrile, b) amidoximated, at two different magnifications (500 X and 1500 X).

4.5.4. Thermal characterization

4.5.4.1. Thermal characterization of trunk nonwoven fabric (NWF) and 150 % GMA grafted NWF

The dynamic and derivative thermograms of the trunk polymer under N_2 atmosphere are shown in Figure 4.21. The thermal degradation of trunk polymer proceeds by a one-step process with a maximum decomposition temperature at 437 °C. Degradation started approximately at 300 °C and ended at 500 °C, giving a 1.23 % residue at 600 °C. Figure 4.22 shows TGA and DTGA curves of 150 % GMA grafted polymer. Two-stage degradation is observed for the decomposition of grafted polymer. Major weight loss of the first step started approximately at 240 °C and ended around 380 °C with an accompanying 65 % weight loss. Since the graft contains 150 % by weight of GMA chains, this loss of ~ 65 % corresponds very well to the loss of GMA units. The second step of degradation started little below 380 °C and ended at 480 °C and approximately 34 % weight loss was observed. The derivative of the second stage weight loss is very similar to the curve obtained for pure trunk polymer. Maximum degradation temperature for first step and second step are 272 °C and 445 °C, respectively. It gives 1.3 % residue at 700 °C.

The course of thermal degradation of GMA grafted trunk polymer was studied by FTIR as well. For this purpose, the samples were heated to different degradation extents in the furnace of TG apparatus and their FTIR spectra were later taken. The FTIR spectra of 150 % GMA grafted polymer and those degraded to 10 %, 30 %, 40 % and 60 % weight losses are shown in Figure 4.23. The progress of degradation is most remarkably represented by the changes in the FTIR spectra in the form of a decrease in the intensity of the 1736 cm^{-1} band due to C=O stretching vibration coming from GMA groups. After 60 % degradation, Figure 4.23e, the spectrum looked very similar with trunk polymer spectrum with the small exception of presence of a band remaining of at around 1700 cm^{-1} . This has further been substantiated by the close overlap of maximum degradation temperature of second step (446 °C) of graft polymer with the maximum

degradation temperature of trunk polymer (437 °C). The characteristic absorption bands of -CH_3 anti-symmetric stretching (2966 cm^{-1}), -CH_2 anti-symmetric stretching (2917 cm^{-1}), and -CH_2 symmetric stretching (2847 cm^{-1}) groups can be observed in the FTIR spectrum of trunk polymer and these bands are also observed in the spectrum of GMA grafted polymer after 60 % degradation. These results show that, during the first stage of thermal degradation, the grafted GMA chains are stripped off leaving behind the trunk polymer.

A simple calculation can be used to support the above reached conclusions; 150 % GMA grafted NW fabric is composed of 60 % GMA and 40 % trunk polymer. Stagewise thermal degradation of grafted polymer takes place around 60 % weight loss. Spectrum of almost pure trunk polymer appears after 60 % weight loss of grafted polymer. Figure 4.24 shows DSC thermograms of trunk polymer and 150 % GMA grafted trunk. The trunk polymer is composed of polypropylene coated with polyethylene. The melting temperature of PP is approximately 166 °C and melting temperature of PE is approximately 129 °C which are very close to the melting temperatures of pure polymers. (Bandrup and Immergut, 1989). In the DSC thermogram of 150 % GMA grafted NWF the melting endotherms due to PE and PP are retained and two broad endothermic peaks with rate maxima at 231 °C and 331 °C appeared. The major difference observed between the two thermograms are these additional endothermic peaks due to decomposition of GMA moieties which was also observed as the weight loss in the first stage in the dynamic TGA curves in Figure 4.22.

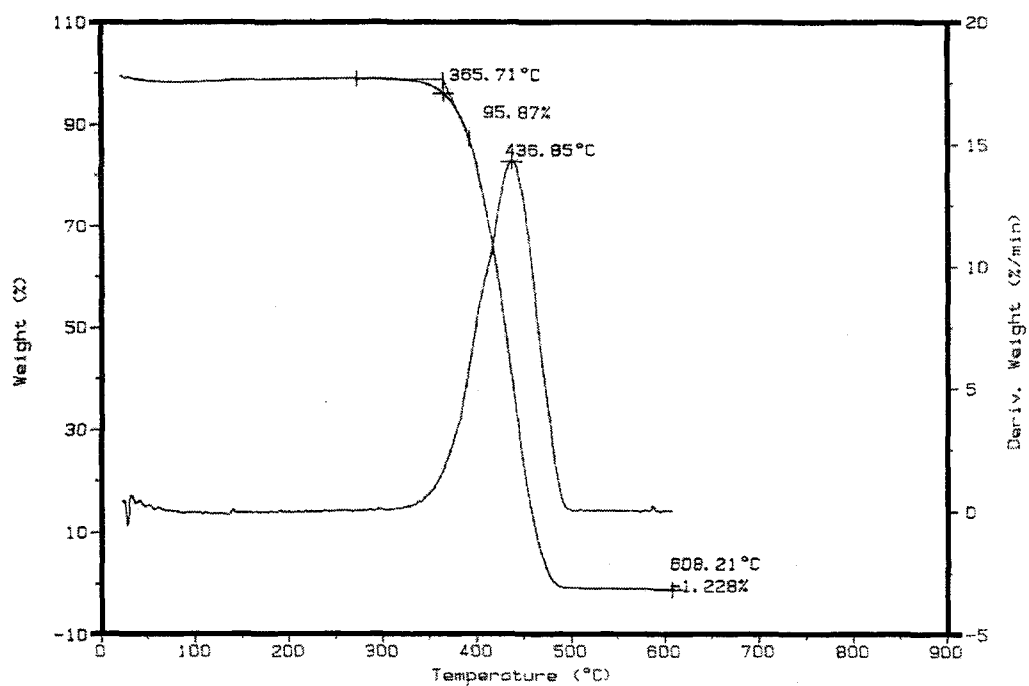


Figure 4.21. The dynamic and derivative thermograms of trunk polymer.

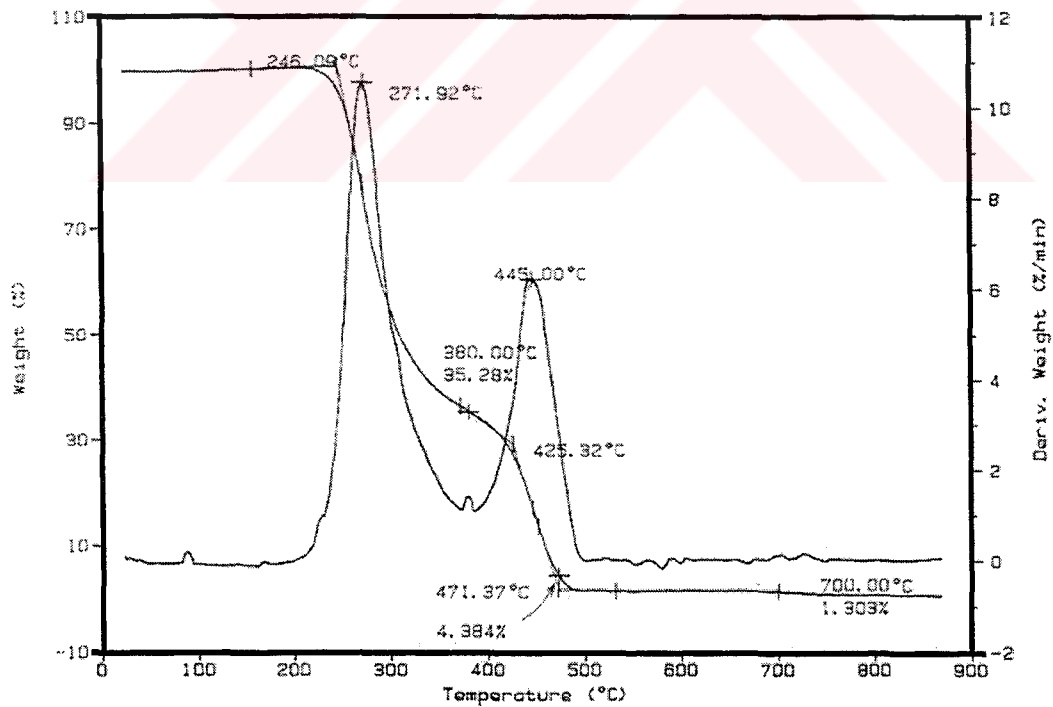


Figure 4.22. The dynamic and derivative thermograms of 150 % GMA grafted polymer.

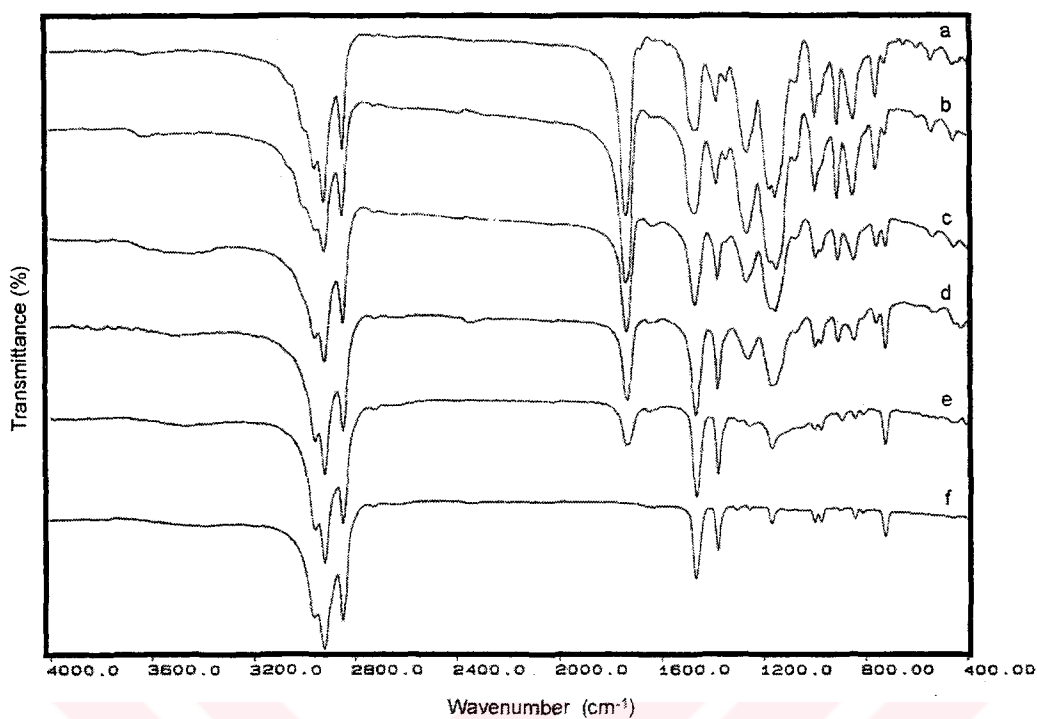


Figure 4.23. The FTIR spectra of thermally degraded 150 % GMA grafted trunk polymer. Spectra corresponding to a) 0 %, b) 10 %, c) 30 %, d) 40 %, e) 60 % weight losses, f) represents trunk polymer.

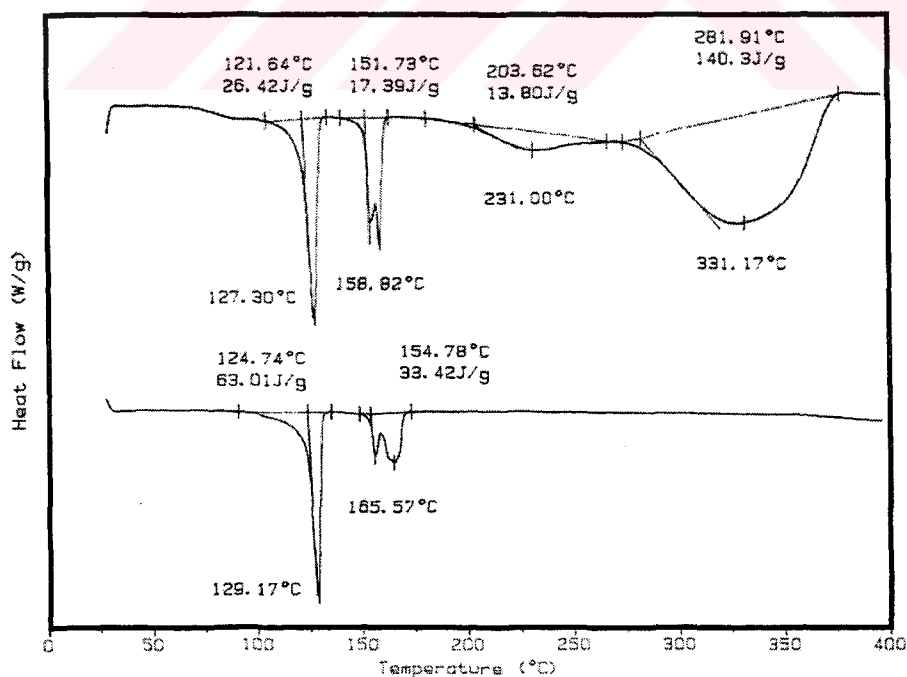


Figure 4.24. DSC thermograms of trunk non-woven fabric, below and 150% GMA grafted sample, above.

4.5.4.2. Characterization of IDPN functionalized graft non-woven fabric

The dynamic thermograms of 150 % GMA grafted polymer modified with iminodipropionitrile are shown in Figure 4.25. Four stages of degradation are evident in these curves. The first stage of weight loss starts approximately at 200 °C and ends around 290 °C. Second stage of degradation starts from about 290 °C and ends around 400 °C. The third and fourth stages of degradation take place between 350 °C and 495 °C overlapping around 450 °C. Complete degradation of sample gives 9.4 % residue at 700 °C.

These degradation steps were also analysed with FTIR spectrometry. Figure 4.26 shows the original FTIR spectrum of IDPN modified NWF and spectra of 25 %, 40 %, 60 % and 70 % degraded samples. Gradual disappearance of CN bands at 2249 cm^{-1} and appearance of shoulders around 1750 cm^{-1} due to formation of anhydrides which is also depicted as C-CO-O-CO-C stretching vibrations at 1011 cm^{-1} and asymmetric and symmetric C=O couple stretching vibration bands at 1806 cm^{-1} , 1764 cm^{-1} , respectively show a behaviour parallel to stagewise degradation observed in Fig. 4.25. This result indicates that, the first step of degradation is due to the decomposition of imino groups on the polymer. After 40 % degradation, the C=O bands of GMA group were kept but the structure of polymer launched into an anhydride structure. The spectrum of 70 % degraded sample is very similar with trunk polymer spectrum and maximum degradation temperature of fourth step (481 °C) can be considered to be close to the maximum degradation temperature of trunk polymer (437 °C).

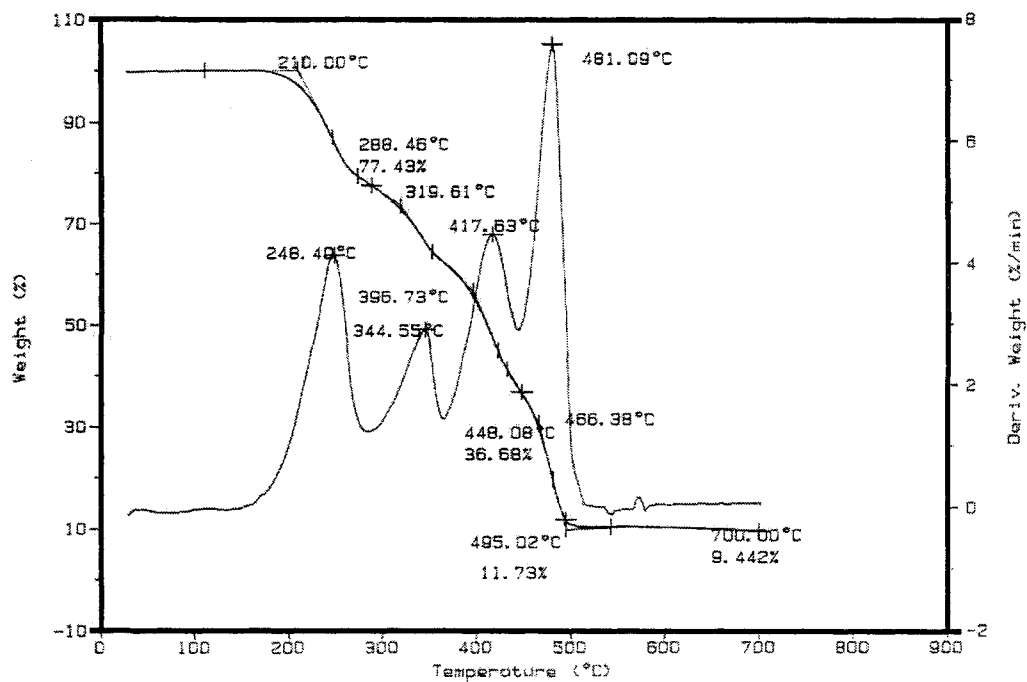


Figure 4.25. The dynamic and derivative thermograms of IDPN modified non-woven fabric.

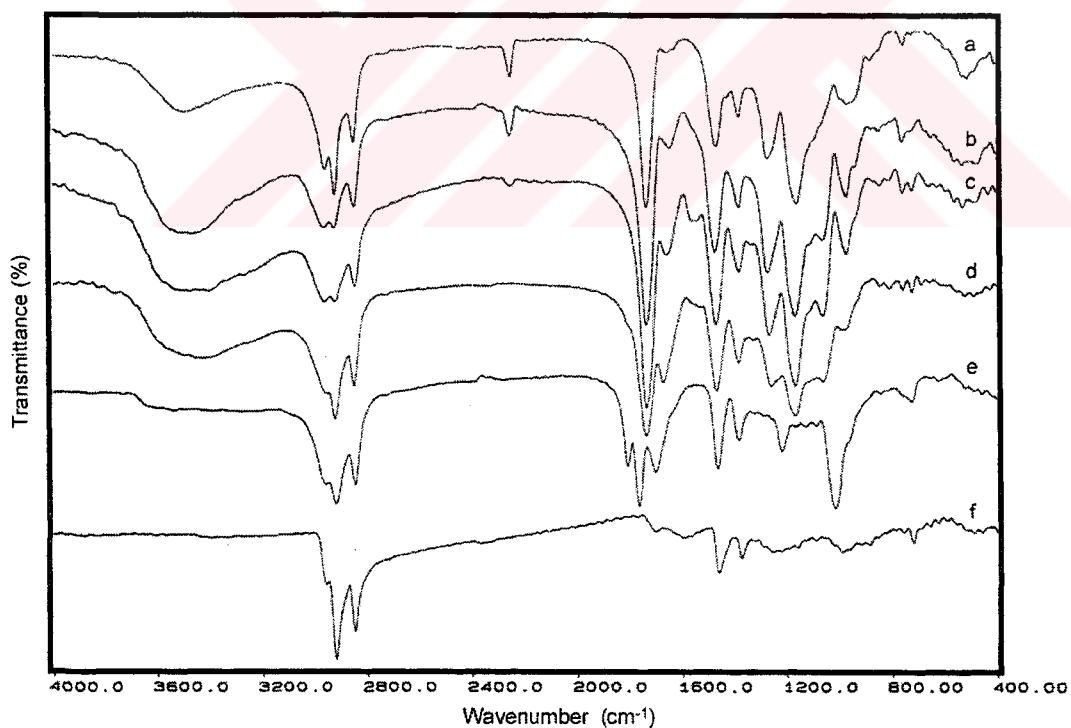


Figure 4.26. The FTIR spectra of thermally degraded IDPN modified graft non-woven fabric taken at the following weight losses: a) 0, b) 25 %, c) 40 %, d) 50 %, e) 65 %, f) 70 %.

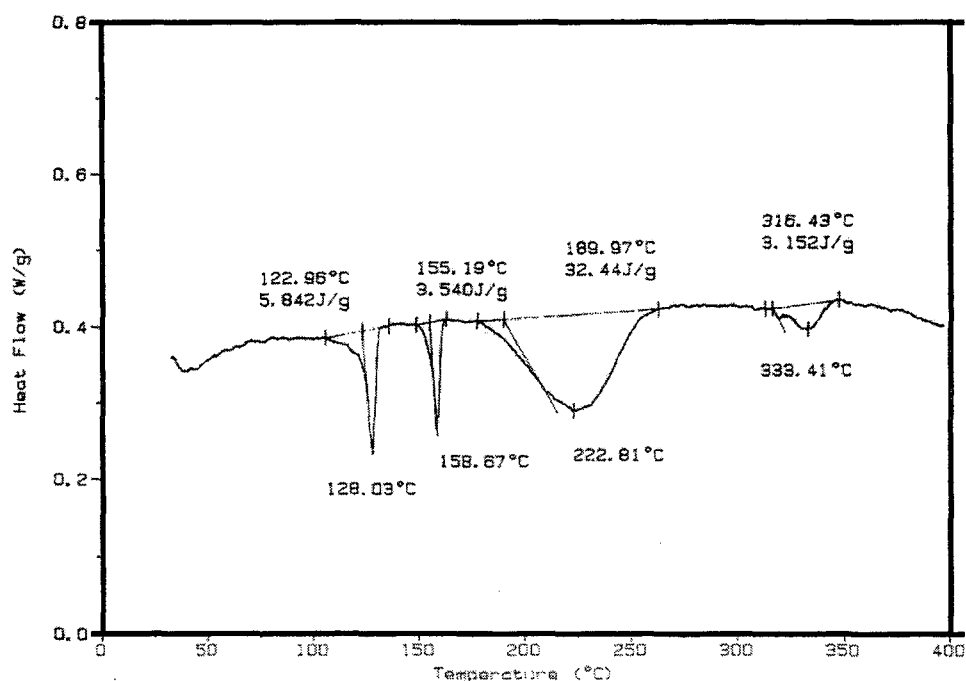


Figure 4.27. DSC thermogram of IDPN modified nonwoven fabric.

Figure 4.27 shows the DSC thermogram of IDPN modified graft NW fabric. The first and second melting peaks are those due to the melting of PE and PP, respectively. The third and fourth endothermic peaks comply with corresponding TGA curve and they are related to the first and second stages of degradation of IDPN modified graft fabric, respectively.

To complete the thermal characterization of final product, i.e. amidoximated fabric, its dynamic thermogram was taken and shown in Figure 4.28. The main difference observed in this thermogram as compared to that given in Figure 4.25 is that upon amidoximation the grafted fabric becomes thermally less stable and degradation starts at around 150 °C. The general trend of four stage weight loss has been mostly retained.

A comparison of Figure 4.26 and Figure 4.29, representing FTIR spectra of thermally degraded non-amidoximated and amidoximated fabrics respectively, show that they follow similar mechanisms ending with the appearance of base material, PE coated PP at 70 % weight loss.

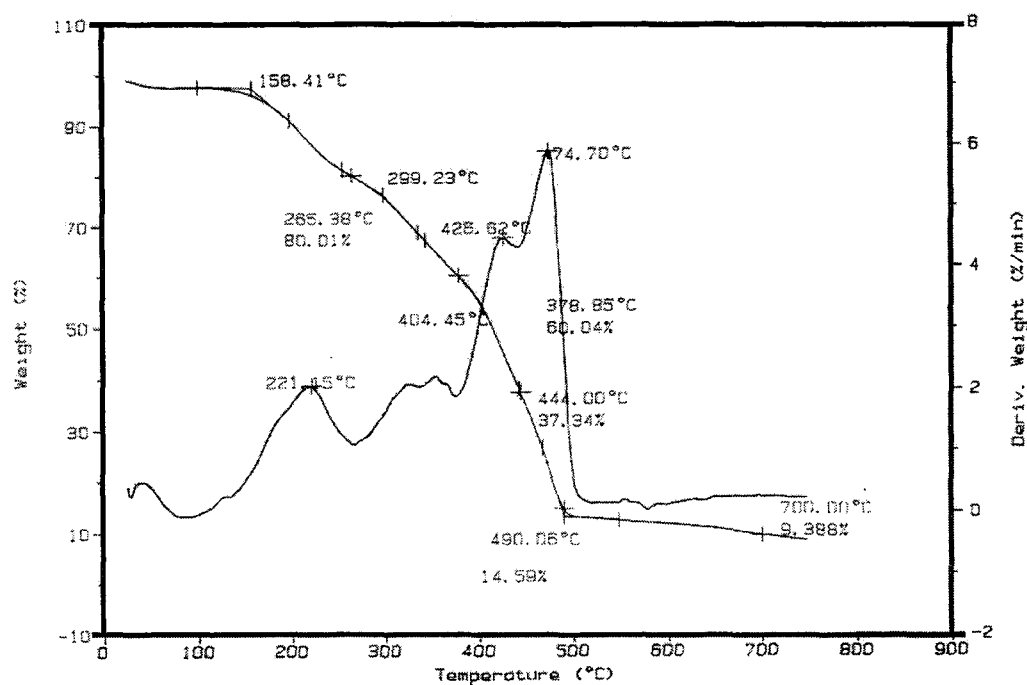


Figure 4.28. Dynamic and derivative thermograms of amidoximated nonwoven fabric.

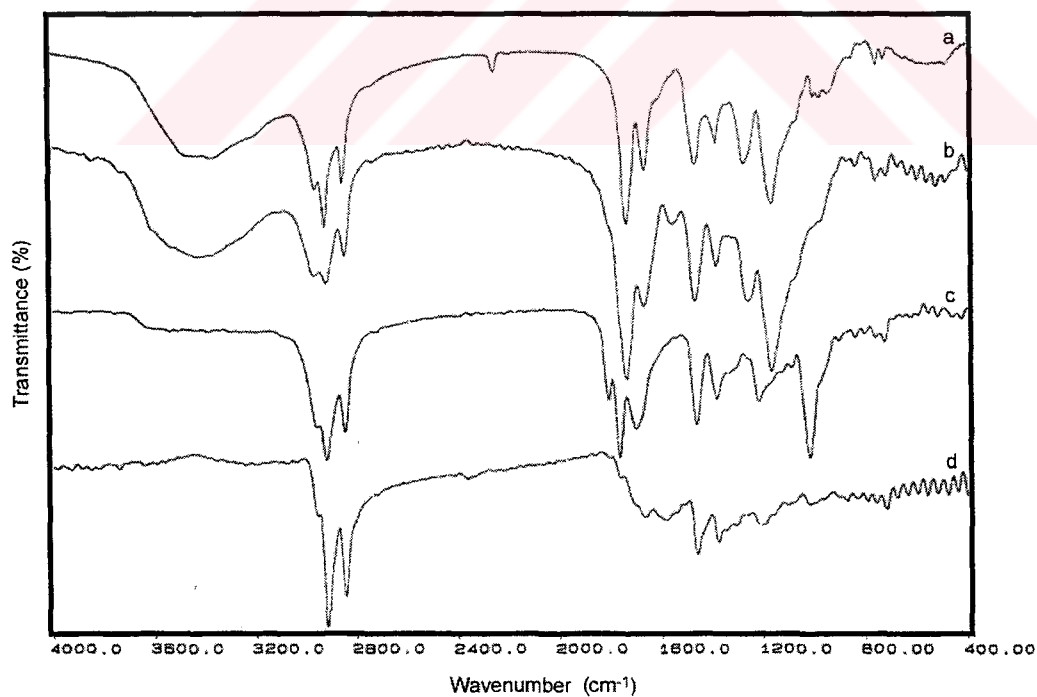


Figure 4.29. The FTIR spectra showing thermally degraded amidoximated nonwoven fabric at the weight losses: a) 0 %, b) 20 %, c) 50 %, d) 70 %.

4.5.5. Adsorption studies for amidoximated nonwoven fabric at low metal ion concentrations

In order to investigate the adsorption kinetics of five different metal ions (U(VI), V(V), Pb(II), Cu(II) and Co(II)) onto modified NWF adsorbent, approximately 0.025 g of adsorbent was contacted with 100 ppb metal ion solutions at pH 5 buffer solution at 25 °C. Figure 4.30 shows the adsorption kinetics of U(VI), V(V), Cu(II), Pb(II) and Co(II) ions onto amidoximated nonwoven fabric. The values were given as the percentage of metal ions adsorbed versus time.

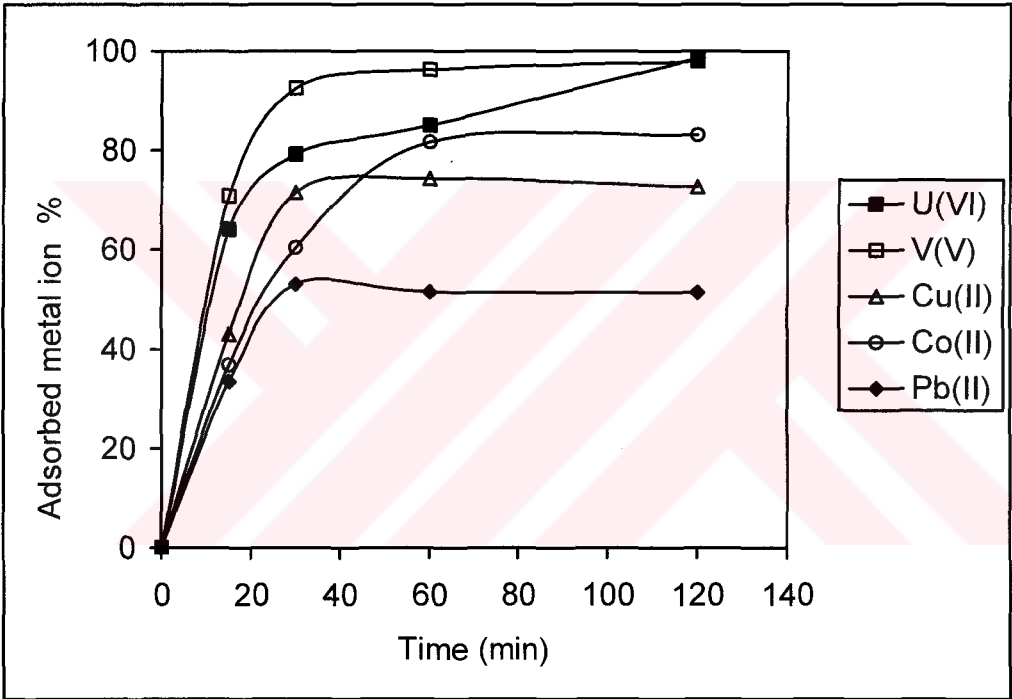


Figure 4.30. Adsorption kinetics of different metal ions from the same initial concentrations onto modified NWF.

High adsorption rates were observed within first 20 min and the plateau values (i.e. adsorption equilibrium) were quickly reached around 30 min for all metal ions investigated. Figure 4.30 shows that the new fabric adsorbent achieved almost 80 % uranium and 92.5 % vanadium loading in the initial 30 min and almost complete removal of these two ions 99 % U(VI) (153,9 $\mu\text{g/g}$) and V(V) (150,1 $\mu\text{g/g}$) within 120 minutes. The adsorption equilibrium of Cu(II), Co(II) and Pb(II) ions were attained in about 30 min and this new adsorbent adsorbed 72.7 %, 83 %, and 50 % respectively.

51.4 % of Cu(II), Co(II) and Pb(II) ions respectively which correspond to equilibrium removal amounts of 134.9 $\mu\text{g/g}$, 112.3 $\mu\text{g/g}$, 56.2 $\mu\text{g/g}$, respectively.

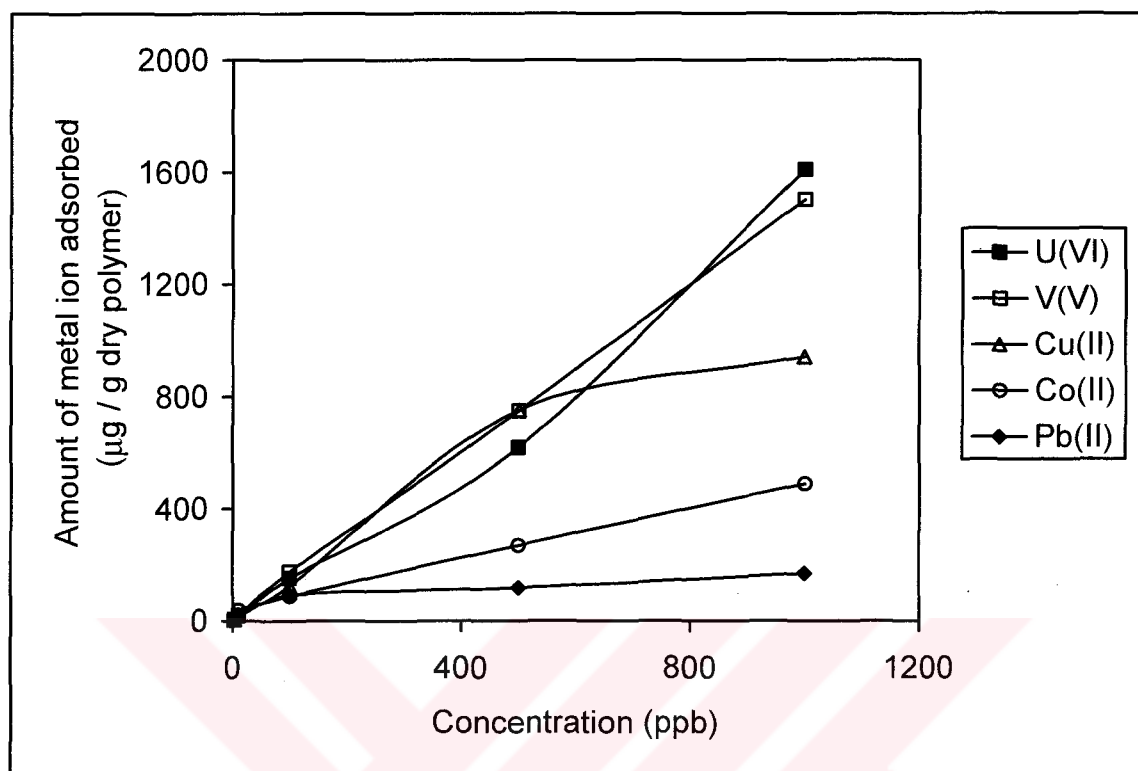


Figure 4.31. Dependence of metal ion uptake on the initial concentrations of metal ions.

The effect of initial concentration of metal ions on the adsorption behavior of amidoximated nonwoven fabric was determined for five different metal ion concentrations (3.3, 50, 100, 500 and 1000 ppb) and given in Figure 4.31. Figure 4.31 shows that the metal ion adsorption increased almost linearly with increase in initial metal ion concentration. The new adsorbent exhibited a higher affinity for U(VI) and V(V) ions, the highest values were found to be 1610 $\mu\text{g/g}$ and 1501 $\mu\text{g/g}$ from 1000 ppb metal ions solution, respectively. 100 % adsorption of uranium and vanadium ions have been reached easily for all concentrations studied. The quantitative removals of other ions are 940 $\mu\text{g/g}$, 489 $\mu\text{g/g}$, 168 $\mu\text{g/g}$ for Cu(II), Co(II) and Pb(II) ions respectively. The adsorption capacity for uranyl ion by the new adsorbent prepared in this work is better than that of the chelating resins prepared by the method of Park et al. and Kise et al. (Park et al, 1996; Kise et al., 1985). The advantages of this new polymeric adsorbent containing two amidoxime

groups per repeating unit of GMA side chains are the presence of these excess amidoxime groups and an additional diethylene spacer unit between the neighboring amidoxime groups in each monomeric unit. It can be said that this adsorbent is the first grafted nonwoven fabric reported in the literature possessing bidentate amidoxime groups. These properties make this new adsorbent more accessible for the adsorption of metal ions in aqueous systems than the conventional adsorbents having only one amidoxime group as the pendant group of the repeating unit.

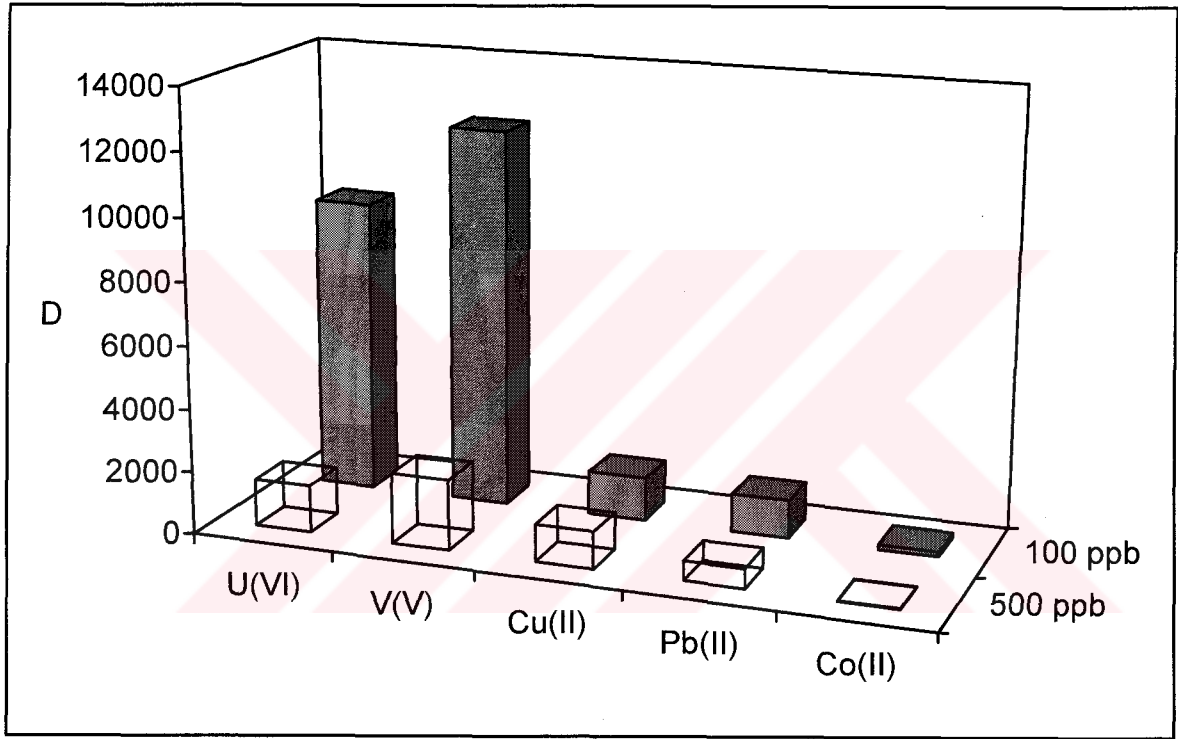


Figure 4.32. Adsorption selectivity of amidoximated nonwoven fabric for the indicated metal ions at two different initial concentrations.

The amidoximated nonwoven fabric shows good stability along with faster rate of equilibrium for all the metal ions studied here. The selectivity of this new adsorbent against certain metal ions was also checked. Figure 4.32 shows the result of the selectivity experiment for amidoximated nonwoven fabric. The selectivity is expressed as the distribution coefficient (D) which is a useful measure of capacity for an adsorbent (Sahni and Reedijk, 1984).

$$D = (\text{mg } M^{n+} / \text{g of dry polymer}) / (\text{mg } M^{n+} / \text{mL of solution})$$

The distribution coefficients of every metal ion were determined under competitive conditions by using the above equation.

For the concentrations studied here adsorptions of U(VI) and V(V) ions have been found to be higher than those of Cu(II), Pb(II) and Co(II). The order of decreasing selectivity is $V(V) > U(VI) \gg Cu(II) \geq Pb(II) \gg Co(II)$ for 100 ppb and 500 ppb solutions of metal ion mixtures. The distribution coefficient calculated for U(VI) and V(V) ions showed that their adsorption from 100 ppb mixture solution is up to 6 times higher than adsorption from 500 ppb mixture solution. These results show that the new adsorbent is suitable for the enrichment of trace amounts of U(VI) and V(V) ions from seawater or other aqueous media. This is in very good accordance with the results previously found and discussed for amidoximated poly(DPAAM). This selectivity follows the same order as found for another amidoxime containing adsorbent (Park et al., 1996).

There have been numerous attempts in developing speciality adsorbents for the uptake of uranyl ions from aqueous solutions and seawater. A comparative evaluation has been made to see the uranyl ion adsorption capacity of adsorbents developed by various groups and the result of such an investigation is given in Table III. The volumes of uranyl ion containing solutions in these batch, semi-batch and continuous systems ranged from 40 mL to 50 L, the most frequently used volume being 20 L. When the efficiencies corresponding to adsorption values normalized for 20 L working solutions are compared as given in the far right column of the Table 4.3, one can see that they can be grouped under three categories: Low efficiency (0.08-0.20 mg/g), medium efficiency (0.34-0.65 mg/g) and high efficiency (0.97-2.50 mg/g) adsorbents. Although this list is far from being complete, the highest uranyl ion adsorption efficiency was obtained with the new adsorbent developed in this work. Further details related to adsorbent properties and adsorption conditions are given in Table 4.3.

Table 4.3. A comparison of uranyl ion adsorption using various amidoximated polymeric adsorbents.

Research groups	Adsorbent [*]	Uranyl ions adsorbed	Uranyl ions adsorbed normalized to 20 L of total working volume
This work ^a	GMA grafted polypropylene/polyethylene nonwoven fabrics modified with 3,3'-iminodipropionitrile	0.005 mg/g U 0.0052 mg/g V	2.5 mg/g U 2.6 mg/g V
Egawa ^b et al. (1991)	Lightly crosslinked poly(acrylonitrile-co-divinylbenzene)	650 µg/g U	0.65 mg/g
Suzuki ^c et al. (2000)	Polypropylene nonwoven fabric grafted with acrylonitrile and methacrylic acid	0.576 mg/g U 1.8 mg/g V	0.576 mg/g U 1.8 mg/g V
Kawai ^d et al. (2000)	Polypropylene fabric cografted with methacrylic acid and acryloylchloride	0.2 mg/g U,	0.2 mg/g
Kise ^e et al. (1985)	Dicyanoethylated polystyrene	0.004 mg/g U	0.08 mg/g
Omichi ^f et al. (1986)	Acrylonitrile grafted onto tetrafluoroethylene-ethylene copolymer	0.2 mg/g U	0.08 mg/g
Kabay ^g et al. (1993)	Polypropylene fiber grafted with acrylonitrile	0.152 mg/g U	0.608 mg/g
Takeda ^h et al. (1991)	Acrylonitrile grafted onto porous polyethylene hollow fiber	0.97 mg/g U	0.97 mg/g
Saito ⁱ et al. (1990)	Acrylonitrile grafted onto porous polyethylene hollow fiber	0.85 mg/g U	0.34 mg/g
Omichi ^j et al. (1985)	Fibrous adsorbent containing acrylic acid and acrylonitrile	0.04 mg/g U	0.08 mg/g

^{*} All PAN containing polymers or copolymers are amidoximated

^a Batch process from 3.3 ppb metal ion mixture solution, volume: 40 mL, the density of amidoxime group (AOD): 2 mmol/g, contact time: 24 h

^b 0.5 g resin, flow rate: 900 mL/h, seawater volume: 20 L, contact time: 10 days.

^c 0.07 g amidoxime fiber, the analysis was carried out for amidoxime fiber, which had been immersed in seawater for 30 days. AOD: 6.3 mmol/g

^d 0.5 g resin, flow rate: 0.47 mL/h, seawater volume: 20 L, contact time: 24 hours. AOD: 3 mmol/g,

^e 0.1 g resin, seawater volume: 1L, contact time: 96 h,

^f Semibatch process (5 L of seawater was intermittently exchanged with fresh seawater), total volume: 50 L, contact time: 10 days,

^g Batch process, seawater volume: 5L, contact time: 24 h,

^h A continuous-flow experiment, a bundle of 230 AO-H fibers, Contact time: 30 days, AOD: 11.3 mmol/g,

ⁱ 0.07 g amidoxime membrane, 1 L of seawater was intermittently exchanged with fresh seawater, total volume: 50 L, contact time: 50 days,

^j 0.1 g resin, semibatch process (2 L of seawater was intermittently exchanged with fresh seawater), total volume: 10 L, contact time: 5 days

4.6. Adsorption Studies for Amidoximated Poly(DPAAM) and Amidoximated Nonwoven Fabric at High Metal Ion Concentrations

The amidoximated poly(DPAAM) and amidoximated nonwoven fabric were added into different concentrations (100-1500 ppm) of four different metal ion solutions at pH 5, until they reach their maximum adsorption equilibrium. The binding properties of these metal ions i.e. $\text{UO}_2(\text{VI})$, $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Co}(\text{II})$ with amidoximated poly(DPAAM) and amidoximated nonwoven fabric were determined in different concentration of aqueous metal solution at pH 5 acetate buffer solution are given in Figure 4.33-4.34. The experimental studies on vanadium ion at high concentrations could not be performed at pH 5 because of the change of colour and maximum wavelength in spectrophotometric measurement which was considered to be due to a change in the oxidation state of vanadium at this pH.

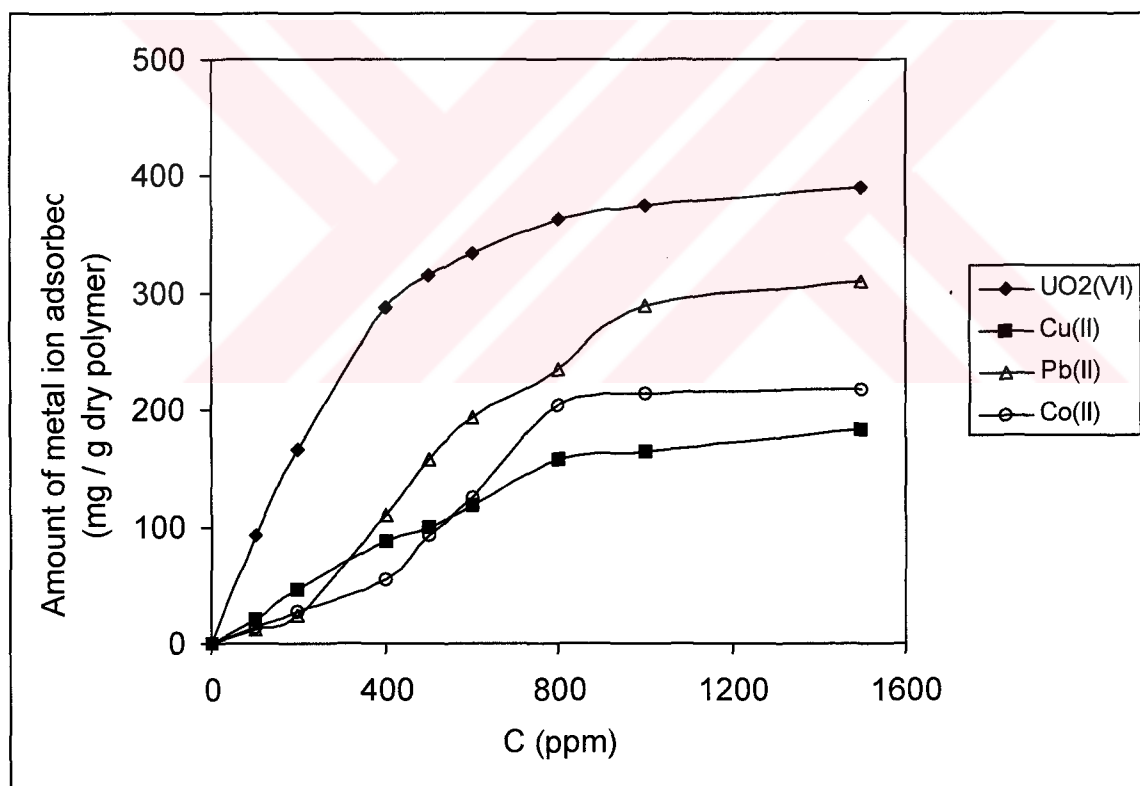


Figure 4.33. Dependence of metal ion uptake on the initial concentrations of metal ions for amidoximated poly(DPAAM).

It was found that the metal ion uptake by amidoximated poly(DPAAM) increased with increasing initial metal ion concentrations and beyond 1000 ppm metal ion

concentration adsorption equilibria were reached as shown in Figure 4.33. At this point adsorption amount of uranyl ion was observed to be 390 mg uranyl ion/g dry amidoximated polymer at pH 5. The adsorption behavior of Pb(II), Cu(II) and Co(II) ions which have lower adsorption capacity according to uranium show similar adsorption trend with $\text{UO}_2(\text{VI})$ ion. It was found that the adsorption capacity of amidoximated poly(DPAAm) for Pb(II), Co(II) and Cu(II) ions at 1500 ppm was 310, 217, 184 mg metal ion/g dry polymer, respectively. The order of affinity based on amount of metal ion uptake (mg metal ion/g dry polymer) is as follows: $\text{UO}_2(\text{VI}) > \text{Pb}(\text{II}) > \text{Co}(\text{II}) > \text{Cu}(\text{II})$.

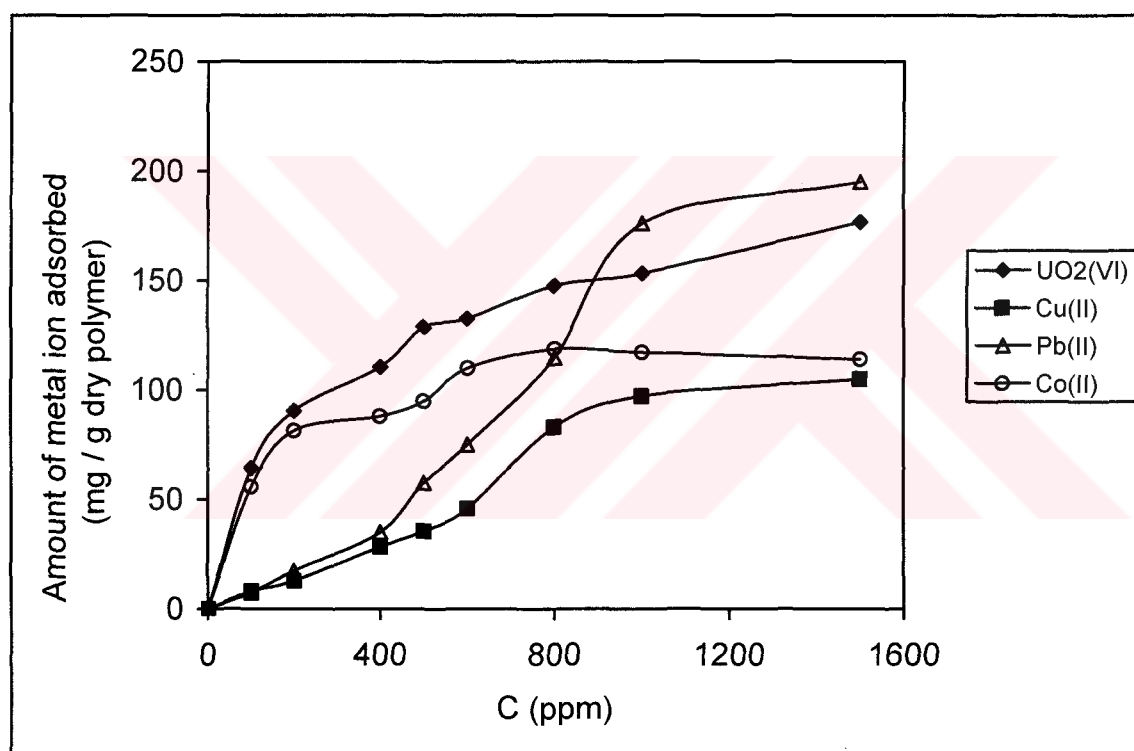


Figure 4.34. Dependence of metal ion uptake on the initial concentrations of metal ions for amidoximated nonwoven fabric.

$\text{UO}_2(\text{VI})$, Pb(II), Cu(II) and Co(II) ions adsorption capacities of the amidoximated nonwoven fabric as a function of initial concentration of metal ions are given in Figure 4.33. As shown in Figure, amidoximated nonwoven fabric showed high affinity for Pb(II) ion as well as $\text{UO}_2(\text{VI})$ ion. Cobalt and copper ions have lower adsorption tendencies compared to lead and uranyl ions as shown in Figure 4.34.

The amount of metal ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased first with increasing the initial concentration of metal ions then reached a plateau value which represents saturation of the active sites (which are available for specific metal ions) on the polymers. It was found that the adsorption capacity of amidoximated nonwoven fabric for Pb(II), UO₂(VI), Cu(II) and Co(II) ions at 1500 ppm was 195, 177, 105 and 114 mg metal ion/g dry polymer, respectively. The order of affinity based on amount of metal ion uptake (mg metal ion/g dry polymer) is as follows: Pb(II) > UO₂(VI) >> Co(II) > Cu(II) for 1500 ppm solutions. The order is different for lower concentration UO₂(VI) being the mostly adsorbed ion. The amidoximated poly(DPAAm) and amidoximated nonwoven fabric exhibited affinity for UO₂(VI) and Pb(II), particularly for uranyl ion, but lower affinity for Cu(II) and Co(II) ions.

The amidoximated poly(DPAAm) has higher adsorption capacity for all metal ions studied in this work than the amidoximated nonwoven fabric as shown in Figure 4.33-4.34. The explanation can be given as follows; poly(DPAAm) was obtained as a homopolymer directly from N,N'-dipropionitrile acrylamide monomer but the amidoximated nonwoven fabric was firstly grafted with GMA (glycidyl methacrylate) and then functionalized with 3,3'-iminodipropionitrile which was not 100 % complete. The conversion of nitrile groups into amidoxime for poly(DPAAm) was higher than for amidoximated nonwoven fabric.

An extensive sorption study on poly(amidoxime) polymer which was obtained from the copolymer of acrylonitrile-divinylbenzene was undertaken especially for extraction of uranium from aqueous solutions by Egawa and Kabay (Egawa et al., 1991; Kabay et al., 1994). They found that the sorption capacity of uranyl ion was about 310 mg/g (the initial concentration of UO₂(VI) ion solution was 2700 ppm). Vernon and Shah prepared a chelating polymer bearing hyrdoxamic/amidoxime groups and the binding of copper and uranium was observed to be 165 and 214 mg/g respectively (the initial concentration of U(VI) ion solution was 0.1 M) (Vernon and Shah, 1983). Lutfor et al. studied the adsorption of uranium ions onto poly(acrylonitrile) grafted sago starch and it was found that uranium ion uptake by this polymer was 283 mg/g (Lutfor et al., 2000). Rivas et al. studied used a commercial poly(amidoxime) chelating polymer and investigated the adsorption

capacity of Cu(II), Cd(II), Hg(II), Pb(II) and UO₂(VI) ions by batch technique (Rivas et al., 2000). It was found that this resin exhibited affinity for UO₂(VI) and Pb(II), but no affinity for the other metal ions. Adsorption capacity of this polymer from 4.98 mM (1344 ppm) initial solution of uranium was 130 mg/g. In this study, adsorption capacities of the new polymers with regard to 1500 ppm solution of uranyl ion was found to be 390 mg/g for amidoximated poly(DPAAm) and 173 mg/g for amidoximated nonwoven fabric. Under the light of these findings, it can be said that bidentate amidoxime polymers developed in this study is more efficient compared to monodentate amidoxime polymers.

Adsorption isotherms of amidoximated poly(DPAAm) and amidoximated nonwoven fabric were analyzed according to the linear form of the Langmuir isotherms for uranyl ion, as,

$$\frac{C_e}{q_e} = (1/K_L q_{mon}) + (1/q_{mon})C_e$$

where C_e is the equilibrium concentration of adsorbate in solution, q_e represents the adsorbed UO₂(VI) ion per unit mass of adsorbent at equilibrium. q_{mon} denotes the amount of adsorption corresponding to complete monolayer coverage. K_L is the Langmuir constant. A plot of C_e/q_e versus C_e would give K_L and q_{mon} (Giles et al., 1960).

The plots of isotherms are shown in Figure 4.35 and seen to be linear over the whole concentration range studied. K_L and q_{mon} values which were calculated from Langmuir equation are given in Table 4.4. The constant, K_L , contains enthalpic interaction of the binding of metal ions with polymer, and can be found from the intercept of the lines given in Figure 4.35. As can be seen from the Table 4.4, K_L value of amidoximated poly(DPAAm) is bigger than amidoximated nonwoven fabric which indicate the favorable interaction of accessible amidoxime sites on the surface of the polymer. q_{mon} is a quantity representing adsorption capacity, also known as monolayer coverage of the surface. q_{mon} values of amidoximated polymer and nonwoven fabric from the Langmuir equation for UO₂(VI) ions were

found to be 400 mg/g and 180 mg/g, respectively. This is very good accordance with the results previously found and discussed on page 103-104.

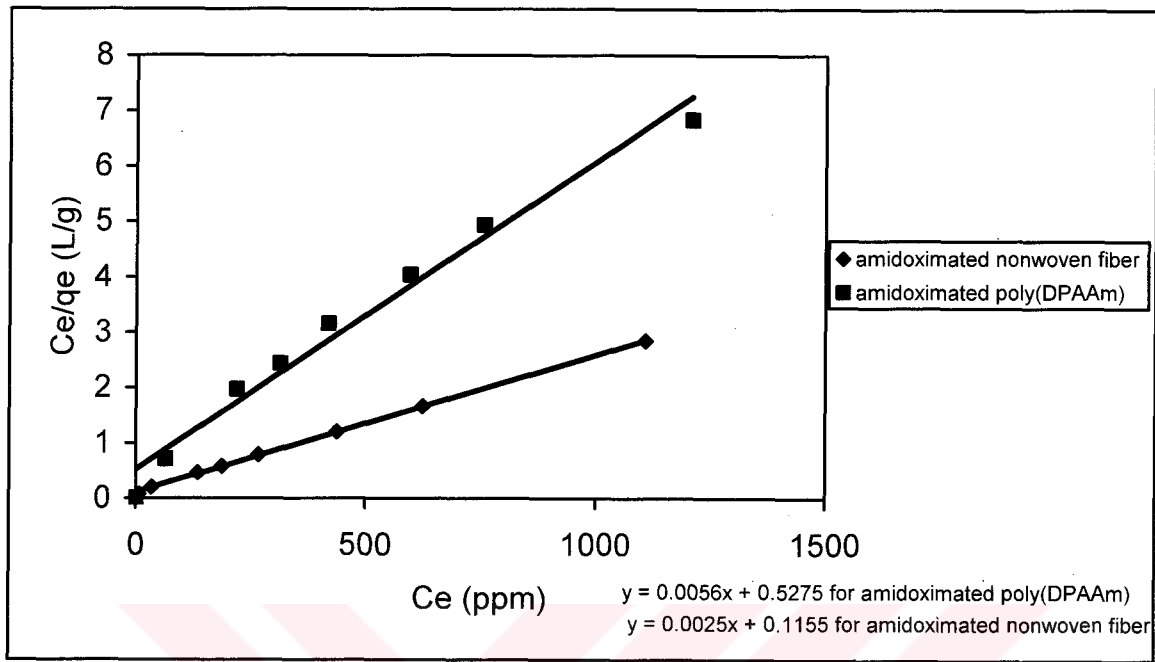


Figure 4.35. Langmuir isotherms for UO₂(VI) ion adsorption on amidoximated poly(DPAAm) and nonwoven fabric.

Table 4.4. K_L and q_{mon} values determined from Fig. 4.35 for the adsorption of UO₂²⁺.

For UO ₂ (VI) adsorption	amidoximated poly(DPAAm)	amidoximated nonwoven fabric
K_L	2.16×10^{-2}	1.06×10^{-2}
q_{mon}	400	180

In order to understand the possible interaction between metal ions and amidoximated poly(DPAAm) and amidoximated nonwoven fabric, FTIR spectra of metal ion adsorbed samples and non-adsorbed samples were taken and shown in Figure 4.36. Due to interactions with UO₂(VI) ions, there is a shift in N-O characteristic bands of polymers. As can be seen from Figure 4.36, after the adsorption of UO₂(VI) ion, the N-O band around at 927 cm⁻¹ shifts to 899 cm⁻¹, as a result of interactions of corresponding groups with UO₂(VI). It was assumed that,

the M^+-O^- bond becomes stronger, exhibit a lower stretching frequency (Dwyer and Mellor, 1964). These differences can be better seen in difference spectrum given in Figure 4.37. According to the difference FTIR spectrum and known literature, a new peak appeared at 904 cm^{-1} assigned to O-U-O stretching vibration (Akkaş and Güven, 2000; Rivas et al., 2000).

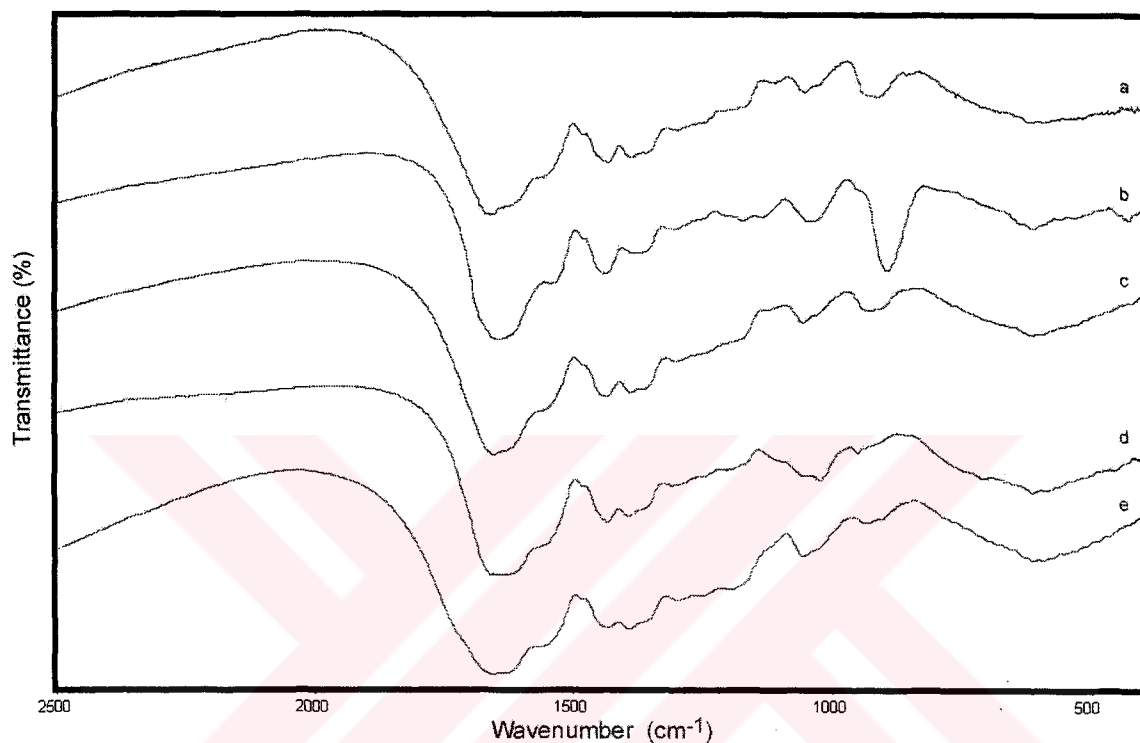


Figure 4.36. FTIR spectra of (a) unadsorbed (b) UO_2^{2+} ion adsorbed, (c) Pb^{2+} ion adsorbed, (d) Cu^{2+} ion adsorbed, (e) Co^{2+} ion adsorbed amidoximated poly(DPAAm).

After the adsorption of other metal ions, the similar differences were observed. For the spectrum of adsorbed Pb, Cu and Co sample, N-O band at around 927 cm^{-1} becomes weaker and shifts to around 920 cm^{-1} .

Figure 4.38 shows the FTIR spectra of amidoximated nonwoven fabric before and after metal ions adsorption. Similarly, it was observed the N-O band around at 940 cm^{-1} shift to 906 cm^{-1} and newly peak appeared at 904 cm^{-1} assigned to O-U-O stretching vibration as can be seen difference spectrum given in Figure 4.39. Similar shifts were observed for the other metal ions. All above results proved the interaction between the metal ions and amidoximated polymer.

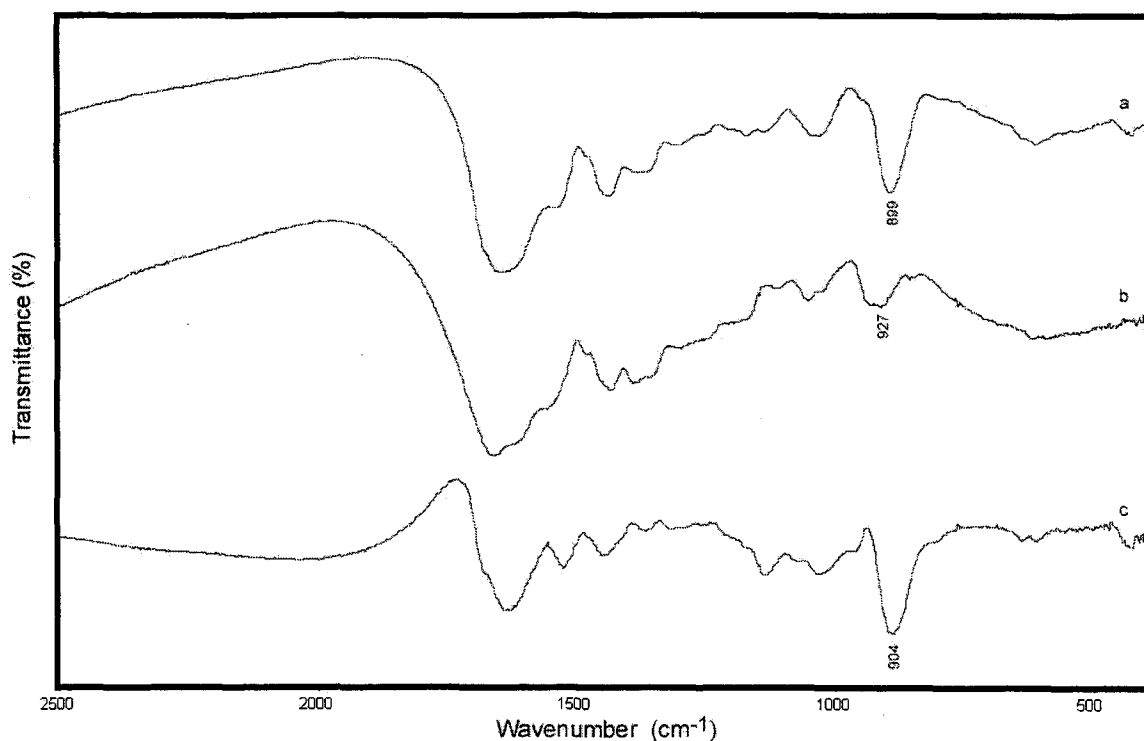


Figure 4.37. FTIR spectra of (a) UO_2^{2+} ion adsorbed and (b) unadsorbed amidoximated poly(DPAAm), (c) spectral differences between (a) and (b).

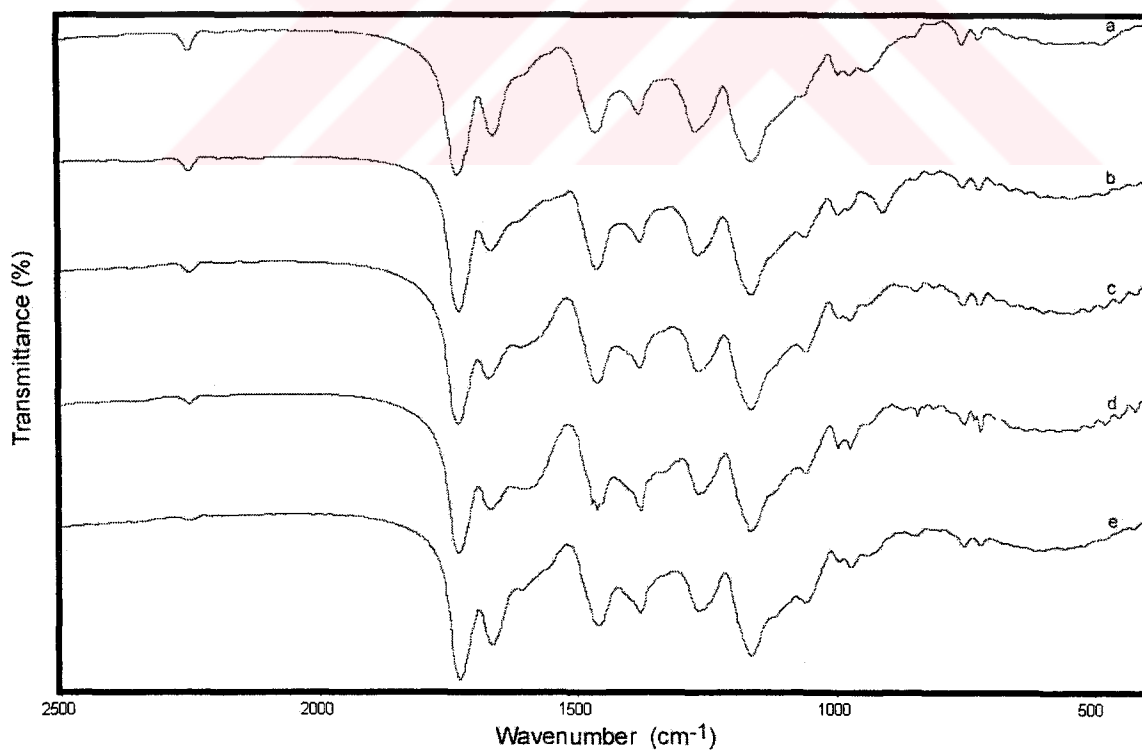


Figure 4.38. FTIR spectra of (a) unadsorbed (b) UO_2^{2+} ion adsorbed, (c) Pb^{2+} ion adsorbed, (d) Cu^{2+} ion adsorbed, (e) Co^{2+} ion adsorbed amidoximated nonwoven fabric.

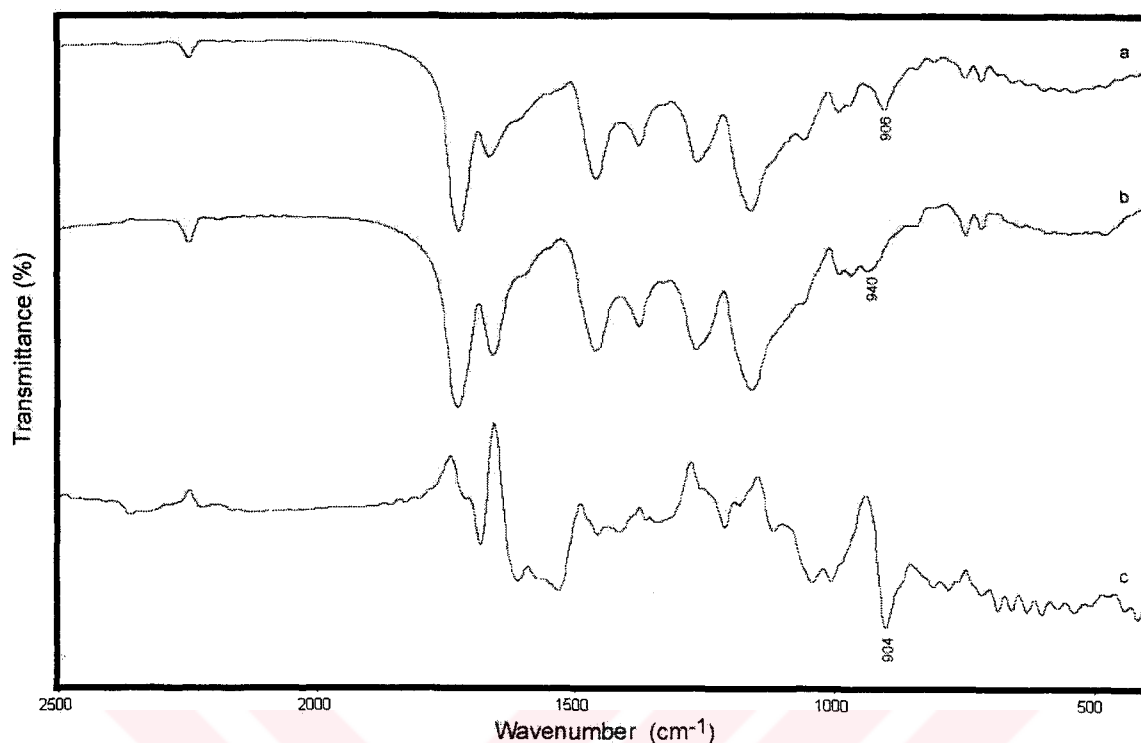


Figure 4.39. FTIR spectra of (a) UO_2^{2+} ion adsorbed and (b) unadsorbed amidoximated nonwoven fabric, (c) spectral differences between (a) and (b).

It was concluded from these results that, the adsorption capacities of these new poly(amidoxime) chelating polymers for uranium and vanadium ions are very high. The advantages of these new polymeric adsorbents containing two amidoxime groups per repeating unit are the presence of these excess amidoxime groups and an additional diethylene spacer units between the neighboring amidoxime groups in each monomeric unit. These properties make these new adsorbents more accessible for the adsorption of metal ions in aqueous systems than the conventional adsorbents having only one amidoxime group per repeating unit.

CONCLUSION

- ❖ A new polymer containing double amidoxime groups per repeating unit was synthesized to enhance the metal ion uptake capacity. For this purpose, N,N'-dipropionitrile acrylamide (DPAAm) monomer was first synthesized by the reaction of 3,3'-iminodipropionitrile and acryloyl chloride. The poly (DPAAm) was synthesized by free radical polymerization reaction using AIBN in ethanol and 77 % conversion was obtained. The polymer synthesized was reacted with hydroxylamine to convert the double nitrile groups in repeat units into amidoximes and after 10 h reaction time 99 % conversion has been reached. The unique advantage of this polymer is that it contains double amidoxime groups per repeating unit, an additional diethylene spacer unit between neighbouring amidoxime groups in each monomeric unit. This polymer is known to be the first acrylic bidentate amidoxime polymer in the amidoxime polymer family reported in the literature.
- ❖ Amidoximated poly(DPAAm) in powder form has shown to provide a rapid uptake within 1 h for the metal ions, U(VI), V(V), Cu(II), Co(II) and Ni(II) studied here with high capacity for U(VI) and V(V) ions. Approximately 100 % adsorption of uranium and vanadium ions for all concentrations (3.3-1000 ppb) have been reached. From the competitive adsorption studies it was seen that the new adsorbent was quite selective for uranium than the other metal ions as depicted by corresponding distribution coefficients (D). The selectivity order determined by calculating D was found to be $U(VI) > V(V) \gg Co(II) = Cu(II) \gg Ni(II)$. This new polymer has a higher vanadium and uranium ion adsorption capacity and adsorption rate from seawater. These results showed that this novel adsorbent containing two amidoxime group per repeating units is quite promising for the enrichment and separation of uranium and vanadium ion from seawater and aqueous solutions.
- ❖ Environmentally stable PE coated PP non-woven fabrics were used as base material for the synthesis of a new adsorbent for metal-ions. In order to introduce specific functional groups to the trunk polymer, GMA was first grafted onto pre-irradiated fabrics. The resultant epoxy groups were opened and

replaced with iminodipropionitrile groups. The IDPN groups were introduced onto the graft chains of PP/PE nonwoven fabric at a conversion of 70 % while maintaining the necessary physical strength of the fabric. The nitrile groups were later converted to amidoxime groups which are known to exhibit good affinity towards several metal-ions, uranyl being the most selected.

- ❖ The structure of newly synthesized (N, N- dipropionitrile acrylamide) monomer, poly(DPAAm) and its amidoximated form were characterized by elemental analysis, FT-IR spectroscopy and thermal analysis methods. The all-nonwoven fabric structures were characterized by using FT-IR, SEM and thermal analysis methods. The binding mechanism of metal ions with amidoxime groups were investigated by using FTIR for amidoximated poly(DPAAm) and amidoximated nonwoven fiber.
- ❖ The new fibrous adsorbent containing two adjacent amidoxime groups in graft chain repeating units has been shown to provide a rapid uptake for the metal ions, U(VI), V(V), Cu(II), Pb(II), Co(II), studied here with high capacity for U(VI) and V(V) ions. 100 % adsorptions of uranium and vanadium ions for all concentrations (3.3-1000 ppb) have been reached. When adsorption was studied from a mixture of ions used here, quite high selectivity has been observed for U(VI) and V(V) ions adsorption in the presence of Pb(II), Cu(II) and Co(II) ions. The order of selectivity which was determined by calculating the distribution coefficient D of metal ions was found to be $V(V) > U(VI) \gg Cu(II) \geq Pb(II) \gg Co(II)$. Uptake of 2.5 mg metal ion/g of adsorbent has been achieved by the adsorption of both uranium and vanadium ions from aqueous solutions with concentrations similar to seawater concentrations.
- ❖ The results of uranyl ion adsorption studies for the two adsorbents developed in this work complied with the Langmuir-type isotherm. The adsorption capacities were found to be 400 mg uranyl ion/g dry polymer and 180 mg uranyl ion/ g dry polymer for amidoximated poly(DPAAm) and nonwoven fabric, respectively. In conclusion, sorption capacities of the newly synthesized poly(amidoxime) chelating polymers for uranium ion were found to be high due to the presence of double amidoxime groups on the repeating units.

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