

**ION SORPTION PROPERTIES OF HEXACYCLENES AND
LEAD IONOPHORE MODIFIED POLYMERS**

**HEKZASİKLEN VE KURŞUN İYONOFOR İLE MODİFİYE
EDİLMİŞ POLİMERLERİN İYON TUTMA ÖZELLİKLERİ**

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Müberra Şen

ABSTRACT

In this submitted thesis, lead ionophore (2-hydroxymethyl-15-crown-5) modified hydrogels (poly(NHMMA-15-crown-5) were synthesized as a specific sorbent for separation, pre-concentration and determination of trace amounts of Pb(II) ions, further more poly(NHMMA-hexacyclene) hydrogels were produced for the specific gold recovery from the samples containing trace amount of gold. Hydrogels were produced by radiation polymerization technique using ^{60}Co -gamma source, related to the irradiation dose and pH, swelling ratios of the hydrogels were determined. For the structural characterization of hydrogels, FT-IR spectra were investigated. The effect of pH, initial concentration and adsorption equilibrium time on the adsorption properties of hydrogels was examined by GF-AAS.

It was observed that gold ion adsorption capacity of the poly(NHMMA-hexacyclene) hydrogels was high at low pH's and reached a maximum value at pH 1.0. Adsorption capacity of the hydrogels for gold ions in acidic media was about 1138 mg/g dry hydrogels and also adsorption equilibrium time was found as 10 h. At least 91.7% recovery was examined using 0.8 M thiourea in 3M HCl solution as a desorption agent.

Poly(NHMMA-15-crown-5) hydrogels showed high selectivity to lead ions at every pH's and adsorption capacity at pH 6.0 was found to be 594 mg/g dry hydrogels. The best desorption agent for the adsorbed lead ions was 3.0 M HNO_3 solution. Adsorption-desorption cycles showed that the feasibility of repeated use was at least 5 times for the hydrogels.

Both of the hydrogels were used for different sample solutions and found that discovered methods worked very well. Validity of the methods showed that methods were efficient for the practical applications. Matrix effects of the other metal ions were eliminated; recovery and pre-concentration of Pb(II) and Au(III) ions were performed perfectly.

Keywords: Hexacyclene, 2-(hydroxymethyl)-15-crown-5, pre-concentration, recovery, hydrogel, matrix elimination, atomic absorption spectrometry.

Supervisor: Prof. Dr. Bekir Salih, Hacettepe University, Department of Chemistry, Physical Chemistry Section.

HEKZASİKLEN VE KURŞUN İYONOFOR İLE MODİFİYE EDİLMİŞ POLİMERLERİN İYON TUTMA ÖZELLİKLERİ

Müberra Şen

ÖZ

Sunulan bu tezde, kurşun iyonofor (2-hidroksimetil-15-taç-5) ile modifiye edilen hidrojeller (poli(NHMMA-15-taç-5) düşük miktardaki kurşun iyonlarının ayrılması, değiştirilmesi ve tayini için seçici bir sorbent olarak sentezlenmiştir, bundan başka düşük miktarda altın içeren maddelerden spesifik olarak altının geri kazanımı için poli(NHMMA-hekzasiklen) hidrojelleri üretilmiştir. Hidrojeller radyasyon polimerizasyonu tekniği ile ⁶⁰Co-gama kaynağı kullanılarak sentezlenmiş, ışınlama dozuna ve pH'a bağlı olarak hidrojellerin şişme oranları tayin edilmiştir. Hidrojellerin karakterizasyonu için FT-IR spektrumları incelenmiştir. Başlangıç metal iyonu derişiminin, pH'ın ve adsorpsiyon denge zamanının hidrojellerin adsorpsiyon özelliklerine olan etkileri GF-AAS kullanılarak gözden geçirilmiştir.

Poli(NHMMA-hekzasiklen) hidrojellerinin altın iyonu kapasitesinin düşük pH'da yüksek olduğu ve pH 1.0'de maximum değere ulaştığı tespit edilmiştir. Hidrojellerin asidik ortamda altın iyonları için adsorpsiyon kapasitesi 1138 mg/g, ayrıca adsorpsiyon denge zamanı da 10 saat olarak bulunmuştur. Desorpsiyon maddesi olarak 3 M HCl içinde 0,8 M tiyoüre çözeltisi kullanılarak geri kazanım en az 91.7% olarak elde edilmiştir.

Poli(NHMMA-15-taç-5) hydrojelleri her pH'da kurşun iyonlarına karşı yüksek seçicilik göstermektedir ve adsorpsiyon kapasitesi pH 6.0'da 594 mg/g olarak bulunmuştur. Adsorplanan kurşun iyonları için en iyi desorpsiyon maddesi 3 M HNO₃ çözeltisidir. Adsorpsiyon-desorpsiyon işlemleri hidrojellerin en az 5 defalık kullanım için uygunluğunu göstermiştir.

Her iki hidrojel değişik çözeltiler için kullanılmış ve bulunan yöntemlerin çok iyi çalıştığı görülmüştür. Metotların doğruluğunu tasdik etmek, onların pratik uygulamalar için verimli olduğunu göstermiştir. Diğer metal iyonlarının matriks etkileri yok edilmiş, altın ve kurşun iyonlarının geri kazanımı ve değiştirilmesi tamamen yerine getirilmiştir.

Anahtar Kelimeler: Hekzasiklen, 2-(hidroksimetil)-15-ta-5, n-deriřtirme, geri kazanım, hidrojel, matriks uzaklařtırma, atomik absorpsiyon spektrometresi.

Danıřman: Prof. Dr. Bekir Salih, Hacettepe Universitesi, Kimya Blm, Fiziko Kimya Anabilim Dalı.

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ABBREVIATIONS

AAS	: Atomic Absorption Spectrometry
NHMMA	: N-(Hydroxymethyl)methacrylamide
FT-IR	: Fourier Transform Infrared Spectrometry
GF-AAS	: Graphite Furnace Atomic Absorption Spectrometry
ICP-MS	: Inductively Coupled Plasma-Mass Spectrometry
ppm	: Part per million
ppb	: Part per billion

1. INTRODUCTION

Macromolecular science had a major impact on the way we live. It is difficult to find an aspect of our lives that is not affected by polymers. Today, polymers are commonly used in thousands of products as plastics, elastomers, coatings, and adhesives. Hydrogels that are known as water swollen crosslinked polymers, have been great interest to scientists for many years because of their hydrophilic character and potential to be biocompatible.

Hydrogels usually contain a much higher amount of water than of polymer. Some gels can reach extremely high portions of water, and are referred to as “superabsorbent” materials. “Permanent” hydrogels require that the polymer chains can be crosslinked by covalent chemical bonds as opposed to reversible interactions such as hydrogen bonds. The crosslinking can be readily achieved using ionizing radiation, which can be employed with a wide range of polymer types, can be done at room temperature. There are easy process control, possibility of joining hydrogel formation and sterilization in one technological step, no necessity to add any initiators and cross-linkers, possibly harmful and difficult to remove, no waste, relatively low running cost for the using irradiation techniques.

Research on the use of radiation in production of hydrogels has become intense during more than a decade, interest has grown continuously, and a large number of papers have been published over the past few years. Numerous applications have been found or envisioned for these materials, particularly in the biomedical area. Uses include: wound dressings, soft contact lenses, controlled-release drug delivery systems, artificial skin, water absorbents, and adsorbents for metal ions or enzymes for purification or catalysis applications.

Heavy Metals can exert detrimental effects on human health and on the environment. Their ecotoxicological properties are generally well known. Therefore separation and determination of heavy metals is a very important process. Also recovery of precious metal ions from other metals at really high concentrations beside the very low concentration of noble metal ions is necessary, too. For this reason, metal complexation polymers have found such application as removal of metal contaminants and extraction of metals from aqueous media. In this way,

very low concentration levels of the metal ions could be determined in various matrices with sufficient sensitivity, selectivity, reliability, accuracy and reproducibility. Recovery of metals from diluted solutions is one classical application for polymeric ligands.

Pre-concentration of trace metals is important in analytical chemistry. In many cases metal ions must be separated from other constituents in the solution that could interfere with the ionic species. Therefore, selective pre-concentration depends on the nature of the sample, the type and concentration of metal ions, and the method to be used for the determination.

For practical analytical applications it is important to combine pre-concentration and separation methods with metal complexation polymers, especially in the presence of interfering components in the analyte solutions. In this way, pre-concentration by functional polymers was successfully applied to the analysis of heavy metals in waters with atomic absorption spectroscopy. The Atomic Absorption Spectrometry (AAS) technique, which offers fast multi-elemental analysis, suffers from a poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples. This drawback can be overcome by a combination of a suitable pre-concentration technique with subsequent AAS determination.

When concentrations in the order of 1 part per million (ppm) or even as low as several part per billion (ppb) are to be determined with less than four different metals, AAS is frequently the choice of the analyst. If more than four different metals are to be determined, in particular on a simultaneous basis, inductively coupled plasma-atomic emission spectrometry (ICP-AES) or the more recent inductively coupled plasma-mass spectrometry (ICP-MS) can be the choice of the analyst.

In this study, hydrogels were synthesized by irradiating from aqueous solutions of N-(Hydroxymethyl)methacrylamide (NHMMA) with known as a lead ionophore, 2-(hydroxymethyl)-15-crown-5, and hexacyclene trisulfate in the ^{60}Co - γ source. Poly(NHMMA-hexacyclene) hydrogels containing amine groups that make specific binding with Au(III) ions and poly(NHMMA-15-crown-5) hydrogels containing oxo

groups that make specific binding with Pb(II) ions were used for the removal, preconcentration and the recovery of gold and lead ions from aqueous media eliminating matrix effects. After the characterization of hydrogels, initial concentration and pH effect on the adsorption capacity, adsorption kinetics, selectivity, recovery and pre-concentration of Au(III) and Pb(II) ions, in the aqueous solutions, onto the synthesized hydrogels were examined. Validity of the methods was tested using spike adding technique and certified sea water. Finally, recovery, pre-concentration and the measurement of the trace level of metal ions in different samples were examined.

2. THEORETICAL

2.1. Heavy Metal Toxicity

There are 35 metals that concern us because of occupational or residential exposure; 23 of these are the heavy elements or "heavy metals". These are antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc. Interestingly, small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (International Occupational Safety and Health Information Centre, 1999).

For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important for us to inform ourselves about the heavy metals and to take protective measures against excessive exposure. If unrecognized or inappropriately treated, toxicity can result in significant illness and reduced quality of life (Ferner, 2001). For persons who suspect that they or someone in their household might have heavy metal toxicity, testing is essential. Appropriate conventional and natural medical procedures may need to be pursued (Dupler, 2001).

The association of symptoms indicative of acute toxicity is not difficult to recognize because the symptoms are usually severe, rapid in onset, and associated with a known exposure or ingestion (Ferner, 2001). The symptoms are cramping, nausea, and vomiting; pain; sweating; headaches; difficulty breathing; impaired cognitive, motor, and language skills; mania; and convulsions. The symptoms of toxicity resulting from chronic exposure (impaired cognitive, motor, and language

skills; learning difficulties; nervousness and emotional instability; and insomnia, nausea, lethargy, and feeling ill) are also easily recognized; however, they are much more difficult to associate with their cause. Symptoms of chronic exposure are very similar to symptoms of other health conditions and often develop slowly over months or even years. Sometimes the symptoms of chronic exposure actually abate from time to time, leading the person to postpone seeking treatment, thinking the symptoms are related to something else.

2.1.1. Definition of a heavy metal

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4 °C (39 °F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide, 1992).

2.1.2. Beneficial heavy metals

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Diagnostic medical applications include direct injection of gallium during radiological procedures, dosing with chromium in potential nutrition mixtures, and the use of lead as a radiation shield around x-ray equipment (Roberts, 1999). Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth (International Occupational Safety and Health Information Centre, 1999). Many of these products are in our homes and actually add to our quality of life when properly used.

2.1.3. Precious metals

The members of platinum group elements (PGEs) and gold are called “precious” or “noble” metals. These metals have interesting physical and chemical properties beside low abundance on earth and high economic value. Catalytic activity and nobility are unique properties of precious metals from these respects. They find wide range application in many field e.g. as catalyst in various chemical processes, in electrical and electronic industries, in medicine and in jewellery.

Gold is one of the rarest elements of earth. Its concentration is about 4 mg/L (ppb) in the upper crust of the earth and 0,01 mg/m³ in seawater. Platinum and palladium have smaller abundance on earth than gold. Growing demand for platinum and palladium resulted from their using in auto-catalyst systems. Platinum complexes, cisplatin and second-generation compounds have been applied in chemotherapy as effective anticancer drugs. Gold is used in electrical circuit materials and in jewellery. High inertness of noble metals toward many chemical reagents also makes the determination of precious metals important.

These metals often occur at trace levels in sample types of complex composition. This situation has improved recently due to developments of instrumental methods and their applications to analysis of precious metals in a variety of matrices. Attention has been given to determination of precious metals in biological, clinical, environmental and industrial samples. But the determination of trace and ultra trace amount of precious metals in natural samples, a pre-concentration procedure is often required. Also separation of precious metal ions from other metal ions at really high concentrations beside the very low concentration of noble metal ions in geological and other natural samples, specific polymeric solvents are necessary. In this way, very low concentration levels of the noble metal ions could be determined in various matrices with sufficient sensitivity, selectivity, reliability, accuracy and reproducibility. For these purpose, variety type of separation methods have been used i.e., adsorption, co-precipitation, cation/anion exchange, complexsation or chelation, oxidation/reduction, liquid-liquid extraction.

Adsorption or solid-phase extraction is moderately using technique for separation of precious metals from interfering matrices to determine. Hydrogels are also very

convenient polymeric sorbents for this aim. Because of their three-dimensional network structure and water is filling the spaces between the polymer chains. They have a number of analytical applications.

2.1.4. Toxic heavy metals

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children (Roberts, 1999). Children may develop toxic levels from the normal hand-to-mouth activity of small children who come in contact with contaminated soil or by actually eating objects that are not food (dirt or paint chips) (Dupler, 2001). Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous (parenteral) nutrition, from a broken thermometer (Smith et al., 1997), or from a suicide or homicide attempt (Lupton et al., 1985).

As a rule, acute poisoning is more likely to result from inhalation or skin contact of dust, fumes or vapours, or materials in the workplace. However, lesser levels of contamination may occur in residential settings, particularly in older homes with lead paint or old plumbing (International Occupational Safety and Health Information Centre, 1999). The Agency for Toxic Substances and Disease Registry (ATSDR) in Atlanta, Georgia, (a part of the U.S. Department of Health and Human Services) was established by congressional mandate to perform specific functions concerning adverse human health effects and diminished quality of life associated with exposure to hazardous substances. The ATSDR is responsible for assessment of waste sites and providing health information concerning hazardous substances, response to emergency release situations, and education and training concerning hazardous substances. In cooperation with the U.S. Environmental Protection Agency, the ATSDR has compiled a Priority List for 2001 called the "Top 20 Hazardous Substances." The heavy metals arsenic (1), lead (2), mercury (3), and cadmium (7) appear on this list.

2.1.5. Commonly encountered toxic heavy metals

As noted earlier, there are 35 metals of concern, with 23 of them called the heavy metals. Toxicity can result from any of these metals. This protocol will address the metals that are most likely encountered in our daily environment. Briefly covered will be four metals that are included in the ATSDR's "Top 20 Hazardous Substances" list. Iron and aluminum will also be discussed even though they do not appear on the ATSDR's list.

2.1.5.1. Arsenic

Arsenic is the most common cause of acute heavy metal poisoning in adults and is the number 1 on the ATSDR's "Top 20 List." Arsenic is released into the environment by the smelting process of copper, zinc, and lead, as well as by the manufacturing of chemicals and glasses. Arsine gas is a common by-product produced by the manufacturing of pesticides that contain arsenic. Arsenic may be also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. Target organs are the blood, kidneys, and central nervous, digestive, and skin systems (Roberts, 1999).

Signs and Symptoms: Exposure to arsenic occurs mostly in the workplace, near hazardous waste sites, or in areas with high natural levels. Symptoms of acute arsenic poisoning are sore throat from breathing, red skin at contact point, or severe abdominal pain, vomiting, and diarrhea, often within 1 hour after ingestion. Other symptoms are anorexia, fever, mucosal irritation, and arrhythmia. Cardiovascular changes are often subtle in the early stages but can progress to cardiovascular collapse.

Chronic or lower levels of exposure can lead to progressive peripheral and central nervous changes, such as sensory changes, numbness and tingling, and muscle tenderness. A symptom typically described is a burning sensation ("needles and pins") in hands and feet. Neuropathy (inflammation and wasting of the nerves) is usually gradual and occurs over several years. There may also be excessive darkening of the skin (hyper pigmentation) in areas that are not exposed to sunlight, excessive formation of skin on the palms and soles (hyperkeratosis), or

white bands of arsenic deposits across the bed of the fingernails (usually 4-6 weeks after exposure). Birth defects, liver injury, and malignancy are possible. (Arsenic has also been used in homicides and suicides).

2.1.5.2. Lead

Lead is the number 2 on the ATSDR's "Top 20 List." Lead accounts for most of the cases of pediatric heavy metal poisoning (Roberts, 1999). It is a very soft metal and was used in pipes, drains, and soldering materials for many years. Millions of homes built before 1940 still contain lead (e.g., in painted surfaces), leading to chronic exposure from weathering, flaking, chalking, and dust. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries. The remainder is used for cable coverings, plumbing, ammunition, and fuel additives. Other uses are as paint pigments and in PVC plastics, x-ray shielding, crystal glass production, pencils, and pesticides. Target organs are the bones, brain, blood, kidneys, and thyroid gland (International Occupational Safety and Health Information Centre, 1999).

Signs and Symptoms: Acute exposure to lead is also more likely to occur in the workplace, particularly in manufacturing processes that include the use of lead (e.g., where batteries are manufactured or lead is recycled). Even printing ink, gasoline, and fertilizer contain lead. Symptoms include abdominal pain, convulsions, hypertension, renal dysfunction, loss of appetite, fatigue, and sleeplessness. Other symptoms are hallucinations, headache, numbness, arthritis, and vertigo.

Chronic exposure to lead may result in birth defects, mental retardation, autism, psychosis, allergies, dyslexia, hyperactivity, weight loss, shaky hands, muscular weakness, and paralysis (beginning in the forearms). Children are particularly sensitive to lead (absorbing as much as 50% of the ingested dose) and are prone to ingesting lead because they chew on painted surfaces and eat products not intended for human consumption (e.g., hobby paints, cosmetics, hair colorings with lead-based pigments, and even playground dirt). In addition to the symptoms found in acute lead exposure, symptoms of chronic lead exposure could be

allergies, arthritis, autism, colic, hyperactivity, mood swings, nausea and numbness, lack of concentration, seizures, and weight loss.

2.1.5.3. Mercury

Number 3 on ATSDR's "Top 20 List" is mercury. Mercury is generated naturally in the environment from the degassing of the earth's crust, from volcanic emissions. It exists in three forms: elemental mercury and organic and inorganic mercury. Mining operations, chloralkali plants, and paper industries are significant producers of mercury. Atmospheric mercury is dispersed across the globe by winds and returns to the earth in rainfall, accumulating in aquatic food chains and fish in lakes. Mercury compounds were added to paint as a fungicide until 1990. These compounds are now banned; however, old paint supplies and surfaces painted with these old supplies still exist. Mercury continues to be used in thermometers, thermostats, and dental amalgam. (Many researchers suspect dental amalgam as being a possible source of mercury toxicity. Medicines, such as mercurochrome and merthiolate, are still available. Algaecides and childhood vaccines are also potential sources. Inhalation is the most frequent cause of exposure to mercury.

Signs and Symptoms: Acute mercury exposure may occur in the mining industry and in the manufacturing of fungicides, thermometers, and thermostats. Liquid mercury is particularly attractive to children because of its beautiful silver color and unique behavior when spilled. Children are more likely to incur acute exposure in the home from ingesting mercury from a broken thermometer or drinking medicine that contains mercury. Because mercury vapors concentrate at floor level, crawling children are subject to a significant hazard when the mercury is sprinkled throughout the house during religious ceremonies or when there is an accidental spill (Zayas et al., 1996). Mercury spills are difficult to clean up, and mercury may remain undetected in carpeting for some time. Symptoms of acute exposure are cough, sore throat, and shortness of breath; metallic taste in the mouth, abdominal pain, nausea, vomiting and diarrhea; headaches, weakness, visual disturbances, tachycardia, and hypertension.

The metallic mercury used by dentists to manufacture dental amalgam is shipped as a hazardous material to dental offices. Symptoms in adults and children could include tremors, anxiety, forgetfulness, emotional instability, insomnia, fatigue, weakness, anorexia, cognitive and motor dysfunction, and kidney damage. People who consume more than two fish meals a week are showing very high serum levels of mercury.

2.1.5.4. Cadmium

Cadmium is a by-product of the mining and smelting of lead and zinc and is the number 7 on ATSDR's "Top 20 list." It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Cadmium may be found in reservoirs containing shellfish. Cigarettes also contain cadmium. Lesser-known sources of exposure are dental alloys, electroplating, motor oil, and exhaust. Inhalation accounts for 15-50% of absorption through the respiratory system; 2-7% of ingested cadmium is absorbed in the gastrointestinal system. Target organs are the liver, placenta, kidneys, lungs, brain, and bones (Roberts, 1999).

Signs and Symptoms: Acute exposure to cadmium generally occurs in the workplace, particularly in the manufacturing processes of batteries and color pigments used in paint and plastics, as well as in electroplating and galvanizing processes. Symptoms of acute cadmium exposure are nausea, vomiting, abdominal pain, and breathing difficulty.

Chronic exposure to cadmium can result in chronic obstructive lung disease, renal disease, and fragile bones. Protect children by carefully storing products containing cadmium, especially nickel-cadmium batteries. Symptoms of chronic exposure could include alopecia, anemia, arthritis, learning disorders, migraines, growth impairment, emphysema, osteoporosis, loss of taste and smell, poor appetite, and cardiovascular disease.

2.1.5.5. Iron

Discussion of iron toxicity in this protocol is limited to ingested or environmental exposure. Iron overload disease (hemochromatosis), an inherited disorder, is discussed in a separate protocol. Iron does not appear on the ATSDR's "Top 20 List," but it is a heavy metal of concern, particularly because ingesting dietary iron supplements may acutely poison young children (e.g., as few as five to nine 30-mg iron tablets for a 30-lb child).

Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption. Most overdoses appear to be the result of children mistaking red-coated ferrous sulfate tablets or adult multivitamin preparations for candy. (Fatalities from overdoses have decreased significantly with the introduction of child-proof packaging. In recent years, blister packaging and the requirement that containers with 250 mg or more of iron have child-proof bottle caps have helped reduce accidental ingestion and overdose of iron tablets by children.) Other sources of iron are drinking water, iron pipes, and cookware. Target organs are the liver, cardiovascular system, and kidneys (Roberts, 1999).

2.1.5.6. Aluminum

Although aluminum is not a heavy metal (specific gravity of 2.55-2.80), it makes up about 8% of the surface of the earth and is the third most abundant element. It is readily available for human ingestion through the use of food additives, antacids, buffered aspirin, astringents, nasal sprays, and antiperspirants; from drinking water; from automobile exhaust and tobacco smoke; and from using aluminum foil, aluminum cookware, cans, ceramics, and fireworks.

Studies suggesting that aluminum might have a possible connection with developing Alzheimer's disease when researchers found what they considered to be significant amounts of aluminum in the brain tissue of Alzheimer's patients. Although aluminum was also found in the brain tissue of people who did not have Alzheimer's disease, recommendations to avoid sources of aluminum received widespread public attention. As a result, many organizations and individuals reached a level of concern that prompted them to dispose of all their aluminum

cookware and storage containers and to become wary of other possible sources of aluminum, such as soda cans, personal care products, and even their drinking water.

However, the World Health Organization (WHO, 1998) concluded that, although there were studies that demonstrate a positive relationship between aluminum in drinking water and Alzheimer's disease, the WHO had reservations about a causal relationship because the studies did not account for total aluminum intake from all possible sources. Although there is no conclusive evidence for or against aluminum as a primary cause for Alzheimer's disease, most researchers agree that it is an important factor in the dementia component and most certainly deserves continuing research efforts. Therefore, at this time, reducing exposure to aluminum is a personal decision. Workers in the automobile manufacturing industry also have concerns about long-term exposure to aluminum (contained in metal working fluids) in the workplace and the development of degenerative muscular conditions and cancer. Target organs for aluminum are the central nervous system, kidney, and digestive system.

Signs and Symptoms: Although aluminum is not a heavy metal, environmental exposure is frequent, leading to concerns about accumulative effects and a possible connection with Alzheimer's disease. Acute exposure is more likely in the workplace (e.g., unintentional breathing of aluminum-laden dust from manufacturing or metal finishing processes).

2.2. Removal Mechanisms of Heavy Metals

2.2.1. Sedimentation and flocculation

Once a heavy metal is in a wetland, whether the water is stagnant or mobile, a number of dynamic transformations may occur (Leewaugh, 1990). It may be transported from one compartment to another, e.g. from water to sediments or biota or suspended solids or vice versa. The process of sedimentation is closely related to the hydrological flow patterns of the wetlands. In calm waters particles, which are denser than water, will settle out. For particles, which are light or less dense than water, sedimentation become possible only after floc formation. Particles of clay and organic minerals, which have surface electronic charge

aggregate to form flocs, which generally settle more rapidly in a wetland than do individual particles. Flocs may also adsorb other types of suspended particles including heavy metals. In wetlands, flocculation is enhanced by increased pH, turbulence, concentration of suspended matters, ionic strength and high algal concentration. Small particles flocculate more easily than larger ones in condition of high pH, low turbulence and high concentration and because of their larger surface area they have proportionally greater adsorption potential. Autochthonous production, re-suspension and in the case of estuaries and brackish waters, salinity, are important facilitators in sedimentation and flocculation.

Sedimentation is not a simple straightforward physical reaction. Other processes like complexation, precipitation and co-precipitation have to occur first. Sedimentation is a physical process after other mechanisms aggregate heavy metals into particles large enough to sink. In this way heavy metals are removed from wastewater and trapped in the wetland sediments, thus protecting the ultimate receiving aquatic environment.

2.2.2. Adsorption

In sediments heavy metals are adsorbed to clay and organic matter by electrostatic attraction (Patrick et al., 1990). Once adsorbed on to humic or clay colloids heavy metals will remain as metal atoms, unlike organic pollutants which will ultimately decompose. Their speciation may change with time as the organic molecules binding them decompose or as sediment conditions change. The extent to which metals ions are adsorbed by cation exchange or non-specific adsorption depends on many factors. These include properties of the metals concerned (valence, radius, degree of hydration and co-ordination with oxygen). Other factors are physico-chemical environment (pH and redox status), the nature of the adsorbent medium (permanent and pH-dependent charge complex-forming ligands), and the concentrations and properties of other metals and soluble ligands present (Alloway, 1992). For chemicals such as heavy metals more than 50% can easily be adsorbed onto particulate matter in the wetland and thus be removed from the water component by sedimentation. The selectivity of clay minerals and hydrous oxide adsorbents in soils and sediments found in wetlands for divalent metals generally follows the order $Pb > Cu > Zn > Ni > Cd$, but some differences occur

between minerals and with varying pH conditions. The selectivity order for peat has been shown to be $Pb > Cu > Cd = Zn > Ca$. In general however, Pb and Cu tend to be adsorbed most strongly and Zn and Cd are usually held more weakly, which implies that these latter metals are likely to be more labile and bioavailable (Alloway, 1990). It is usually found that adsorption of metal ions onto solids is described by either the Langmuir or the Freundlich adsorption isotherms equations. Metal adsorption onto manganese oxide can be described by the Langmuir equation for a range of metal concentrations, over about one order of magnitude only (Van den Berg, 1982).

2.2.2.1. Freundlich isotherm

Freundlich isotherm is the oldest and most widely used adsorption equation for solid–liquid system. The empirically derived Freundlich isotherm can be defined as follows:

$$\frac{x}{m} = K_f C_e^{1/n} \quad (2.1)$$

where x/m is unit of adsorbate added per unit of adsorbent (mg/kg), C_e is equilibrium concentration of adsorbate in solution (mg/L). K_f and n can be determined experimentally by determining the degree of adsorption x/m at different concentrations C_e . The information can then be plotted using the following equation.

$$\log \left(\frac{x}{m} \right) = \log K_f + \frac{1}{n} \log C_e \quad (2.2)$$

In a plot of the above equation, $\log K_f$ will be the intercept of the line when C_e is 1 mg/L, and it indicates the adsorption capacities of the solid waste, $1/n$ is the gradient assuming a linear relationship (Onay et al., 2005).

2.2.2.2. Langmuir isotherm

Langmuir (Langmuir, 1918) proposed the first isotherm model which assumed monolayer coverage of the adsorbent surface. The most commonly used

expression of the Langmuir equation for describing adsorption data for solid–liquid systems is

$$\frac{x}{m} = \frac{K_L M C_e}{1 + K_L C_e} \quad (2.3)$$

where x is the amount or concentration of the solute adsorbed in mg, m is the mass of the adsorbent in kg, C_e is the equilibrium concentration of the solute in mg/L, K_L and M are constants. The linearized expression of this equation is

$$\frac{1}{x/m} = \frac{1}{K_L M C_e} + \frac{1}{M} \quad (2.4)$$

This equation is called the “Double-Reciprocal Langmuir Equation” and more suitable for situations in which the distribution of equilibrium concentrations tends to be skewed towards the lower end of the range of the equilibrium concentrations. It was concluded that the Langmuir constant or affinity parameter (K_L) is related to the bonding energy between the adsorbed ion and the adsorbent, but that specific functional relationship is uncertain (EPA, 1992). Kinniburgh noted that K_L is best estimated from the slope of the adsorption isotherm at very low concentrations. The constant M is accepted as the adsorption maximum of the adsorbent with respect to the specific solute and is interpreted as the maximum amount or concentration that an adsorbent can retain.

2.2.3. Co-precipitation

Co-precipitation of heavy metals with secondary minerals, including the hydrous oxides of Fe, Al and Mn is an important adsorptive mechanism in wetland sediments. Cu, Mn, Mo, Ni, V and Zn are co-precipitated in Fe oxides and Co, Fe, Ni, Pb and Zn are co-precipitated in Mn oxides.

Pyrite (FeS_2) forms in reducing conditions when sulphate become reduced to sulphide, producing H_2S which then reacts with Fe^{2+} to form FeS and FeS_2 . The oxidation of sulphides such as pyrite causes marked acidification of wetland soils. This causes heavy metals to go back into solution.

The heavy metals normally found co-precipitated with secondary minerals in soil sediments are (Soposito, 1983):

Fe oxides : V, Mn, Ni, Cu, Zn, Mo

Mn Oxides : Fe, Co, Ni, Zn, Pb

Ca carbonates : V, Mo, Fe, Ni, Co, Cd

Clay minerals : V, Ni, Co, Cr, Zn, Cu, Pb, T, Mn, Fe

2.2.4. Precipitation

Precipitation is one of the major mechanisms by which metals are removed from water in wetlands and deposited in the sediments. The formation of insoluble heavy metal precipitates is one of many factors limiting the bioavailability of heavy metals to many aquatic ecosystems. Precipitation depends on the solubility product (K_{sp}) of the metal species involved, pH of the wetland and concentration of metal ions and relevant anions. Precipitation from a saturated solution of a sparingly soluble heavy metal salt may be represented by the dynamic equilibrium. The constant governing the equilibrium is the rate of removal of metal ions in the form of a precipitate equals the rate of their dissolution from the precipitate. When the values of the concentration of cation and anion are such that their product exceeds K_{sp} , precipitation occurs (Matagi et al., 1998).

2.2.5. Cation and anion exchange

Ion exchange can occur between the counter ions balancing the surface charge on the sediment colloids and the ions in the wetland water. Negative charges on the sediment colloids are responsible for cation exchange, in which exchange of a hydrogen ion for the metal occurs. The extent to which the sediment constituents can act as cation exchangers is expressed as the cation exchange capacity (CEC), measured in cmol_c/kg. Sediment organic matter has a higher capacity than sediment colloids and plays a very important part in adsorption reactions in most soils even though it is normally present in much smaller amount (1-10%) than clays (80%).

Anion exchange occurs when anions are attracted to positive charges on sediment colloids. Hydrous oxides of Fe and Al are usually positively charged and so tend to be the main sites for anion exchange in sediments. Most sediments have smaller capacities for anion exchange than cation exchange. Some anions such as NO_3^- and Cl^- are not adsorbed to any marked extent but others such as HPO_4^{2-} and H_2PO_4^- are strongly adsorbed. Some organic pesticides, such as phenoxyalkanoic acid herbicides, exist as ions at normal sediment pHs and are adsorbed to a limited extent by hydrous oxides and by H_2 bonding to humic polymers.

2.2.6. Complexation

Complexation is a reaction whereby heavy metal ions replace one or more coordinated water molecules in the co-ordination sphere with other nucleophilic groups or ligands. Complexation reactions are important regulators of heavy metal ion speciation in water. In turn, speciation affects metal reactivity and toxicity (Brezonik, 1994). In the case of wetlands the ligands are mainly multidentate organic molecules. These are natural organic matter, including humic, tannic and fulvic acids (HA, TA, & FA). An understanding of heavy metal organic interactions is therefore important in developing realistic models for heavy metal speciation in natural waters. The adsorption of cations on organic substances is mainly due to the general negative charge of these colloidal substances. Redox potential and pH are among some of the factors affecting this process. However the nature of HA and FA poses serious problems in this regard. They are polydispersed defined and this has resulted in a range of different models being advocated for the treatment of their interactions with heavy metals (Buffle, 1984).

Heterogeneous complexants exhibit at least three major distinguishing features.

- Their polyfunctionality, i.e. many complexing sites of different nature present on the same physical structure.
- Their polyelectrolytic character (i.e. possible existence of high electric charge densities due to the presence of large numbers of dissociable functional groups per physical entity).

- The importance of conformational factors (e.g. reaction on surfaces, formation of aggregates etc.) The ability of dissolved organic matter to form complexes with ions in wetlands is of interest because of the associated biological implications, such as bioavailability and toxicity of heavy metals to living organisms and because of its relevance to efforts of understanding geochemical cycles of metals in the environment. The sequences of stability of complexes established by Jonasson (Jonasson, 1977) is $\text{HgCu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cu}$.

2.2.7. Oxidation/Reduction

The redox state of a heavy metal in solution is an important speciation parameter because it can drastically affect its toxicity, adsorptive behaviour and metal transport (Mertz and Cornazer, 1971; Florence et al., 1983). The redox state of the heavy metals depends on whether there are anoxic or oxic conditions in the wetlands. Micro-organisms, such as *Thiobacillus* spp catalyse the oxidation of sulphides. In the case of pollution by tailings from metalliferous mining, particles of ore minerals in the soils, such as, PbS , ZnS and CuFeS_2 become oxidized, releasing metal cations Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} into the sediment when they are adsorbed. Some organic pollutant molecules on the soil surface will undergo photolytic decomposition due to exposure to UV wavelengths in daylight and hence release the metal originally adsorbed on them. Oxidation of organic pollutants occurs by the action of oxygenase enzymes secreted by microorganisms (Moffet and Zika, 1987). Changes in redox potential (E_h) under reducing conditions allows the metals to precipitate as metal sulfides.

2.2.8. Heavy Metal Uptake by Wetlands

Mafabi (Mafabi, 1995) defined wetlands as places where water stays long enough for plants and animals to become adapted to waterlogged conditions. In the case of wetlands plants, Denny (Denny, 1987) recognized the following categories; emergent, surface floating, rooted leaves and submerged macrophytes. Denny (Denny, 1980 and 1987) further noted that main route of heavy metal uptake in wetland plants was through the roots in the case of emergent and surface-floating plants, while euhydrophytes (plants that have completely submerged leaves or both floating and submerged leaves) take up heavy metals through leaves and

roots. Welsh and Denny (Welsh and Denny, 1979) demonstrated that lead was taken from the sediments into the submerged plants *Potamogeton crispus* L. and *Potamogeton pectinatus* L. by minimal translocation to leaf tips, dead regions and in lower older leaves, while extensive acropetal translocation for copper was observed in particular sites of accumulation.

Micro-organisms remove heavy metals directly from wetlands by two major mechanisms; the first is a metabolism dependent uptake of metals into their cells at low concentrations (some toxic metal ions are micronutrients for the micro-organism); the second is bio-sorption which is a non-active adsorption process binding metal ions to the extra cellular charged materials or the cell walls. In micro-organisms, hydrophilic heavy metals ions are believed to be transported across the hydrophobic space of a biomembrane by the "shuttle" process of facilitated diffusion (or host-mediated transport) where a receptor molecule, e.g. a protein on the outer membrane surface binds a metal ion (Langton and Bryan, 1984; Boudon et al., 1983). The hydrophilic metal-receptor complex then diffuses to the interior of the membrane and releases the metal ion into the cytosol where it is trapped, perhaps by reaction with a thiol compound. The receptor then diffuses back to the other surface of the membrane where it may collect another metal ion.

2.3. Hydrogels

Hydrogels are well known as networks of hydrophilic polymers, which can absorb a significant amount of water (> 20% of their dry mass) without dissolving or losing their structural integrity (Peppas and Mikos, 1986; Park et al., 1993). Both chemical and physical methods have been used to create hydrogels. In chemically crosslinked gels, covalent bonds are presented between different polymer chains. In physically crosslinked gel, dissolution is prevented by physical interactions, which exist between different polymer chains (Hennink and Nostrum, 2002). Schemes of chemical and physical hydrogels are presented in Figure 2.1 and 2.2.

Chemical hydrogels may be generated by crosslinking of water-soluble polymers, or conversion of hydrophobic polymers to hydrophilic polymers plus crosslinking to form a network. In the crosslinked state (Figure 2.1), crosslinked hydrogels reach

an equilibrium swelling level in aqueous solutions, which depends mainly on the crosslinked density.

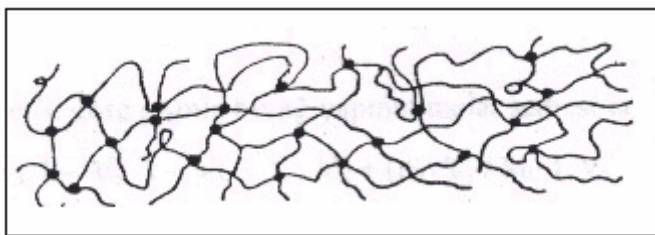


Figure 2.1. Chemical crosslinking

Like physical hydrogels, chemical hydrogels are not homogeneous. They usually contain regions of low water swelling and high crosslinking density, called 'clusters', that are dispersed within regions of high swelling, and low crosslink density. This may be due to hydrophobic aggregation of crosslinking agents, leading to high crosslink density clusters (Drumheller et al., 1995).

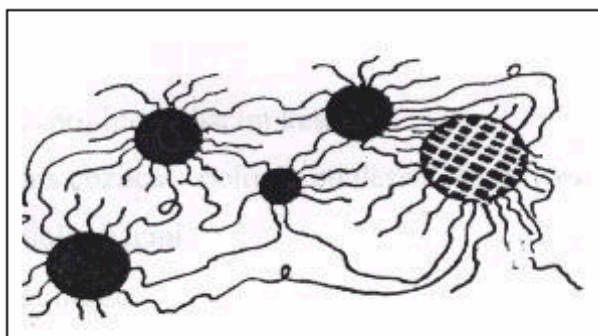


Figure 2.2. Physical crosslinking

For physical hydrogels, networks are held together by molecular entanglements, and/or secondary forces including ionic, H-bonding or hydrophobic forces (Campoccia et al., 1998; Prestwich et al., 1998). Physical hydrogels are not homogeneous, since clusters of molecular entanglements, or hydrophobically- or ionically- associated domains, can create inhomogeneities (Figure 2.2). Free chain ends or chain loops also represent transient network defects in physical gels (Hoffman, 2002).

2.4. Chemically Crosslinked Gels

2.4.1. Crosslinking by radical polymerization

It is possible to obtain gels by polymerizing an appropriate monomer, crosslinking agent, and initiator in a good solvent of the polymer, as in the example of vinyl monomers in the presence of divinyl compounds. Ethylene glycol dimethacrylate and methylene bisacrylamide are often used as crosslinking agents. Free radical initiators start polymerization at a low temperature, so there are times when redox initiators are occasionally used. In these initiators, there is an optimum temperature (high temperature initiator, normal initiator, low-temperature (redox initiator) and very low-temperature initiator) that creates radicals. Therefore, it is important to select the initiators by matching them with the conditions of gel synthesis.

When creating a gel with a uniform network structure, it is important to select a combination where the reactivities of the monomer and the crosslinking agent are similar. It is ideal to have monomers with copolymer reactivity ratios $r_1=r_2=1$ as such a combination leads to random polymerization. However, it is not easy to find such a combination. Generally, it would mean looking for a combination of a monomer with a similar reaction ratio and a crosslinking agent, but the above mentioned relationship is possible only in a low degree of polymerization. When the degree of polymerization is increased, a slight difference between r_1 and r_2 increases the difference in the consumption rates of the monomer and the crosslinking agent, it is necessary to use caution, as this offsets the crosslink density and distribution.

2.4.2. Crosslinking by chemical reaction of complementary groups

Water-soluble polymers owe their solubility properties to the presence of functional groups (mainly OH, COOH, NH) that can be used for the formation of hydrogels. Covalent linkages between polymer chains can be established by the reaction of functional groups with complementary reactivity, such as an amine-carboxylic acid or an isocyanate OH/NH reaction, or by Schiff base formation (Hennink and Nostrum, 2002).

2.4.2.1. Crosslinking with aldehydes

Water-soluble polymers with hydroxyl groups (e.g. poly (vinyl alcohol)) can be crosslinked using glutaraldehyde (Peppas and Berner, 1980; Dai and Barbari, 1999). In order to establish crosslinking, rather drastic conditions have to be applied (low pH, high temperature, methanol added as quencher). In contrast, amine containing polymers can be crosslinked with the same reagent under mild conditions whereby so-called Schiff bases are formed. This has especially been investigated for the preparation of crosslinked proteins (e.g. albumin) (Willmott et al., 1984) and gelatin (Tabata and Ikada, 1989; Yamamoto et al., 2000) and amine containing polysaccharides (Jameela and Jayakrishnan, 1995). Because glutaraldehyde is a toxic compound that even at low concentration shows cell-growth inhibition, alternatives have been developed crosslinking of gelatin using polyaldehydes obtained by partial oxidation of dextran has been reported (Draye et al., 1998). These gels were designed for application in wound treatment and epidermal growth factor (EFG) was incorporated to promote wound healing.

2.4.2.2. Crosslinking by addition reaction

Water-soluble polymers can be converted into hydrogels using bis (or higher) functional cross linking agents which react with functional groups of water-soluble polymers via addition reactions. Polysaccharides can be crosslinked with 1, 6-hexa methylenediisocyanate (Brondsted, 1995), divinylsulfone (Gehrke, 1998), or 1, 6-hexanedibromide (Coviello et al., 1999) and many other reagents. The network properties can be easily tailored by the concentration of the dissolved polymer and the amount of crosslinking agent. The crosslinking reactions are preferably carried out in organic solvents, because water can also react with the crosslinking agent. Further, since the crosslinking agents are generally speaking very toxic, the gels have to be extracted extensively to remove traces of unreacted agents. Once these matrices are aimed for the release of pharmaceutically active agents, they have to be loaded after the gel formation and extraction process. This means that protein molecules can be loaded in meshes of the gels, which are larger than the protein and these systems therefore show typically first-order release. This often results in a limited duration of the release. Finally, between the polymer chains, linkages are established which are rather stable. This means that

degradation only occurs once the polymer backbone is degraded by enzymes (Brondsted et al., 1998).

2.4.2.3. Crosslinking by condensation reaction

Condensation reactions between hydroxyl groups or amines with carboxylic acids or derivatives here of are frequently applied for the synthesis of polymers to yield polyesters and polyamides, respectively. These reactions can also be used for the preparation of hydrogels. Crescezi et al. described the synthesis of polysaccharide hydrogels via the Passerini and Ugi condensation reactions (Nooy et al., 1999; Nooy et al., 2000). In the Passerini condensation a carboxylic acid and an aldehyde or ketone are condensed with an isocyanide to yield an α -(acryloxy) amide. In the Ugi condensation an amine is added to this reaction mixture finally yielding an α -(acylamino) amide. The reaction can be carried out in water at slightly acidic pH and at room temperature. Since the Passerini condensation yields hydrogels with ester bonds in their cross-links, these gels degrade at ambient temperature and pH 9.5. The degradation time varied, depending on their composition, from 1 to 8 days. Since gels prepared using the Ugi condensation contain amide bonds in their cross-links, these gels were stable under these conditions.

2.4.3. Crosslinking by high energy irradiation

Hydrogels can be obtained by radiation technique in a few ways, including irradiation of solid polymer, monomer (in bulk or in solution) or aqueous solution of polymer. The first method, i.e. irradiation of hydrophilic polymer in a dry form (e.g. Burillo and Ogawa, 1986; Nedkov and Tsvetkova, 1994), has some draw-backs. It may require special sample preparation (like pressing or melting), and some difficulties may be encountered in obtaining homogeneous macroscopic hydrogels. Moreover, it requires usually much higher doses to obtain a gel compared to irradiation in solution, and, furthermore, it may be difficult to remove fully the oxygen, that can promote unwanted side reactions (cf. Rosiak et al., 1995b). One of the reasons for the high gelation doses in dry state is that radiation-chemical yield of radicals that are the precursors of cross-links, is usually lower than in aqueous solution. Also the restricted motion of the radical-bearing chains limits the

effectiveness of crosslinking. One has to note, however, that from the necessity to use higher doses for gelation in the solid state it does not follow that more energy is needed for the formation of an average link between the chains. Radiation doses are calculated as energy per mass unit of the system. If we assume that gelation occurs when, on average, one crosslink is formed per each polymer chain (Charlesby, 1960). It is obvious that more cross-links are needed for the gelation of 1 kg of a solid polymer sample, than for gelation of 1 kg of its dilute solution.

More frequently the method of monomer irradiation is applied (e.g. Rosiak, 1991, 1994). In this technique polymerization takes place in the first stage, followed by crosslinking of the formed chains. This way is possibly most convenient when the chosen monomer is easily available but its polymer is not. Since many of the monomers used are harmful or even toxic (usually contrary to the corresponding polymers), particular care has to be taken when using this method for the formation of hydrogels for biomedical use to ensure that either all the monomer has reacted or its unreacted residues have been fully extracted afterwards, in a separate operation. Since during irradiation of monomer many consecutive and parallel reactions occur, the system is rather complicated and difficult for qualitative description, although some attempts were undertaken (Rosiak et al., 1983, 1988a, b; Tobita, 1993a, b). It is a frequent practice to add some bifunctional monomer to the mixture to increase the efficiency of crosslinking. It has to be stressed that in many cases this synthesis method works very well. There are rare cases, like with poly (vinyl alcohol) gels, where it cannot be used because of the instability of the monomer.

The irradiation of polymers in aqueous solution, since such systems, containing neither monomers nor crosslinking agents (otherwise frequently used to enhance gel formation), are easier to control and study, lower number of usually unwanted processes occurs, as, for example, homo-grafting of monomer on a polymer chain that may lead to branched structures, and, last but not least, hydrogels formed in this way are suitable for biomedical use (certainly, provided that a proper polymer is chosen) with no need of further purification. Typical examples of simple, synthetic polymers used for hydrogel formation by this method are poly (vinylalcohol) (PVA), poly (vinylpyrrolidone) (PVP), poly (-ethylene oxide) (PEO),

polyacrylamide (PAAm), poly (acrylic acid) (PAAc) and poly (vinyl methyl ether) (PVME). Gels obtained from two latter substrates belong to the group being of particular interest as the components of "intelligent biomaterials", since their properties are sensitive to environmental stimuli-pH, ionic strength (PAA) and temperature (PVME). Useful set of basic physical and chemical data as well as general literature survey on water-soluble polymers, were published by Molyneux (Molyneux, 1987).

2.4.4. Crosslinking using enzymes

Sperinde et al. published an interesting method using an enzyme to synthesize PEG-based hydrogels. In their approach, a tetrahydroxy PEG was functionalized with glutaminy groups (PEG-Q_a). PEG net-works were then formed by the addition of trans-glutaminase to aqueous solutions of PEG-Q_a and poly (lysine-co-phenylalanine). This enzyme catalyzes the reaction between the γ -carboxamide group of the PEG-Q and the ϵ -amine group of lysine to yield an amide linkage between the polymers. The gel properties could be tailored by the ratio of the PEG-Q_a and the lysine copolymer. Under suitable conditions, gels were formed with an equilibrium water content of 90% (Sperinde, 1997).

2.5. Application Fields of Hydrogels

A number of interesting variations on hydrogel materials have been reported in recent years. Hydrogels have been grafted onto surfaces, or into pores of materials, for purposes of achieving hydrophylic characteristics or biocompatibility. Fabrics having hydrophylic materials grafted to their surfaces are being investigated as reinforcing agents for use in enhancing the strength of hydrogels (Lopérgolo et al., 2000). Radiation crosslinking of naturally occurring polymers such as polysaccharides, is being investigated for production of biodegradable hydrogels (Paparella et al., 1996) (Aso et al., 1999). "Nanogel" materials, consisting of individual macromolecules that are internally crosslinked by irradiation of dilute solutions, have been described (Ulański et al., 1998).

Specially modified hydrogels are being studied for wastewater purification. Gels containing acid groups have been made to bind ions, including uranium and nickel, for use in removal of metals from aqueous media (Kantoğlu, 1999; Pekel, 2000).

Other hydrogels have been used to demonstrate the scavenging of textile dye molecules for purification of wastewater streams (Duran et al., 1999). Enzyme adsorption into hydrogels has been studied for use in industrial processes. For example amylase (used in the fermentation industry) was shown to retain its activity for a longer time when bound to a gel (Tümtürk et al., 1999). Bound catalysts have a number of advantages including easy separation after processing.

Recently hydrogels have found a wide range of biomedical applications including controlled drug delivery systems, replacement blood vessels, wound dressing, soft tissue substitution and contact lenses. A variety of other uses for responsive hydrogels are being investigated, including such things as artificial muscles, valves and actuators (Ichijo et al., 1995). Hydrogels are generally found to be very well tolerated when implanted in vivo and can be easily tailored to suit the many functions of prosthetics in contact with blood or tissues. The success of hydrogels as biomaterials lies in their resemblance to living tissue because of their relatively high water content which minimizes the frictional irritation of surrounding tissue. Additional advantages of hydrogels are their non-toxicity, non-antigenicity, non-irritability, and chemical stability. The relatively high water content of hydrogels made them also permeable to small molecules like oxygen, nutrients, and metabolites. The high solute permeability of hydrogels made them ideal materials of choice as devices for the controlled release of drugs and other active agents. Much of the research on hydrogels has been focused on the application in controlled drug delivery. By proper design of hydrogels it is possible to control the kinetics delivery of active ingredients.

Hydrogel materials exhibiting the responsive phenomenon have received much attention for application in controlled release of drugs (Şen, M. and Güven, O., 1995). By repeated contraction/expansion cycles, it is possible to release pulses of small molecules dissolved in the hydrogel matrix (Miyajima et al., 1995). An on- off device based on an electroresponsive hydrogel that releases a drug molecule is being developed (Kaetsu, 1995).

2.6. Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) was discovered in the early 1950s, and has become a well-used and widely accepted technique for trace metal determination in a wide variety of samples. The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength, which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

2.6.1 Quantitative analysis by atomic absorption

The atomic absorption process is illustrated in Figure 2.3. Light at the resonance wavelength of initial intensity, I_0 , is focused on the flame cell containing ground state atoms. The initial light intensity is decreased by an amount determined by the atom concentration in the flame cell. The light is then directed onto the detector where the reduced intensity, I , is measured. The amount of light absorbed is determined by comparing I to I_0 .

2.6.1.1. Theoretical concepts and definitions

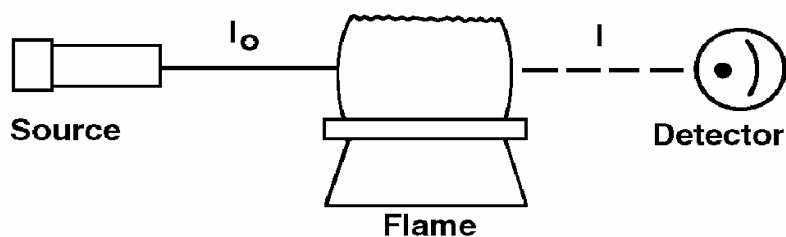


Figure 2.3. The atomic absorption process.

Several related terms are used to define the amount of light absorption, which has taken place. The “transmittance” is defined as the ratio of the final intensity to the initial intensity.

$$T = I/I_0 \quad (2.5)$$

Transmittance is an indication of the fraction of initial light which passes through the flame cell to fall on the detector. The “percent transmission” is simply the transmittance expressed in percentage terms.

$$\%T = 100 \times I/I_0 \quad (2.6)$$

The “percent absorption” is the complement of percent transmission defining the percentage of the initial light intensity which is absorbed in the flame.

$$\%A = 100 - \%T \quad (2.7)$$

These terms are easy to visualize on a physical basis. The fourth term, “absorbance”, is purely a mathematical quantity.

$$A = \log (I_0/I) \quad (2.8)$$

Absorbance is the most convenient term for characterizing light absorption in absorption spectrometry, as this quantity follows a linear relationship with concentration. Beer’s Law defines this relationship:

$$A = abc \quad (2.9)$$

where “A” is the absorbance; “a” is the absorption coefficient, a constant which is characteristic of the absorbing species at a specific wavelength; “b” is the length of the light path intercepted by the absorption species in the absorption cell; and “c” is the concentration of the absorbing species. This equation simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions.

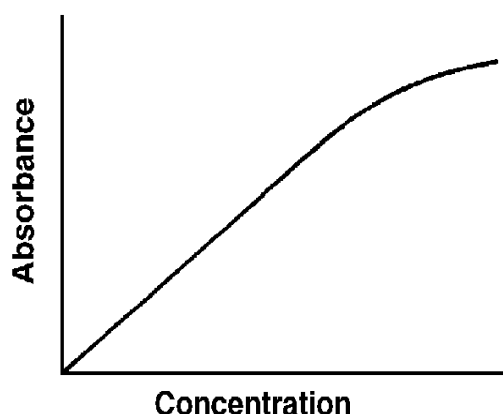


Figure 2.4. Concentration versus absorbance.

This directly proportional behaviour between absorbance and concentration is observed in atomic absorption. When the absorbances of standard solutions containing known concentrations of analyte are measured and the absorbance data are plotted against concentration, a calibration relationship similar to that in Figure 2.4 is established. Over the region where the Beer's Law relationship is observed, the calibration yields a straight line. As the concentration and absorbance increase, non-ideal behavior in the absorption process can cause a deviation from linearity, as shown.

After such a calibration is established, the absorbance of solutions of unknown concentrations may be measured and the concentration determined from the calibration curve. In modern instrumentation, the calibration can be made within the instrument to provide a direct readout of unknown concentrations. Since the advent of microcomputers, accurate calibration, even in the nonlinear region, is simple.

2.6.2. The basic components

Every absorption spectrometer must have components, which fulfill the three basic requirements. There must be: (1) a light source; (2) a sample cell; and (3) a means of specific light measurement.

In atomic absorption, these functional areas are implemented by the components illustrated in Figure 2.5. A light source which emits the sharp atomic lines of the

element to be determined is required. The most widely used source is the hollow cathode lamp. These lamps are designed to emit the atomic spectrum of a particular element, and specific lamps are selected for use depending on the element to be determined.

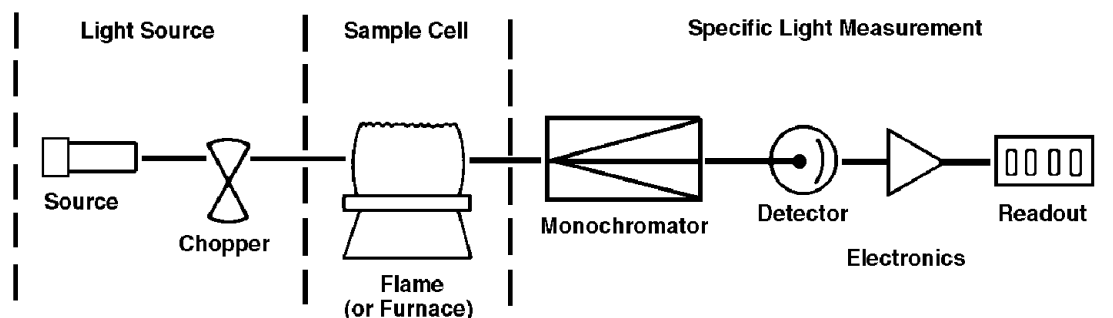


Figure 2.5. Basic AA spectrometer.

It is also required that the source radiation be modulated (switched on and off rapidly) to provide a means of selectively amplifying light emitted from the source lamp and ignoring emission from the sample cell. Source modulation can be accomplished with a rotating chopper located between the source and the sample cell, or by pulsing the power to the source.

Special considerations are also required for a sample cell for atomic absorption. An atomic vapor must be generated in the light beam from the source. This is generally accomplished by introducing the sample into a burner system or electrically heated furnace aligned in the optical path of the spectrophotometer. Several components are required for specific light measurement. A monochromator is used to disperse the various wavelengths of light which are emitted from the source and to isolate the particular line of interest. The selection of a specific source and a particular wavelength in that source is what allows the determination of a selected element to be made in the presence of others.

The wavelength of light which is isolated by the monochromator is directed onto the detector, which serves as the “eye” of the instrument. This is normally a photomultiplier tube, which produces an electrical current dependent on the light intensity. The electrical current from the photomultiplier is then amplified and processed by the instrument electronics to produce a signal which is a measure of

the light attenuation occurring in the sample cell. This signal can be further processed to produce an instrument readout directly in concentration units.

2.6.3. Atomization of the sample

Two systems are commonly used to produce atoms from the sample. Aspiration involves sucking a solution of the sample into a flame; and electrothermal atomization is where a drop of sample is placed into a graphite tube that is then heated electrically. Some instruments have both atomization systems but share one set of lamps. Once the appropriate lamp has been selected, it is pointed towards one or other atomization system.

2.6.3.1. Flame aspiration

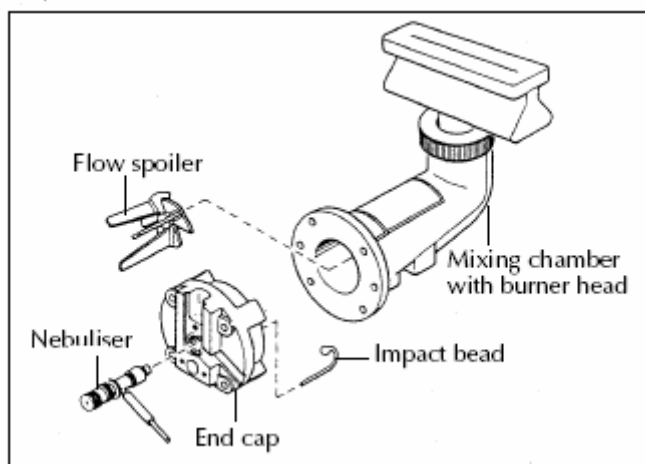


Figure 2.6. Typical burner and spray chamber

Figure 2.6 shows a typical burner and spray chamber. Ethyne/air (giving a flame with a temperature of 2200–2400 °C) or ethyne/dinitrogen oxide (2600–2800 °C) are often used. A flexible capillary tube connects the solution to the nebuliser. At the tip of the capillary, the solution is 'nebulised' – *ie* broken into small drops. The larger drops fall out and drain off while smaller ones vaporize in the flame. Only *ca* 1% of the sample is nebulised.

2.6.3.2. Electrothermal atomization

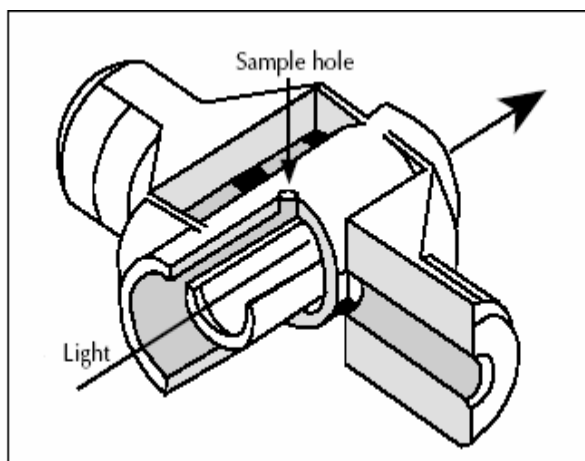


Figure 2.7. Hollow graphite tube with a platform

Figure 2.7 shows a hollow graphite tube with a platform. 25 μL of sample (*ca* 1/100th of a raindrop) is placed through the sample hole and onto the platform from an automated micropipette and sample changer. The tube is heated electrically by passing a current through it in a pre-programmed series of steps. The details will vary with the sample but typically they might be 30–40 seconds at 150 $^{\circ}\text{C}$ to evaporate the solvent, 30 seconds at 600 $^{\circ}\text{C}$ to drive off any volatile organic material and char the sample to ash, and with a very fast heating rate (*ca* 1500 $^{\circ}\text{C s}^{-1}$) to 2000–2500 $^{\circ}\text{C}$ for 5–10 seconds to vaporize and atomize elements (including the element being analyzed). Finally heating the tube to a still higher temperature – *ca* 2700 $^{\circ}\text{C}$ – cleans it ready for the next sample. During this heating cycle the graphite tube is flushed with argon gas to prevent the tube burning away. In electrothermal atomization almost 100% of the sample is atomized. This makes the technique much more sensitive than flame AAS.

2.6.4. Background absorption

It is possible that other atoms or molecules apart from those of the element being determined will absorb or scatter some radiation from the light source. These species could include unvaporized solvent droplets or compounds of the matrix (chemical species, such as anions, that tend to accompany the metals being

analyzed) that are not removed completely. This means that there is a background absorption as well as that of the sample.

One way of measuring and correcting this background absorption is to use two light sources, one of which is the hollow cathode lamp appropriate to the element being measured. The second light source is a deuterium lamp.

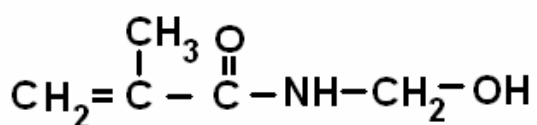
The deuterium lamp produces broad band radiation, not specific spectral lines as with a hollow cathode lamp. By alternating the measurements of the two light sources – generally at 50 –100 Hz – the total absorption (absorption due to analyte atoms plus background) is measured with the specific light from the hollow cathode lamp and the background absorption is measured with the light from the deuterium lamp. Subtracting the background from the total absorption gives the absorption arising from only analyte atoms.

3. EXPERIMENTAL

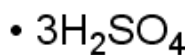
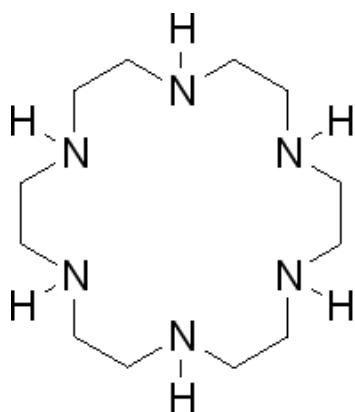
3.1. Synthesis and Characterization of Hydrogels

3.1.1. Materials

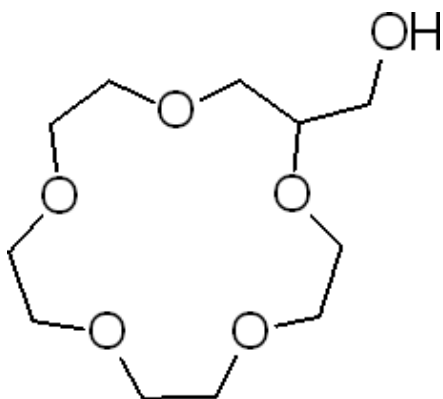
Hexacyclene trisulfate, 2-(hydroxymethyl)-15-crown-5 (lead ionophore) and N-(Hydroxymethyl)methacrylamide (NHMMA) were purchased from Aldrich (Milwaukee, USA) and used as received. IR grade KBr was obtained from Merck (Germany). All chemicals were used as received without further purification. Open structure of the monomer and the ligands are given in Figure 3.1.



N-(Hydroxymethyl)methacrylamide



Hexacyclene trisulfate



2-(Hydroxymethyl)-15-crown-5

Figure 3.1. Chemical structure of monomer and the ligands.

3.1.2. Preparation of hydrogels

About 1 mL of NHMMA-hexacyclene-water and NHMMA-2-(hydroxymethyl)-15-crown-5-water ternary mixtures containing different amount of the monomer, hexacyclene, 2-(hydroxymethyl)-15-crown-5 and water were placed in poly vinyl chloride (PVC) straws of 3 mm diameter and irradiated in a ^{60}Co - γ source (Russian made PX-30 Isslodovatelj, 1.97 kGy/h) at a variable dose rates. Hydrogels were taken out from straws and washed several times with distilled water to remove all unreacted monomers and low molecular weight polymeric materials from hydrogels. Firstly, hydrogels were dried in air and in vacuum oven at 60 °C for 5 days, and then stored in desiccators until use.

3.1.3. Water uptake of hydrogels

Water uptakes of the hydrogels were determined to study the swellability of the hydrogels. The experiment was conducted as follows: 0.2 g weighed dry hydrogel was placed in 100 mL cylindrical glass tube containing 50 mL of deionized water. The hydrogels were allowed to swell at room temperature with occasional shaking. Periodically removed hydrogels were weighed using an electronic balance to calculate the swellability of the hydrogels. The weight ratio of dry and wet samples was recorded. The swelling ratios of the hydrogels were calculated by using the following expression.

$$\text{Swelling ratio (\%)} = [(W_{\text{swollen}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100$$

3.1.4. Elemental analysis

The amount of hexacyclene content into poly(NHMMA-hexacyclene) hydrogels and 2-(hydroxymethyl)-15-crown-5 content into poly(NHMMA-15-crown-5) hydrogels were determined by elemental analysis data of the dried samples obtained using an elemental analyzer (Leco, CHNS-932, USA). Between 1.0 and 2.0 mg of synthesized hydrogels, at different mixture and at different irradiated doses, were placed in to the tin capsule and introduced inside furnace of the elemental analyzer system to obtain the percent of C, H and N.

3.1.5. FT-IR spectra

FT-IR spectra of the synthesized hydrogels at different monomer ratios and radiation doses were obtained by using an FT-IR spectrometer (Mattson 10000 FT-IR Spectrometer, Unicam, UK). Around 0.02 g of poly(NHMMA-hexacyclene) and poly(NHMMA- 15-crown-5) hydrogels were dried in vacuum oven at 60 °C for 5 days to remove all adsorbed water and then powder form of the hydrogels were thoroughly mixed with 0.1 g of KBr to obtain homogeneous mixtures. These mixtures were pressed to form tablets after mixing well, and then the FT-IR spectra were recorded.

3.2. Treatment of Au(III) Ions onto Poly(NHMMA-hexacyclene) Hydrogels and Pb(II) Ions onto Poly(NHMMA- 15-crown-5) Hydrogels

3.2.1. Reagents

1980.7 mg L⁻¹ Au(III) standart was prepared from solid NaAuCl₄ (BDH, England); 1000 mg L⁻¹ Pb(II) standart was prepared from solid Pb(NO₃)₂ (BDH, England). Other solutions were prepared from these stock solutions daily. Hydrochloric acid, nitric acid and pure sodium hydroxide pellets were used to adjust pH of sample solutions. Thiourea and H₃PO₄ were used as desorption agents. All of these chemicals were purchased from Merck (Germany). De-ionized water of 18.2 MΩ.cm resistivity obtained from a Milli Q-water purification system (Millipore) served for preparation of all solutions.

3.2.2. Apparatus

Table 3.1. Working conditions of hallow cathode lamps.

ELEMENT	WAVELENGTH	SLIT WIDTH	CURRENT
Au	242.8 nm	0.7 nm	8 mA
Pb	247.6 nm	0.2 nm	20 mA

A Perkin Elmer Analyst 100 Atomic Absorption spectrometer with HGA 800 Electrothermal Atomization unit, equipped with deuterium lamp background correction was employed. Hallow cathode lamp of gold (Nuffield Road) and lead (Perkin Elmer) were used. The working conditions are given in Table 3.1. Pyrolitic coated graphite furnaces (Perkin Elmer) were used for analyses.

For analyses of matrix elimination on the Au(III) ion determination and selectivity of poly(15-crown-5) hydrogels; metal ion concentrations were measured by inductively coupled plasma-mass spectrometry equipped with AS-510 autosampler (ICP-MS, 7500a series, Agilent –UK). Argon plasma was used and flow rate of all gases were set 15.0, 0.90 and 1.11 L min⁻¹, spray chamber was cooled by water, scan acquisition mode was set and pulse counting detector was used with 320 μ s channel⁻¹ dwell time.

3.2.3. Adsorption of the metal ions

Adsorption of Au(III) and Pb(II) ions from aqueous solutions was investigated in batch experiments. Effects of the pH, adsorption kinetics and the initial concentration of the ions in the adsorption media were studied.

20 mL gold ion solution was treated with ~12 mg of the poly (NHMMA-hexacyclene) hydrogels at different pH values (in the range of 1.0–8.0) (adjusted with HCl–NaOH). For the gold ion uptake from a single solution, 20 mL of aqueous gold ion solutions with different concentrations (in the range of 1–1980.7 mg/L) were treated with ~12 mg of the poly (NHMMA-hexacyclene) hydrogels at pH 1.0 (adjusted with HCl–NaOH).

Aqueous lead ion solution of 20 mL at different pH values (in the range of 1.0–8.0, adjusted with HNO₃–NaOH) were treated with ~12 mg poly(NHMMA-15-crown-5) hydrogels. For the effect of the initial concentration, lead ion solutions of 20 mL with different concentrations (in the range of 1–1000 mg/L) were treated with the ~12 mg poly(NHMMA-15-crown-5) hydrogels at pH 6.0.

To find the adsorption kinetics of the Pb(II) and Au(III) ions, 10 and 100 ppm of 20 mL of metal ion solutions were treated with ~0.05 g of modified hydrogels. To examine kinetic behaviour of the poly(NHMMA-hexacyclene) hydrogels for gold ions, pH of the solutions were adjusted to 1.0. Kinetics of the lead ion adsorption onto the poly(NHMMA-15-crown-5) hydrogels were studied at pH 4.0. During the experiments, at some times about 100 μ L samples were taken out.

48 h agitation time and 400 rpm agitation speed (at room temperature) was applied in glass bottles in order to prevent complete adsorption for all experiments.

The hydrogels were separated from the adsorption mediums after the sufficient time for adsorption, and the remaining concentration of the metal ions in the aqueous phases were measured by GF-AAS after the dilutions. The amounts of adsorbed metal ions were obtained by using the following expression.

$$\text{Metal ions adsorbed} = [(C_o - C_A) \times V] / [m \times 1000]$$

C_o and C_A are the concentrations of the metal ions in the initial solution and in the aqueous phase after adsorption respectively (mg L^{-1}). V is the volume of the aqueous phase (mL), and m is the amount of the polymer (g).

3.2.4. Desorption of the metal ions

Hydrogels loaded with metal ions were washed several times with deionized water. 20 mL of 0.8 M thiourea in 3 M HCl solution was used to desorb all gold ions adsorbed onto the poly(NHMMA-hexacyclene) hydrogels. Desorption of lead ions from the poly(NHMMA-15-crown-5) hydrogels were achieved by using 20 mL of 3 M HNO_3 . Metal ions adsorbed polymeric materials were placed in desorption mediums and stirred at 400 rpm for 48 h. At the end of desorption period, a part of the supernatant solutions were removed and measured by GF-AAS. Desorption ratio was obtained by using the following expression.

$$\text{Desorption ratio} = \frac{\text{quantity of metal desorbed to the elution medium}}{\text{quantity of metal ions adsorbed onto the sorbent}}$$

3.2.5. Pre-concentration of the metal ions

$5 \times 10^{-2} \mu\text{g L}^{-1}$ Au(III) ion solution was prepared from standard solution of this metal ion separately. After adjusting pH to 1.0 by using concentrated hydrochloric acid; volume was adjusted to 1.0 L with deionized water. Then 0.02 g of poly (NHMMA-hexacyclene) hydrogel was treated with solution at the conditions of 400 rpm agitation rate. After 48 h adsorption time, supernatant was separated and Au(III) ion adsorbed poly (NHMMA-hexacyclene) hydrogel was placed in 2 mL of 3 M of HCl containing 0.8 M of thiourea for the desorption of gold ions from the hydrogel for 48 h.

For the pre-concentration of Pb(II) ions, $5 \times 10^{-2} \mu\text{g L}^{-1}$ of 1.0 L of Pb(II) ion solution was treated with poly(NHMMA-15-crown-5) hydrogel at the conditions of 400 rpm agitation rate after adjusting pH to 4.0 by using 1 M NaOH. After the 48 h incubation period, the hydrogel was separated from solution and washed with deionized water, then by using 3 M HNO_3 , lead ions were desorbed in 2 mL during 48 h.

Then the metal ion contents of desorption mediums were analyzed by GF-AAS. Pre-concentration of the metal ions were calculated by using the initial and final amounts of them.

3.3. Determination of Pb(II) Ions in Sea Water, Tap Water, Drinking Water and Well Water

Recovery and pre-concentration steps are necessary for the determination of Pb(II) ions in sea water, tap water, drinking water and well water. For recovery of Pb(II) ions, into the 20 mL of sea water (19 Mayıs- Samsun), tap water (Beytepe- Ankara), drinking water (Kabalak- Ankara) and well water (19 Mayıs- Samsun), 1 M NaOH was added to adjust the pH to 4.0 and ~10 mg of the poly(NHMMA-15-crown-5) hydrogels were placed into the solutions. After 48 h of agitation period at 400 rpm, the hydrogels were separated from solutions and washed with deionized water. Then hydrogels were placed into the 20 mL desorption mediums containing 3 M HNO_3 solutions.

For the pre-concentration of Pb(II) ions; 250 mL of each solutions were treated with hydrogels after adjusting the pH to 4.0 and desorbed into 5 mL of desorption agents as described in the recovery experiments.

Then lead ion concentrations were measured in aqueous phases by GF-AAS. From the experimental data, recovery and pre-concentration results were calculated for the Pb(II) ions.

3.4. Selectivity of Poly(NHMMA-15-crown-5) Hydrogels

The selectivity of poly(NHMMA-15-crown-5) hydrogels for lead ions was examined at three different pH values (2.0, 4.0 and 6.0). Solutions that Pb(II), Cu(II), Ni(II), Co(II), Ag(I), Cr(II), Cd(II), Fe(III) and Zn(II) ions were mixed, containing 0.5 mM of

each metal ions were treated with poly(NHMMA-15-crown-5) hydrogels. In a second experiment, beside 0.5 mM Cu(II), Ni(II), Co(II), Ag(I), Cr(II), Cd(II), Fe(III) and Zn(II) ions, Pb(II) ion concentrations were decreased 100-fold. The metal ion concentrations were measured after the 48 h, by ICP-MS. In all experiments, 20 mg of hydrogels and 50 mL of metal ion mixture solutions were used.

3.5. Determination and Recovery of Au (III) Ions in Anode Slime

3.5.1. Decomposition of anode slime

An anode slime sample obtained from an electrolytic copper production plant (HES Cable, Kayseri, TURKEY) was prepared in solution form as follows. Homogenized anode slime was dried at 110°C in an oven overnight and after weighing 5 g of sample it was transferred into 200 mL beaker. It was heated on a hotplate for 3 times with 50 mL of aqua regia solution containing 1.0 mL Br₂ solution and heated until dryness at 150°C. Final residue was dissolved using 50 mL of 1.0 M of HCl solution and filtered into a 250 mL beaker using filter paper (Whatmann, no: 4). Filter paper and beaker was washed with 0.5 M HCl into a 100 mL volumetric flask and completed the volume with 0.5 M HCl.

3.5.2. Method validation for gold ion analysis

For the validation of the method, 10 mL solubilized anode slime samples were mixed with 200 and 400 µg L⁻¹ standart gold ion solutions in 1:1 ratio to get 100 and 200 µg L⁻¹ gold ion concentrations. Solubilized anode slime samples were treated with 10 mg of dried poly(NHMMA-hexacyclene) hydrogels at pH 1.0 for 48 h with an 400 rpm agitation rate. Gold ion adsorbed polymeric materials were placed in 10 mL desorption mediums (0.8 M thiourea in 3 M HCl solution) and stirred at 400 rpm for 48 h. The metal ion concentration released from polymeric materials into the aqueous phase was measured by GF-AAS. Finally, the gold ion recovery was calculated to examine the validity of the discovered method, for leading to gold ion uptake.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis and Characterization of Poly(NHMA-Hexacyclene) and Poly(NHMA-15-crown-5) Hydrogels

In this study, two different hydrogels were synthesized for the specific Au(III) and Pb(II) ion removal, recovery and pre-concentration from different natural samples either in their aqueous or solid forms. For the gold ion removal hexacyclene was chosen as a specific ligand because of the positive ion form of that one in the acidic media and 2-(hydroxymethyl)-15-crown-5 was chosen for lead ion removal because of highly selectivity of this ligand to ionic lead in the solutions beside the other toxic and transition metal ions. The chemical structures of these ligands are given in Figure 3.1. From the Figure 3.1, it has been seen clearly that hexacyclene could produce multiple positive charges easily on its amino groups at low pHs and 2-(hydroxymethyl)-15-crown-5 shows activity only to the lead ion because of the internal cavity size that fits only for lead ion in the aqueous solutions. Solutions obtained from the combination of N-(hydroxymethyl)methacrylamide with hexacyclene and 2-(hydroxymethyl)-15-crown-5 were irradiated in ^{60}Co -gamma radiation source at different irradiation doses to obtain hydrogels containing maximum amount of hexacyclene and 2-(hydroxymethyl)-15-crown-5 responsible for the specific gold and lead ion adsorption. From the elemental analyses results, it has been observed that hexacyclene and 2-(hydroxymethyl)-15-crown-5 content in the hydrogels increased when the irradiation doses were increased. In each case, the content of 2-(hydroxymethyl)-15-crown-5 was set the 11.6 % and finally, content of the hexacyclene was found to be maximum 9% in the synthesized hydrogels. This is the maximum content of the ligands in the synthesized hydrogels even higher content (more than 15%) of hexacyclene and 2-(hydroxymethyl)-15-crown-5 were used in the irradiated mixtures and used more than 0.8 kGy dose for the synthesise of the hydrogels. In the metal ion adsorption experiments, the hydrogels containing 9% hexacyclene and 11.6% 2-(hydroxymethyl)-15-crown-5 were used.

4.1.1. Swelling behaviour of the hydrogels

For the characterization of the hydrogels, swelling behaviours of them were studied. In order to examine the effect of the irradiation dose on the swelling behaviour of the poly(NHMMA-hexacyclene) hydrogel, the hydrogels synthesized at 0.25, 0.3, 0.4, 0.5, 0.6 and 0.8 kGy were used. The results of these experiments are shown in Figure 4.1.

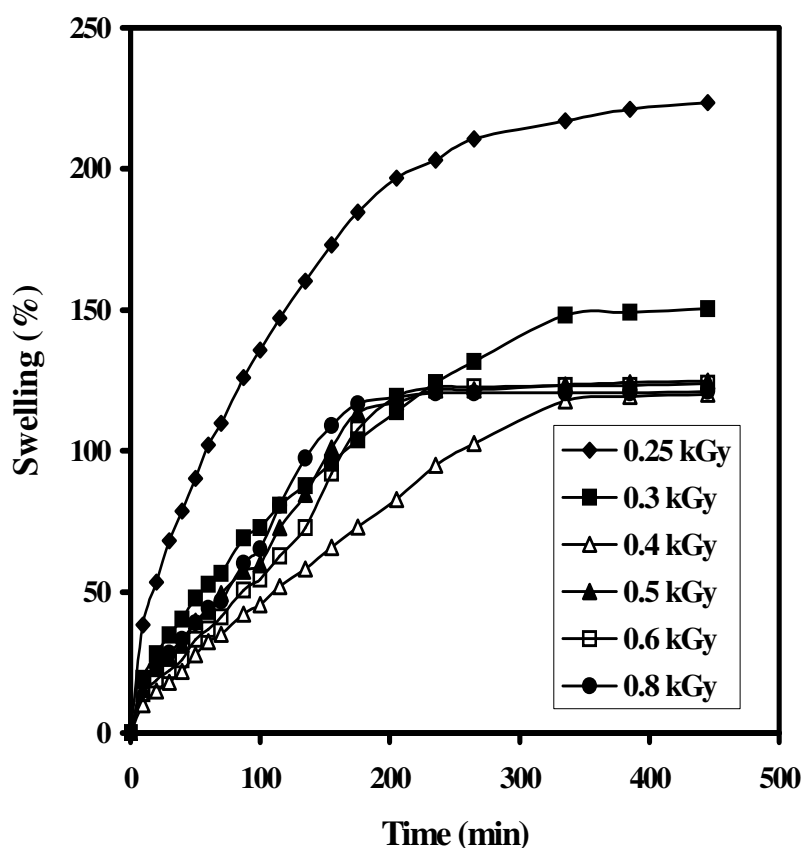


Figure 4.1. Swelling of poly(NHMMA-hexacyclene) hydrogels obtained at different irradiation doses.

It has been clearly shown from Figure 4.1 that the swelling ratio of the hydrogels decreased when the irradiation time increased. When the irradiation dose was increased from 0.2 kGy to 0.4 kGy, swelling ratio of the hydrogels decreased dramatically and reached almost to 120. After 0.4 kGy irradiation doses, swelling behavior of the hydrogels did not change. The decrease in the swelling ratio of the hydrogels synthesized at high irradiation dose is a result of the high degree of crosslinking and hexacyclene content occurring inside the hydrogel.

Swelling behaviour of the hydrogels (produced at 0.8 kGy irradiation dose) was also investigated at different pHs. The swelling ratio of these hydrogel was given in Figure 4.2.

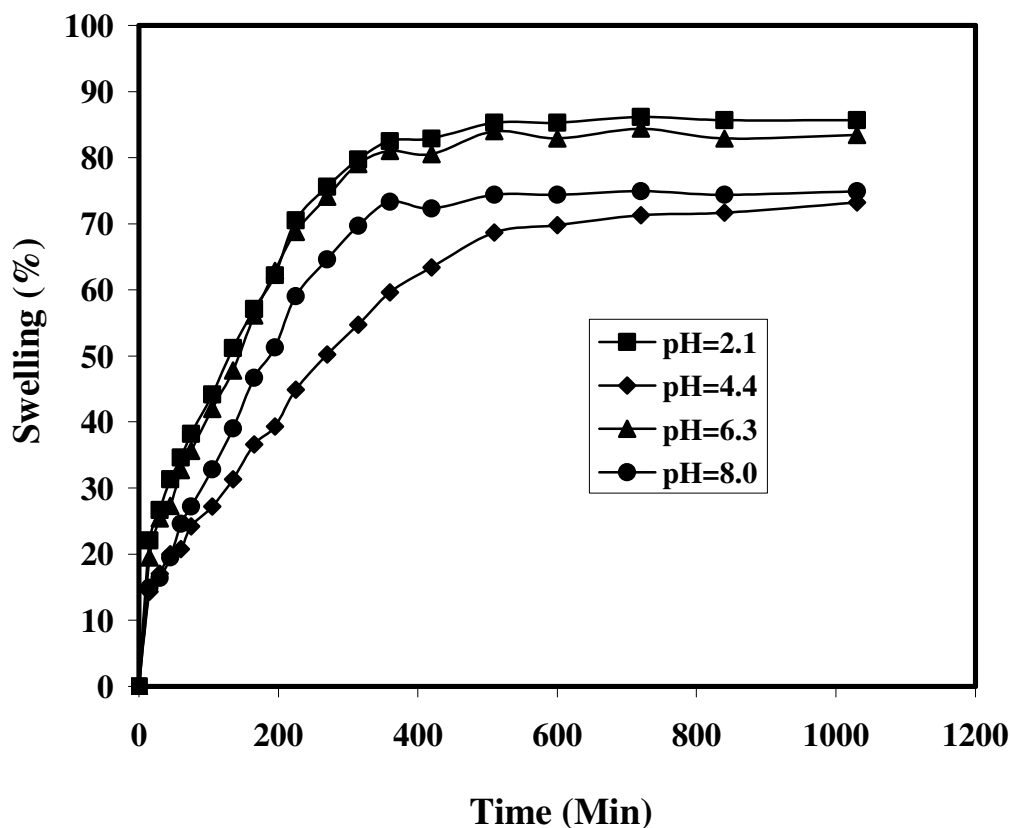


Figure 4.2. Swelling behaviour of the poly(NHMMA-15-crown-5) hydrogel obtained at different pHs.

It was observed that there was no critical changing on the swelling ratio of the hydrogels in the pH solutions. This is logical because of the more rigid and non-protonated structure of the 2-(hydroxymethyl)-15-crown-5. Also, 2-(hydroxymethyl)-15-crown-5 containing hydrogels swelled less than the hexacyclene containing hydrogels synthesized at the same conditions. This is the case of the more hydrophilic structure of the hexacyclene compared to the 2-(hydroxymethyl)-15-crown-5.

4.1.2. Characterization of the hydrogels by FT-IR

For structure characterization of the hydrogels, FT-IR spectra were used. In Figure 4.3, FT-IR spectra of the poly(NHMMA-hexacyclene) hydrogels in the irradiated mixture and at different irradiation doses are given. From these spectra, main changing was observed on the broad absorption peak at around 3450 cm^{-1} . The broad absorption band between 3100 and 3600 cm^{-1} is corresponding N-H and O-H stretching absorption bands. The broadening of this band results from the existence of intermolecular hydrogen bonds of many functional groups from the monomer and the ligand. The wideness of this peak increased with increasing radiation dose. This shows that hexacyclene content in the hydrogels increased when the irradiation dose was increased. Similar results were obtained from elemental analyses results.

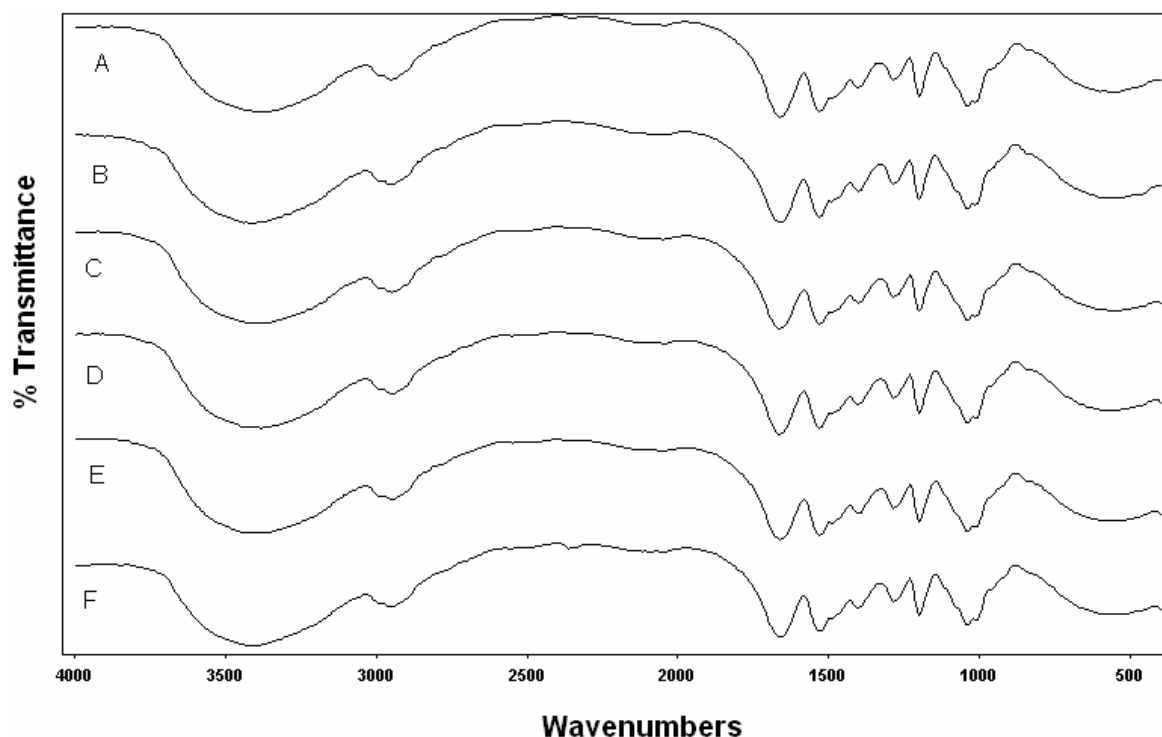


Figure 4.3. FT-IR spectra of the poly(NHMMA-hexacyclene) hydrogels (obtained from the irradiation mixture containing 15% hexacyclene) irradiated at different doses: 0.25 kGy (A); 0.3 kGy (B); 0.4 kGy (C); 0.5 kGy (D); 0.6 kGy (E); 0.8 kGy (F).

The absorption band at 1062 cm^{-1} is dominant in the polymer structure. Mainly this absorption band corresponds to the C-O vibration onto the N-(hydroxymethyl)methacrylamide. This is the reasonable effect because of the high

content of N-(hydroxymethyl)methacrylamide in the hydrogel. The other absorption bands at 1687 and 1636 characterize the existence of C-N vibrations.

For the poly(NHMMA-15-crown-5) hydrogels, almost similar FT-IR spectra was observed. In the case of poly(NHMMA-15-crown-5) hydrogels, two hydrogels were synthesized using 15% content of 2-(hydroxymethyl)-15-crown-5 and at 0.8 kGy irradiation dose as a parallel experiments and the FT-IR spectra are given in Figure 4.4.

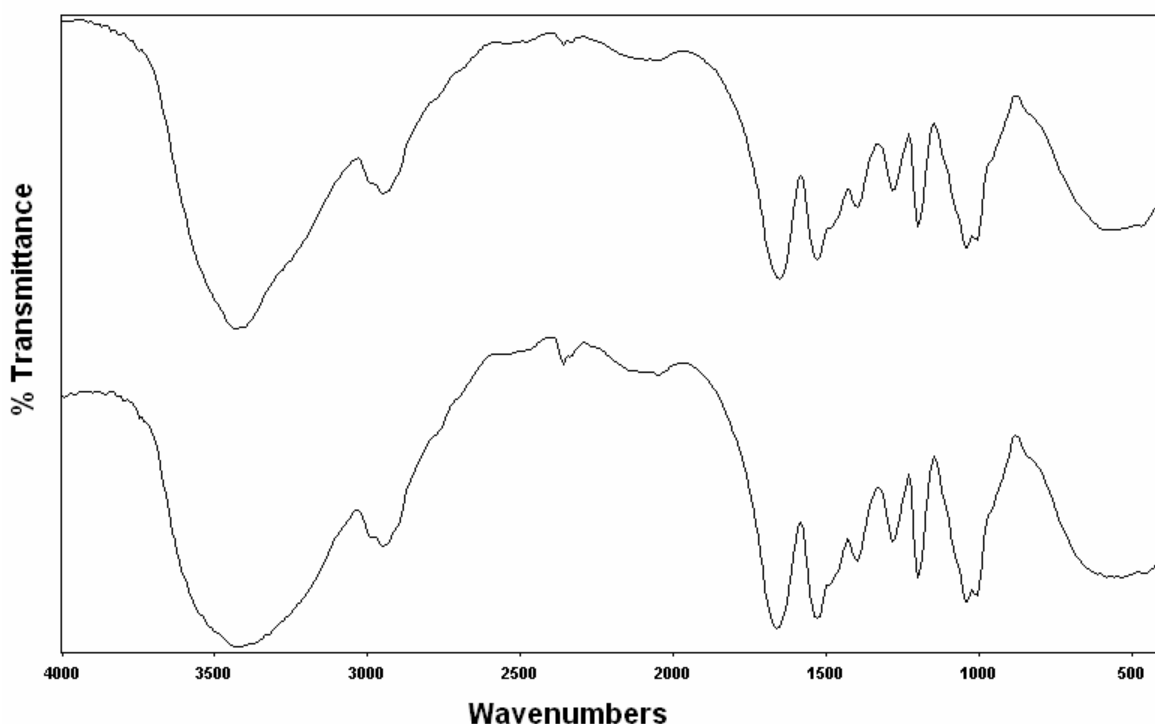


Figure 4.4. FT-IR spectra of the poly(NHMMA-15-crown-5) hydrogels (obtained from the irradiation mixture containing 15% 2-(hydroxymethyl)-15-crown-5) irradiated at 0.8 kGy irradiation dose as a parallel experiments.

From Figure 4.4, it has been observed that synthesis of the poly(NHMMA-15-crown-5) hydrogel could be performed repeatedly. The absorption band at around 3300 cm^{-1} is more sharp compared to absorption band at 3450 cm^{-1} wavenumber on the FT-IR spectra of poly(NHMMA-hexacyclene) hydrogels. This intense absorption band at around 3300 cm^{-1} characterizes the O-H vibration absorption band mainly resulted from N-(hydroxymethyl)methacrylamide and 2-(hydroxymethyl)-15-crown-5. Two bands at 1265 cm^{-1} responsible for C-O-C bond on poly(NHMMA-15-crown-5) hydrogel.

4.2. Au(III) Ion Adsorption onto The Poly(NHMMA- Hexacyclene) Hydrogels

4.2.1. pH Effect on the adsorption capacity

For selective adsorption, beside the use of specific ligand modified sorbent, selectivity could be achieved by adjusting a medium pH. A detailed study was conducted in order to determine the influence of pH on adsorption characteristics of Au(III) ions onto poly(NHMMA-hexacyclene) hydrogels. In this study, the uptake percent of Au(III) ions onto the poly(NHMMA-hexacyclene) hydrogels is selective at low pHs, which means in an acidic media.

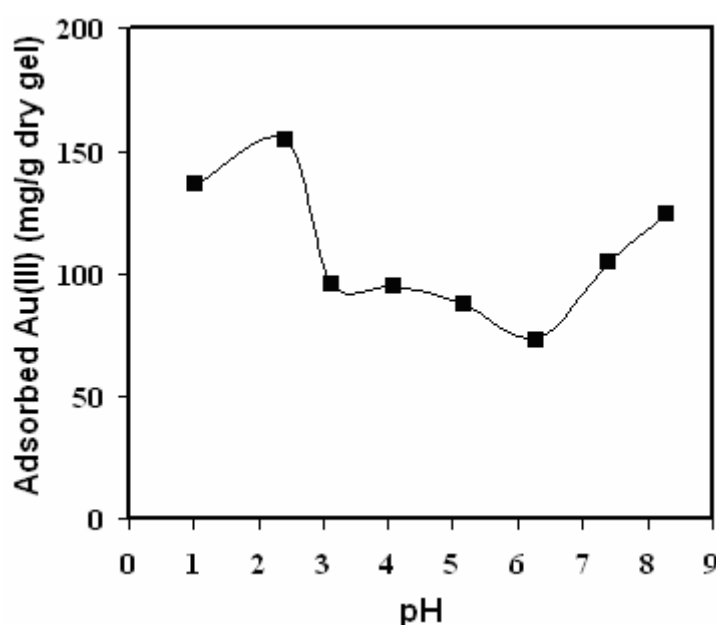


Figure 4.5. Effect of pH on the adsorption capacity of poly(NHMMA-hexacyclene) hydrogel for Au(III) ions. Initial concentration for Au (III): 100 ppm; sample volume: 20 mL; amount of hydrogels: ~12 mg; temperature: 25°C; agitation rate: 400 rpm; agitation period: 48 h.

As seen in Figure 4.5, the removal of gold ions, at low pH values up to 1.03, from gold ion solution by poly(NHMMA-hexacyclene) hydrogel increased and reached about 136.6 mg g⁻¹ dried hydrogel. The adsorption capacity of gold ions was as 72.87 mg g⁻¹ dry gel at pH 6.3. Affecting from the pH parameter is an advantage for this adsorption process. High adsorption capacity at low pH around 1.0 is really important to eliminate the adsorption of the other metal ions that make interference to gold ion.

4.2.2. Initial Au(III) ion concentration effect

As shown in the Figure 4.6, the adsorption process was affected by various concentrations of Au(III) ions when pH of gold ion solutions were set to pH 1.0. The uptake of gold ion increased with the increasing initial gold ion concentrations until plateau value which represents the saturation of the active sides of the sorbent. It was found that maximum gold ion adsorption was about 1138 mg gold g⁻¹ dry gel.

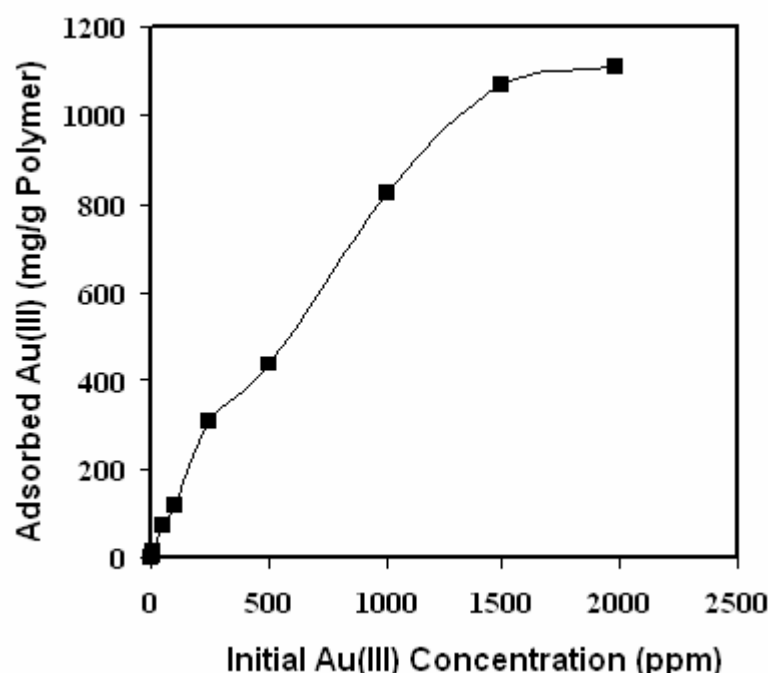


Figure 4.6. Effect of initial concentration on the adsorption capacity of the poly(NHMMA-hexacyclene) hydrogel for Au (III) ions. Sample volume: 20 mL; amount of hydrogels: ~12 mg; pH: 1.0; temperature: 25°C; agitation rate: 400 rpm; agitation period: 48 h.

In literatures, by using modified and non-modified sorbents maximum gold adsorptions were reported. A wide range of adsorption capacities were examined in these studies. Wasikiewicz et al. investigated absorption ability of gold ions into EB-radiation crosslinked carboxymethylchitin (CMCht) and carboxymethylchitosan (CMChts). A high capacity of metal ions adsorption by CMChts is believed to be caused by a large number of amino groups which are able to exchange hydrogen atoms to metal ones. The maximum adsorption capacity of gold is 10.86 and 7.65 mg g⁻¹ for CMChts and CMCht, respectively (Wasikiewicz et al., 2005). Kavaklı et al. studied with the poly(*p*-chloromethylstyrene–ethylene glycol dimethacrylate), (poly(*p*-CMS–EGDMA)), microbeads for the selective adsorption of gold. The

uptake of gold ions onto the microbeads was 6.18 mmol g^{-1} at pH 3.0 (Kavaklı et al., 2002). Kılıç et al. synthesized poly(acrylamide-1-allyl-2thiourea) hydrogels, to use for the specific gold recovery from single and competitive media. Adsorption capacity of the hydrogels for gold ions was found about 940 mg g^{-1} dry hydrogel (Kılıç et al., 2005). Sanchez et al. evaluated new resins, with a functional group based on triisobutyl phosphine sulphide and containing different spacer arms between polymeric matrix and the functional group in order to determine and characterize the mechanism of the metal adsorption process. Selectivity of them were between $0.4 - 6.5 \text{ mmol Au/g}$ for Au (III) (Sanchez et al., 2001). Arrescue et al. were prepared four derivatives of chitosan by crosslinking and grafting of sulfur compounds. Maximum uptake capacity reaches 600 mg Au g^{-1} (about 3 mmol g^{-1}) (Arrescue et al., 2003). Jermakowicz et al. obtained two resins with different matrices, both bearing aminoguanidyl ligands and used for gold sorption from hydrochloric acidic and from alkali solutions. For resin 2 which expanded poly(vinylbenzyl chloride-co-divinylbenzene) copolymer (VBC/DVB), sorption of gold from acidic and alkali solutions was 68 and 23 mg/g , respectively (Jermakowicz et al., 2002). Kolarz et al. synthesized anion exchangers with alkyl substituted guanidyl groups by the reaction of cyanamide(alkyl substituted cyanamides) and carbodiimides with amino groups in modified polystyrene. From the solution containing 2 ppm of gold the sorption is high as 30 mg/g (Kolarz et al., 2001). Döker found adsorption capacity of poly (NHMA-allylthiourea) (poly(NHMMA-AT))hydrogel for Au(III) ions as 651.39 mg g^{-1} (Döker, 2004).

The obtained results show that adsorbed Au(III) ion value using poly(NHMMA-hexacyclene) hydrogels, is really high and satisfactory.

4.2.3. Effect of adsorption time on Au(III) ion adsorption

The adsorption rate of Au (III) ions onto the poly(NHMMA-hexacyclene) hydrogels are shown in Figure 4.7. From the Figure 4.7, it was observed that gold ion adsorption capacity increased up to 10 h adsorption time and then reached the equilibrium adsorption time at around 20 h .

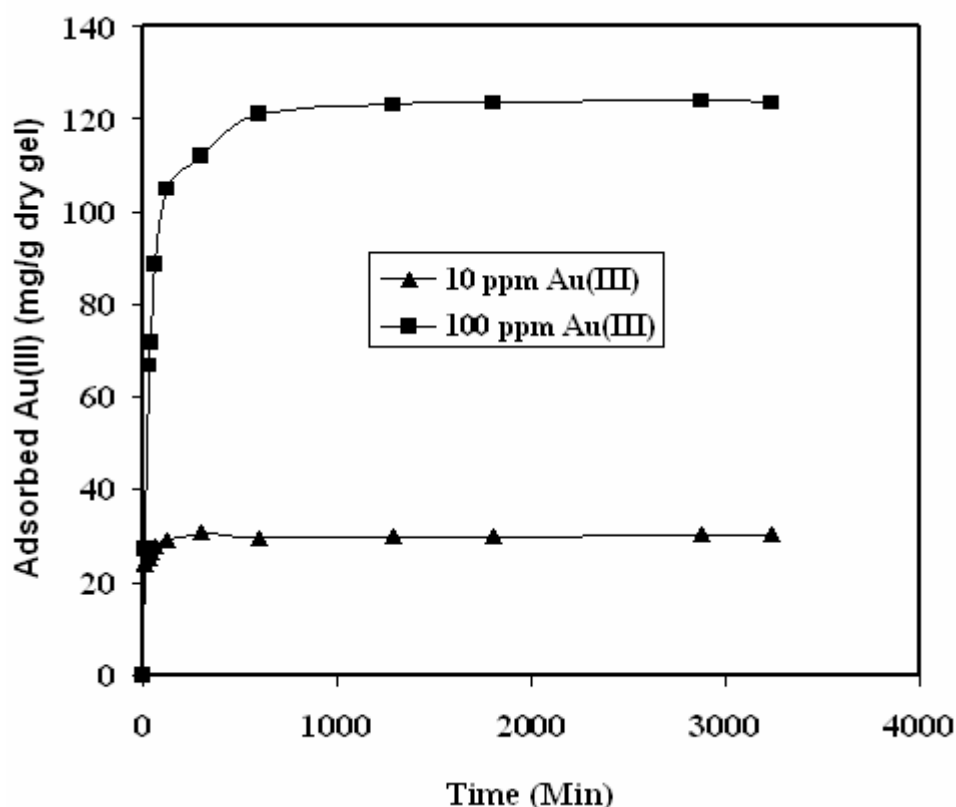


Figure 4.7. Effect of time on Au(III) ion adsorption capacity by poly(NHMA-hexacyclene) hydrogel. Sample volume: 20 mL; pH: 1.0; amount of hydrogels: ~ 0.05 g; temperature: 25°C; agitation rate: 400 rpm; agitation period: 48 h.

Döker showed the adsorption rate of Au(III) ions onto the poly (NHMA-AT) hydrogel, respectively. Adsorption equilibrium time for Au(III) ions were 8 h (Döker, 2004). Kavaklı et al. considered 24 h as equilibrium time in their Au (III) ion adsorption kinetic studies in which they used cyclam modified poly(*p*-CMS-EGDMA) polymeric microbeads (Kavaklı et al., 2002). Kılıç et al. studied gold ion uptake kinetics onto the hydrogels containing different amounts of 1-allyl-2-thiourea and produced at different irradiation dose rates. It was observed that gold ion adsorption capacity reached the equilibrium adsorption time at around 90 h (Kılıç et al., 2005). Sanchez et al., considered 150 h as a short equilibrium time in their gold adsorption kinetic studies, in which they used phosphine sulphide-type chelating polymers beared different spacer arms (Sanchez et al., 2001). Wasikiewicz et al. investigated sorption properties of various metal ions on carboxymethylchitin and carboxymethylchitosan. Kinetic studies showed that adsorption of Au(III) ions occurred in a relatively short period of time (2 h) (Wasikiewicz et al., 2005). Arrescue et al. studied gold adsorption on chitosan derivatives. Sorption kinetics was influenced by pH and the type of chitosan

derivatives. Necessary contact time to reach the equilibrium was changed between 12 and 24 hours (Arrescue et al., 2003).

Adsorption equilibrium time for the synthesized hydrogels in this study has been showed that adsorption equilibrium time is short (about 10 h) and it was feasible in the real application processes.

4.2.4. Au(III) ion desorption from the poly(NHMMA-hexacyclene) hydrogels

0.8 M thiourea in 3 M HCl was used as desorbing agent, to examine the desorbed gold ion concentration. Desorbed gold ion concentrations were measured by GF-AAS.

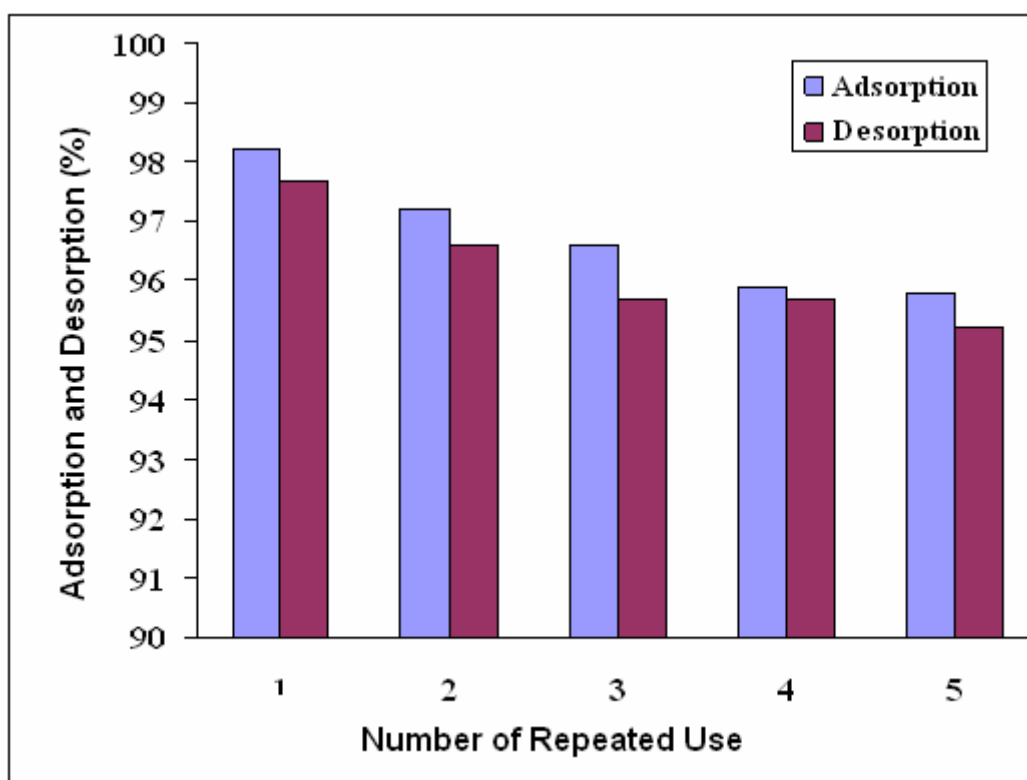


Figure 4.8. Reuse of the hydrogels for the adsorption and desorption of Au(III) ion.

As shown in Figure 4.8, the minimum desorption was found as 95%. This desorption ratio is suitable for at least 5 repeated process for the same hydrogels without losing more than 3 % adsorption capacity of the hydrogels.

4.2.5. Recovery and matrix elimination for Au(III) ions

To examine the recovery and matrix elimination for Au(III) ion in the real samples by using synthesized poly(NHMA-hexacyclene) hydrogels, anode slime sample solution was used. Back-ground and atomic absorption signal was recorded by GF-AAS and the signals are given in Figure 4.9. As seen from Figure 4.9 (a), back-ground signal is really high compared to the atomic absorption signal of gold ions. This is the case of the existing of the other interferences and their effects on the gold ions. Also, the shape of the atomic absorption signal of gold ion is not regular.

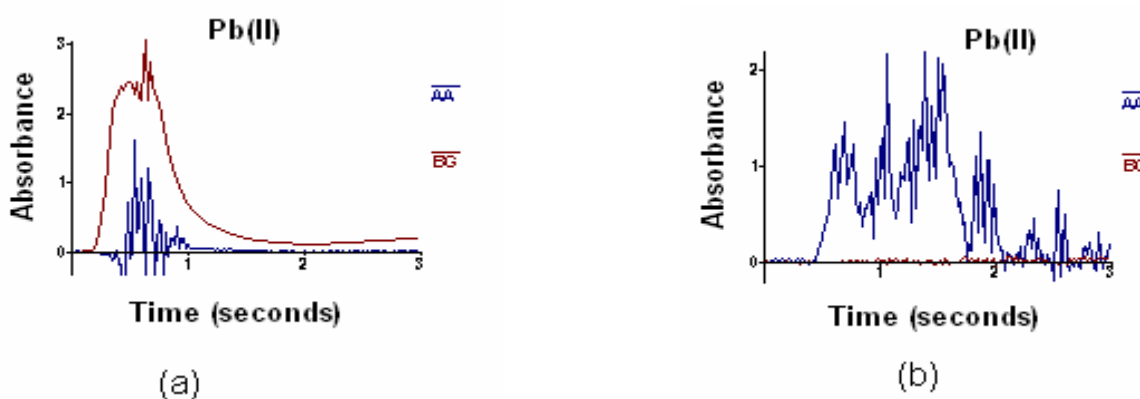


Figure 4.9. Atomization signal curves of the Au(III) ions. (a) Directly measured from anode slime sample solution. (b) After the adsorption-desorption cycle applied to the anode slime sample solution.

When the anode slime sample solution was treated with the synthesized hydrogels and the adsorbed gold ions were desorbed to the desorption solution, back-ground and atomic signal of the gold ions were measured once more. These results are given in Figure 4.9 (b). As shown from Figure 4.9 (b), back-ground signal was diminished completely and the atomic signal of the gold ions was increased. If the interferences were removed from the sample solution by the adsorbing sorbents, more reproducible and accurate results could be obtained. In our case, it has been clearly seen that system was working very well when the synthesized poly(NHMA-hexacyclene) hydrogels were used. In this way, also pre-concentration could be done using high volume adsorption solution and less amount of desorption solution.

4.2.6. Recovery and pre-concentration of Au(III) ions onto the poly(NHMMA-hexacyclene) hydrogels

To examine the recovery and pre-concentration factor of Au(III) ions onto the poly(NHMMA-hexacyclene) hydrogels 1.0 L $5 \times 10^{-2} \mu\text{g L}^{-1}$ gold ion solution was treated with 0.02 g of poly(NHMMA-hexacyclene) hydrogels at pH 1.0. Then the adsorbed gold ions were desorbed into the 2 mL of desorption solution which was containing 0.8 M thiourea in 3M HCl. In the desorption media, gold ion concentrations were measured by GF-AAS, then the recovery and pre-concentration of the gold ions were calculated. All of the results obtained from the experiment are given in Table 4.1. As seen from Table 4.1, recovery was found to be 91.7 and pre-concentration factor was obtained as 500-fold.

Table 4.1. Recovery and pre-concentration factors of Au(III) ions from very dilute solution.

Metal Ion	Volume (mL)	Concentration ($\mu\text{g L}^{-1}$)	pH	Desorption solution	Recovery (%)	Pre-concentration Factor
Au(III)	1000	5×10^{-2}	1.0	2 mL of 0.8 M thiourea in 3.0 M HCl	91.7	500

4.2.7. Method validation

In these type application processes, method validation is very important and shows the method efficiency. For the validation of the method, the solubilized anode slime sample solutions(containing 0, 100 and 200 $\mu\text{g L}^{-1}$ standart gold ions) were measured by GF-AAS after the adsorption-desorption cycle.

Recovery of the Au(III) ions were calculated and given in Table 4.2. From the Table 4.2, it could be seen that recovery of the Au(III) ions was found to be not less than 94 %. It is concluded that discovered method is satisfactory for the recovery process of Au(III) ions.

Table 4.2. Recovery of gold ions from anode slime sample solution.

Element	Concentration (ppb)			
	Found (n = 5)	Added	Sum (n = 5)	Recovery (%)
Au	29.2 ± 0.5	-	28.7 ± 0.8	98.3
Au	29.2 ± 0.5	100.0	124.9 ± 1.3	96.7
Au	29.2 ± 0.5	200.0	217.2 ± 2.1	94.8

4.2.8. Matrix elimination on the Au(III) ion determination using poly(NHMMA-hexacyclene) hydrogels

To examine the elimination of the matrices in the real sample affecting the Au(III) ion recovery, and pre-concentration, concentrations of the main metal ions and the Au(III) ion were measured by ICP-MS before and after the treatment of the anode slime solution with poly(NHMMA-hexacyclene) hydrogels at pH 1.0 for 48 h adsorption time. The results are given as bar graphics in Figure 4.10 that shows the metal ion concentrations before and after the treatments.

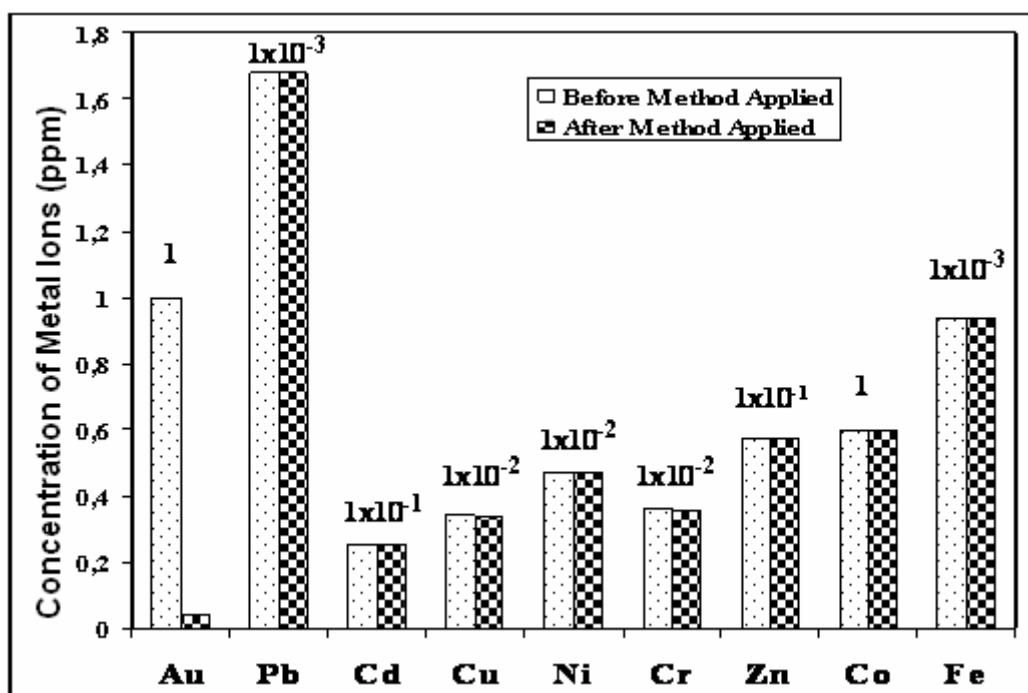


Figure 4.10. The effect of some transition metal ions for the adsorption of gold ion onto the poly(NHMMA-hexacyclen) hydrogels in anode slime solution.

Only the gold ion concentrations were reduced and reached less than 4% compared to its original value before the adsorption. The concentration of the

other studied ions such as Pb, Cd, Cu, Ni, Cr, Zn, Co and Fe were not changed. This shows that hydrogels showed the affinity only the Au(III) ions beside the other transition metal ions. This means that, the other metal ions left in the solution and only Au(III) ions adsorbed onto the poly(NHMMA-hexacyclene) at pH 1.0. In this way, all the interferences affecting gold ion measurement, could be eliminated. Recovery and pre-concentration processes by using poly(NHMMA-hexacyclene) hydrogels give an advantage for the elimination of matrix effects.

4.2.9. Application of the method to the some real geological samples

For the real samples collected from the volcanic region of the west part of TURKEY near İzmir city, solubilization technique used as done for the anode slime and 10 mL solutions from the final solutions were treated with the poly(NHMMA-hexacyclene) hydrogel at the same conditions as studied for the anode slime. After the adsorbed Au(III) ions were desorbed into the desorption solutions, the gold ion concentration released from the hydrogel into the aqueous phase was measured by GF-AAS. The content of the Au(III) ions in each sample were calculated as g/ton and given in Table 4.3.

Table 4.3. Au(III) ion content of digested geological samples.

Geological Samples	Sample Number	Au (g/ton)
Sample 1	1	18.83 $\pm$ 1.04
Sample 2	2	0.51 $\pm$ 0.16
Sample 3	3	0.61 $\pm$ 0.05
Sample 4	4	1.08 $\pm$ 0.24
Sample 5	5	3.09 $\pm$ 0.23

The Au(III) ion content in the studied samples was varied between 0.51 and 18.83 g/ton. For the feasible gold ion production from the real samples, gold ion content should be higher than 1 g/ton. From these results, it could be concluded that three

of the samples seem to be feasible for Au(III) ion recovery and also one of them has high content of Au(III) ion which is about 18.83 g/ton. The high Au(III) ion content of the samples is because of the volcanic rock nature. In the literatures, it is well known that volcanic rocks can contain high amount of gold ion.

4.3. Pb(II) Ion Adsorption Onto Poly(NHMA-15-crown-5) Hydrogels

4.3.1. pH Effect on the adsorption capacity

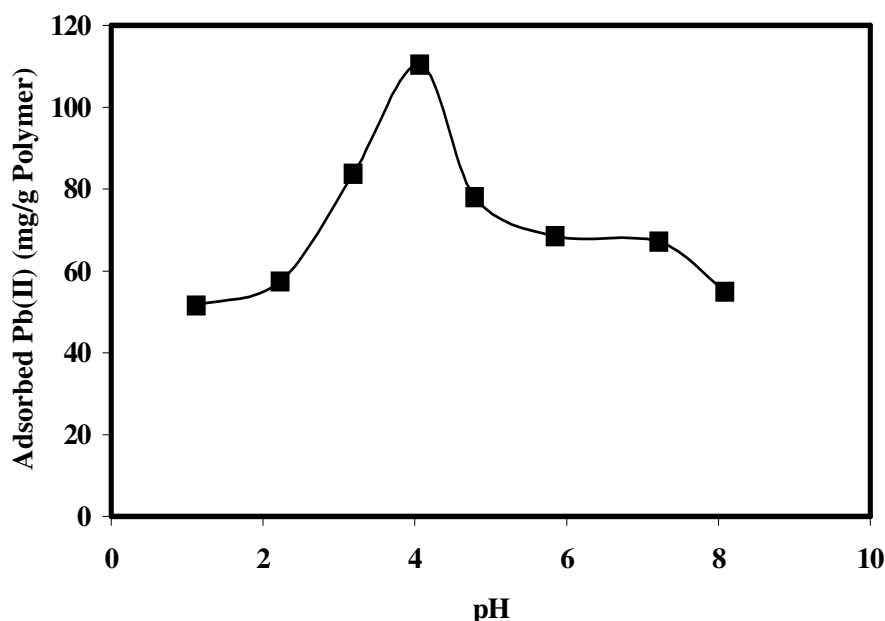


Figure 4.11. Effect of pH on the adsorption capacity of the poly(15-crown-5) hydrogel for Pb(II) ions. Initial concentration for Pb (II):100 ppm; sample volume: 20 mL; amount of hydrogels: ~12 mg; temperature: 25°C; agitation rate: 400 rpm; agitation period: 48 h.

Crown ethers have been demonstrated as highly selective complexing agents for many metal ions. They can be applied in separation and determination of metal ions through molecular recognition (Weber et al., 1989). Of the divalent metal cations, complexation of Pb(II) ions by certain crown ethers (cyclic polyethers) is particularly strong (Izatt et al., 1985). Therefore, an investigation was undertaken to determine the efficiency and selectivity of hydrogels which have 15-crown-5 groups that sorbs Pb(II) ions from dilute aqueous solutions.

The effect of pH on lead ion uptake for the poly(NHMA-15-crown-5) hydrogels was examined for aqueous lead solutions. For this study, uptake of lead in mg g^{-1}

gel units with changing pH values is shown in Figure 4.11. Lead ion adsorption capacity increased rapidly up to pH 4.0, then decreased until pH 6.0 and reached the equilibrium adsorption at around pH 7.0. At pH 4.0, the solvated Pb(II) ion size is exactly fit to get in the cavity of the lead ionophore. However, lead ion adsorption capacity of the poly(NHMMMA-15-crown-5) hydrogels seem to be reasonable at the other pHs also. The minimum adsorption capacity is not less than 52 mg/g dried hydrogels.

4.3.2. Initial concentration effect on the adsorption capacity

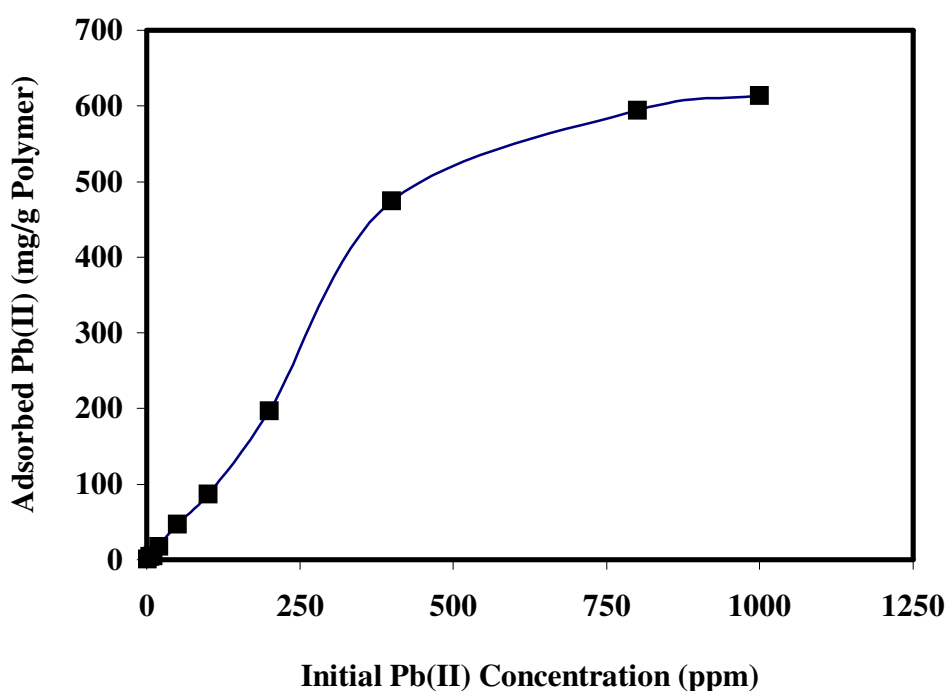


Figure 4.12. Effect of initial concentration on the adsorption capacity of the poly(15-crown-5) hydrogel for Pb (II) ions. Sample volume: 20 mL; amount of hydrogels: ~12 mg; pH: 6.0; temperature: 25°C; agitation rate: 400 rpm; agitation period: 48 h.

Treatment of processes for lead ion removal from aqueous media affected from initial lead ion concentration at constant pH (pH 6.0). In this study concentration of the lead ions in the aqueous phase was measured with GF-AAS, and it was found that maximum lead ion adsorption was about 594 mg g⁻¹ dried hydrogel. All the results for the concentration experiments are given in Figure 4.12.

The adsorption capacities of some sorbents for lead ion were studied by scientists. Erdem and Özverdi investigated the ability of siderite to remove Pb(II) ions from

aqueous solution. Adsorption capacities of siderite at 25, 30 and 35° C were found to be 10.32, 12.45 and 14.06 mg Pb²⁺/ g siderite, respectively (Erdem and Özverdi, 2005). Malcı et al. used the ligand attached microbeads, poly (p-CMS-EGDMA-S4HD) to examine the adsorption capacity of Pb(II) ions. It was found 2.21 mg g⁻¹ polymer for Pb(II) (Malcı et al., 2005). Denizli et al. synthesized poly (hydroxyethylmethacrylate-N-methacryloyl-(L)-glutamic acid) copolymer beads for removal of lead ions. The adsorption capacities were 42.5 mg g⁻¹ for Pb²⁺, 26.8 mg g⁻¹ for Hg⁺² and 17.6 mg g⁻¹ for Cd²⁺ at 0.5 mol/L metal concentration (Denizli et al., 2005). A R. Reddy and K. H. Reddy investigated metal ion uptake properties of polystyrene-supported chelating polymer resins functionalized with (i) glycine, (ii) hydroxyl benzoic acid, (iii) Schiff base and (iv) diethanol amine. The maximum lead uptake capacities of the CMPS-GL, CMPS-HB, CMPS-AH and CMPS-DE are 10.970 mg g⁻¹, 10.570 mg g⁻¹, 12.965 mg g⁻¹, 13.705 mg g⁻¹ (A. R. Reddy and H. Reddy, 2003). As seen from all literature values, lead adsorption capacity of poly(NHMA-15-crown-5) hydrogels synthesized in this study is really useful and feasible for the removal of lead ions from the real samples.

4.3.3. Effect of the adsorption time on Pb(II) ion adsorption

A wide range of metal ion adsorption times onto the polymeric sorbents have been reported. For example Malcı et al. examined poly (*p*-chloromethylstyrene-ethyleneglycoldimethacrylate) microbeads at 0.1 and 1.0 mM Pb (II) ion solutions with the time at pH 5.0. They found the adsorption equilibrium time as 30 minutes. Denizli et al. considered 2 h as a short equilibrium time in their lead ion adsorption kinetic studies, in which they used poly(hydroxyethyl methacrylate-N-methacryloyl-(l)-glutamic acid) beads (Denizli et al., 2005). A. R. Reddy and H. Reddy studied metal ion-uptake properties of polystyrene-supported chelating resins. The removal of Pb(II) ions at different time intervals suggest that an hours time is sufficient for maximum and constant uptake (A.R. Reddy and K. H. Reddy, 2003). Erdem and Özverdi investigated lead ion adsorption capacity of siderite, the adsorption yield also increases with contact time and attains a maximum value at 90 min; thereafter, it remains almost constant (Erdem and Özverdi, 2004).

As can be seen from the Figure 4.13, adsorption of lead ions onto the poly(NHMA-15-crown-5) increased with the increasing adsorption time and

reached a plateau value. To provide ultra low detection of elements, determination of lead ions was done with GF-AAS.

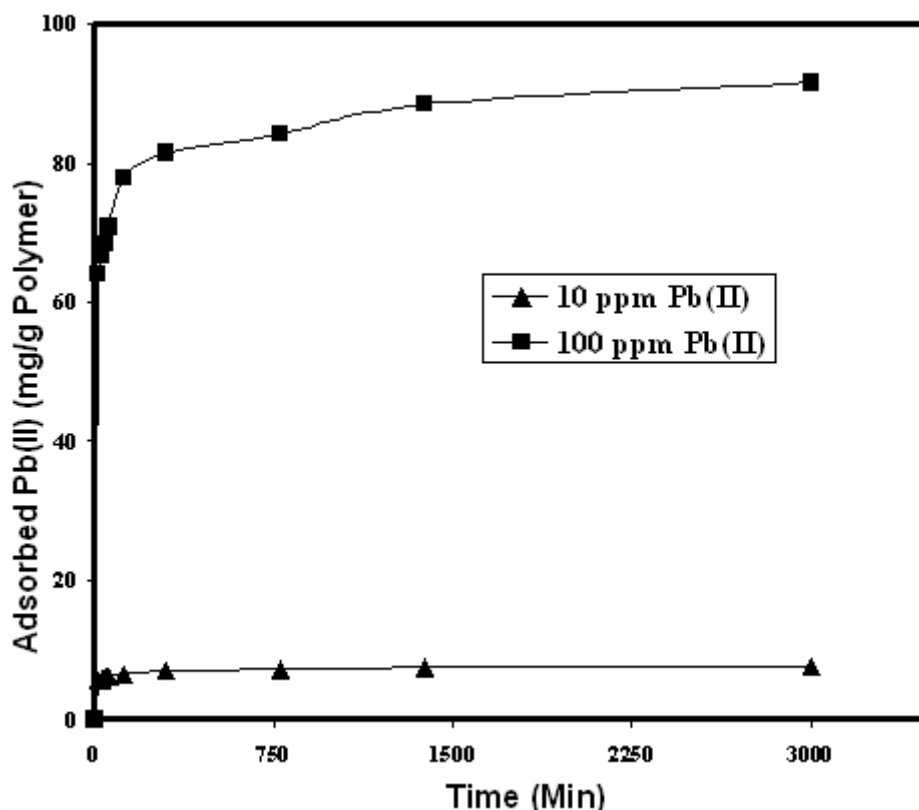


Figure 4.13. Effect of time on Pb(II) adsorption capacity by poly(NHMMA-15-crown-5) hydrogels. Sample volume: 20 mL; amount of hydrogels: ~0.05 g; pH: 4.0; temperature: 25°C; agitation rate: 400 rpm; agitation period: 48 h.

Different adsorption rates of metal ions can be considered to separate the ions from each other. In this study, equilibrium adsorption capacity was attained at around 2h. This period is really reasonable for the equilibrium adsorption period.

4.3.4. Pb(II) ion desorption from poly(NHMMA-15-crown-5) hydrogels

To examine the reusability of poly(NHMMA-15-crown-5) hydrogels in a continuous lead ion adsorption process, desorption of lead ions from hydrogels were examined. Elution of Pb(II) ions from the hydrogels was carried out with 20 mL of 3 M HNO₃. The amount of Pb(II) ions eluted were further analyzed by GF-AAS. Repeated use experimental results are given in Figure 4.14 with the adsorption and desorption per cent together for five adsorption-desorption cycle by using the same hydrogels. In the adsorption-desorption cycle experiments, adsorption

capacity loss was found to be less than 5% after 5 repeated use. This result shows that poly(NHMMA-15-crown-5) hydrogels can be used efficiently for the recovery and pre-concentration experiment of lead ions repeatedly.

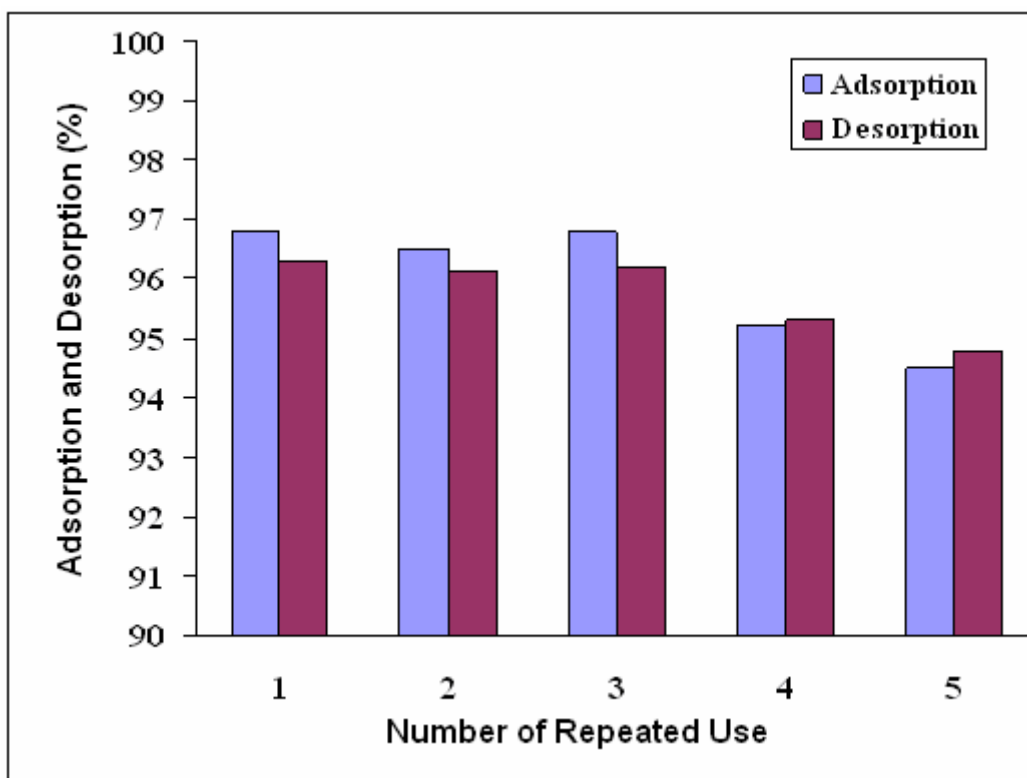


Figure 4.14. Repeated use of the lead ions onto the poly(NHMMA-15-crown-5) hydrogels.

4.3.5. Selectivity of the poly(NHMMA-15-crown-5) hydrogels to Pb(II) ions in the mixture of metal ions

To test the lead ion selectivity of poly(NHMMA-15-crown-5) hydrogels, 50 mL of 0.5 mM of Pb(II), Cu(II), Ni(II), Co(II), Ag(I), Cr(II), Cd(II), Fe(III) and Zn(II) ion mixture was treated with 20 mg of hydrogel after adjusting the pH 2.0. The same procedure was done for metal ion mixtures a pH 4.0 and 6.0.

In the second part of the experiment lead ion concentration in the metal ion mixture was decreased 100-fold. After the adsorption equilibrium time, which was the 48 h, hydrogels were separated from adsorption medium. Finally metal ion concentrations were measured by ICP-MS and the results are given in Figure 4.15.

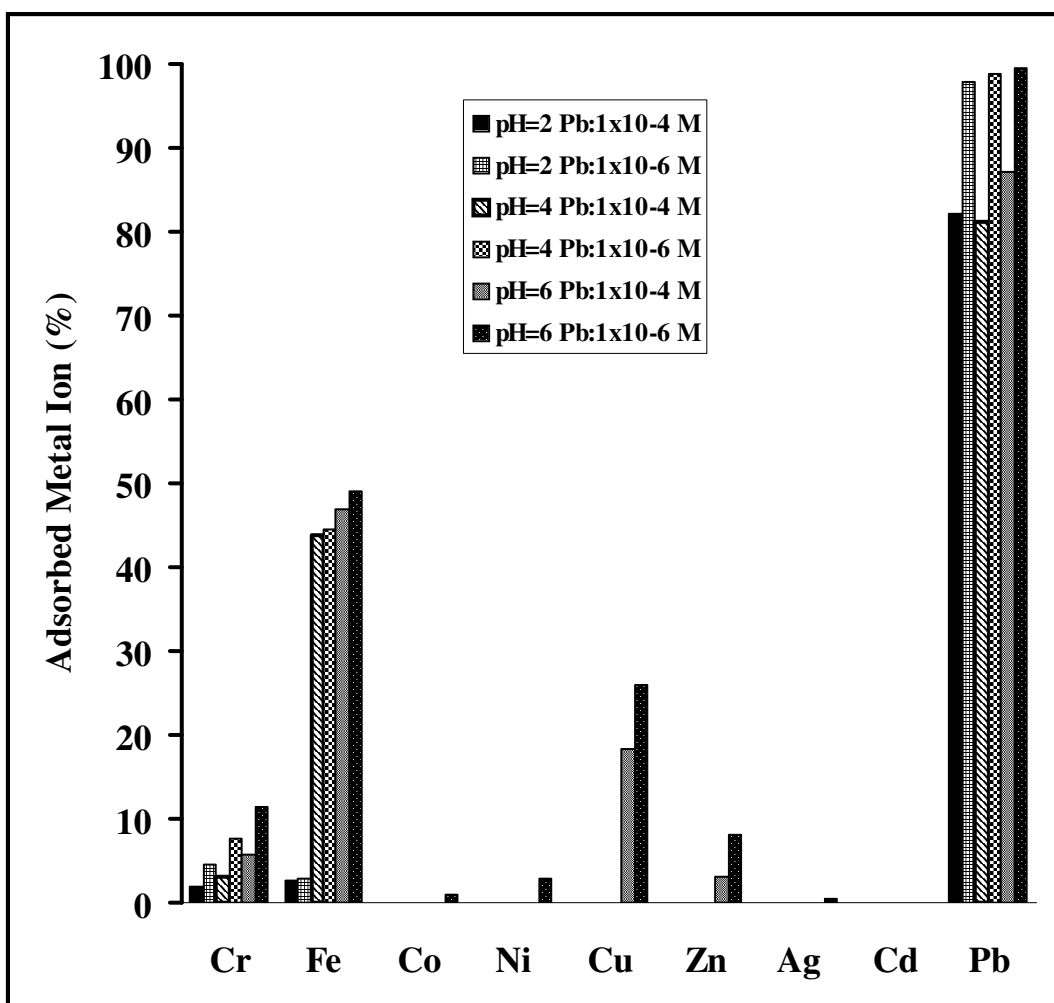


Figure 4.15. Interference effects of the transition metal ions onto the lead ion adsorption by the poly(NHMMA-15-crown-5) hydrogels.

As seen from Figure 4.15, lead ion adsorption of the hydrogel did not change significantly with pH. Lead ion adsorption capacity of the hydrogels was found more than 97% when lead ion concentration was the same as the other studied metal ions in the mixture, and also lead ion adsorption was found to be at least 86% when its concentration was set to 100-fold less compared to the other metal ions even at pH 2.0. Beside lead ion, only Fe and less amount of Cr ion showed interference effects. But, interference effect was found to be less than 6% for iron ion and less than 2% for the Cr ion at pH 2.0. This shows that at pH 2.0, all interference effects were diminished dramatically and only lead ions could be recovered and pre-concentrated from the solutions even its concentration 100-fold less compared to the concentration of the other metal ions. As a result,

poly(NHMMA-15-crown-5) hydrogels could be used efficiently and selectively for the recovery and pre-concentration of lead ions from the natural samples.

4.3.6. Method validation for the Pb(II) ion adsorption onto poly(NHMMA-15-crown-5) hydrogels

For the validation of the method, certified sea water material (BCR CRM 403) which is containing low amount of Pb, Cd, Cu, Mo, Ni, Pb and Zn ions was measured directly and after the adsorption-desorption cycle by GF-AAS. The recovery of lead ions was calculated and given in Table 4.4. As seen from Table 4.4, recovery of lead ions was found to be 95.7% which was a useful value for the method validation by using international standard.

Table 4.4. Method validation results obtained from certified sea water material (BCR CRM 403).

Metal Ions	Metal Ion Concentrations (nmol kg ⁻¹)		% Recovery
	Certified value	Found *	
Cd(II)	0.175	-	-
Cu(II)	3.9	-	-
Mo(II)	103	-	-
Ni(II)	4.4	-	-
Pb(II)	0.117	0.112 ± 0.002	95.7 ± 0.6
Zn(II)	25.7	-	-

* The results were given with average of 5 parallel experimental results

4.3.7. Determination of Pb(II) ions in different natural aqueous samples after pre-concentration onto the poly(NHMMA-15-crown-5) hydrogels

Lead concentration in different natural aqueous solutions such as drinking, tap, well and sea water samples were measured by GF-AAS directly and after the discovered method was applied. For the application of the method to the natural aqueous solutions, 50-fold pre-concentration was performed. The analytical results are given in Table 4.5. For the direct measurements, no lead ion was measured for drinking water and tap water. Lead ion concentration could be measured for the other two natural aqueous samples, but with high standard deviation because of the interferences. When the method was applied to the sample, lead ion

concentrations in all samples were measured with high precision. This shows that standard deviation of the measured results were very high for direct measurements compared to the results obtained after pre-concentration and matrix elimination procedures applied to the water samples. In other words, it concluded that discovered method was really suitable for the measuring low concentration of lead ions specifically in the natural aqueous samples.

Table 4.5. Measured concentrations of lead ions in drinking, tap, well and sea water samples by GF-AAS directly and after the pre-concentration method applied.

Sample	Concentration of lead (ppb)	
	Direct	After pre-concentration
Drinking Water	nd	0.0127 ± 0.0012
Tap Water	nd	0.085 ± 0.006
Well Water	0.96 ± 0.73	0.41 ± 0.03
Sea Water (Costal)	0.68 ± 0.47	0.046 ± 0.003

4.3.8. Matrix elimination for Pb(II) ion analysis by using the discovered method; controlling the atomic and back-ground signals in AAS

To examine the matrix elimination from the aqueous samples containing very low amount of Pb(II) ion, discovered method in this study was applied following adsorption-desorption cycle and then the atomic and back-ground signal shapes were tested. For this purpose, drinking, sea and well waters were used; the atomic and back-ground signals of all samples were obtained before adsorption and after the desorption. Adsorption- desorption cycle was tested for the same volume of sample solutions and also 50-fold pre-concentration was performed for drinking water. The results are given in Figure 4.16, (a) for before adsorption, (b) after 1:1 adsorption-desorption cycle applied and (c) after 50:1 (50-fold pre-concentration) adsorption-desorption cycle applied.

In Figure 4.16 (a), atomic and back-ground signals obtained from drinking water by GF-AAS showed that the intensity of the atomic and the back-ground signal level

was very weak because of the low content of the Pb(II) ions and high content of the interferences. Low intensity atomic signal not let to measure the concentration of Pb(II) ions in drinking water due to below the detection limit.

When 50-fold pre-concentration technique was applied to the drinking water by using discovered method, the atomic signal intensity of Pb(II) ions increased enormously and produced a very pure and symmetric signal curve (Figure 4.16 (c)).

When the discovered method applied in 1:1 adsorption-desorption cycle, background signal intensity was lowered and atomic signal intensity of the Pb(II) ions was increased (Figure 4.16 (b)). All these results showed that, high amount of matrices can be eliminated, and that measurements are possible in a GF-AAS system for lead ion determination using the poly(NHMMA-15-crown-5) hydrogels after the adsorption-desorption cycle.

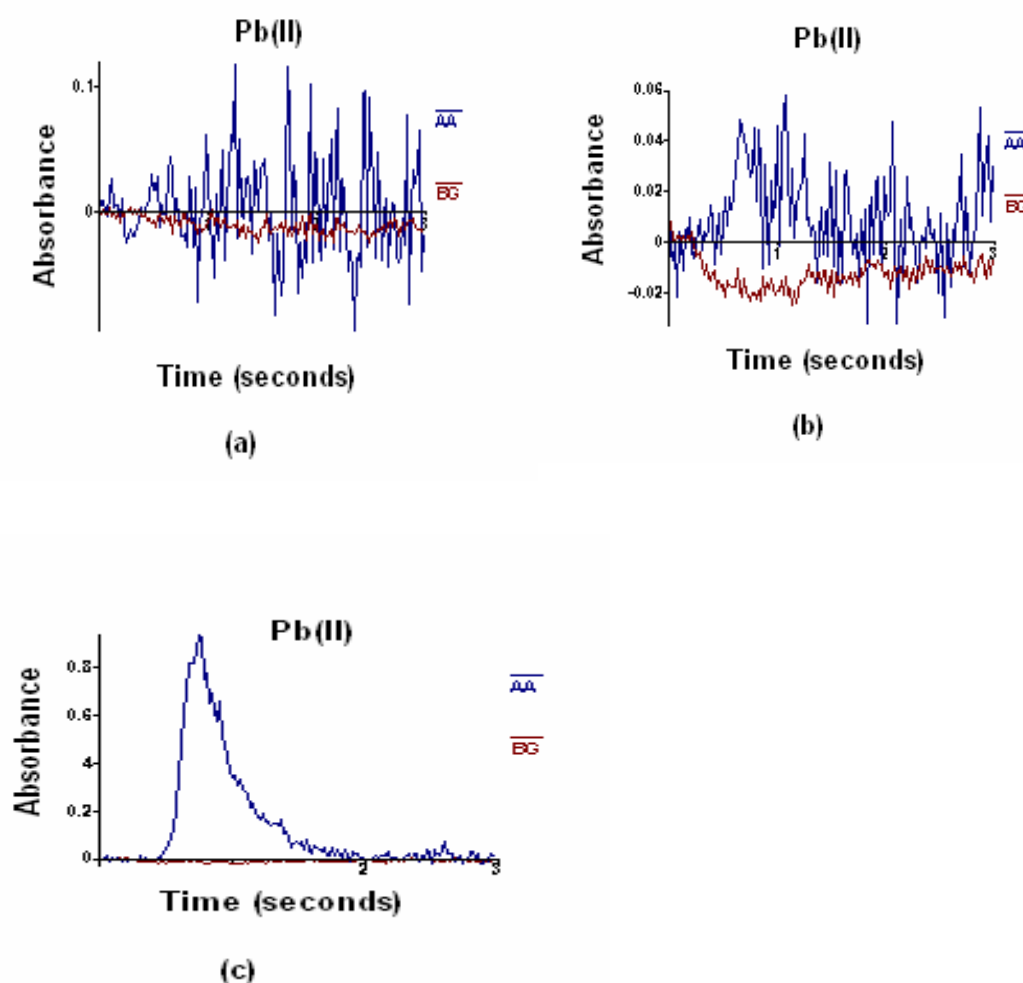


Figure 4.16. Atomization signal curves of the Pb(II) ions in the drinking water. (a) Directly measured. (b) After 1:1 adsorption-desorption cycle applied. (c) After 50:1 (50-fold pre-concentration) adsorption-desorption cycle applied.

Similar experiments which were carried out for drinking water were repeated for well water, sea water and international standard sea water samples. In Figure 4.17 (a), (b) and (c), atomic and back-ground signals of well water measured directly, after the 1:1 adsorption-desorption cycle applied and after 50-fold pre-concentration technique applied by the poly(NHMMA-15-crown-5) hydrogels were seen.

In Figure 4.17 (a), atomic signal intensity of Pb(II) ion is really low because of the concentration of Pb(II) ion that is under the detection limit, the back-ground signal intensity is low too. But after the pre-concentration onto the hydrogels, lead ion atomic signal intensity increased dramatically in spite of there was no signal intensity increment on the back-ground signal. When the pre-concentration

technique was applied to the well water using poly(NHMA-15-crown-5) hydrogels, very low level of Pb(II) ion in well waters could be performed (Figure 4.17 (c)). If only 1:1 adsorption-desorption cycle applied to the well water, (Figure 4.17 (b)) Pb(II) ion concentration could be measurable in well water having a little bit high Pb(II) ion content compared to the drinking water in Figure 4.16 (b).

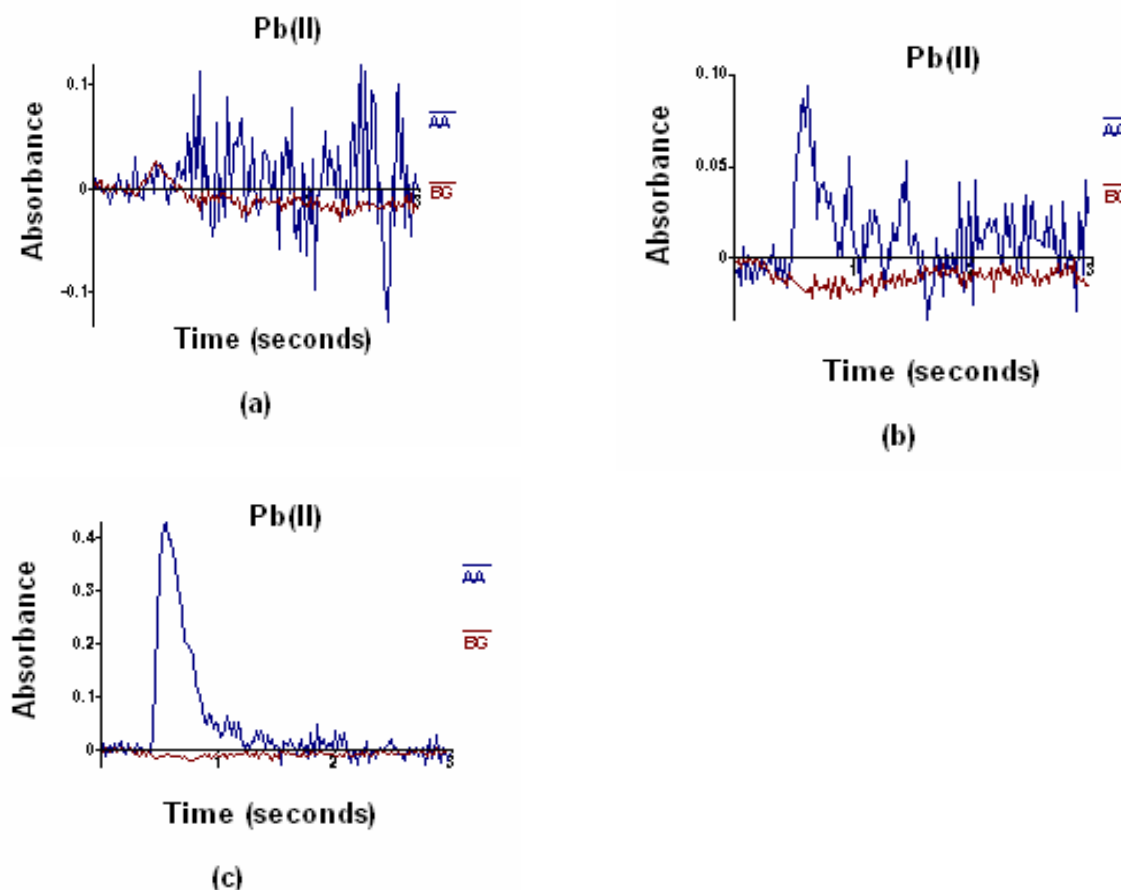


Figure 4.17. Atomization signal curves of the Pb(II) ions in the well water. (a) directly measured. (b) After 1:1 adsorption-desorption cycle applied. (c) After 50:1 (50-fold pre-concentration) adsorption-desorption cycle applied.

Sea water is a kind of different aqueous sample in order to contain high amount of interferences. For this reason, it was aimed to test the sea water collected from costal and internal standard sea water. For the costal natural sea water, three different methods were applied such as direct measurement, 100-fold pre-concentration and 1:1 adsorption-desorption cycle applications. For the direct measurement of sea water with GF-AAS, atomic and back-ground signals could

be seen on the Figure 4.18 (a). High intensity back-ground signal was observed beside the very weak atomic signal for Pb(II) ions, also atomic signal of Pb(II) ions did not have a suitable shape because of high amount of interferences.

When the pre-concentration technique was applied, back-ground signal intensity was diminished because of well working method application and the atomic absorption signal intensity of Pb(II) ions was increased beside the regular atomization shape of the lead ions (Figure 4.18 (c)). Because of the trace level of Pb(II) ion in sea water, atomic signal of Pb(II) ion was not observed clearly when 1:1 adsorption-desorption cycle was applied using the synthesized hydrogels (Figure 4.18 (b)).

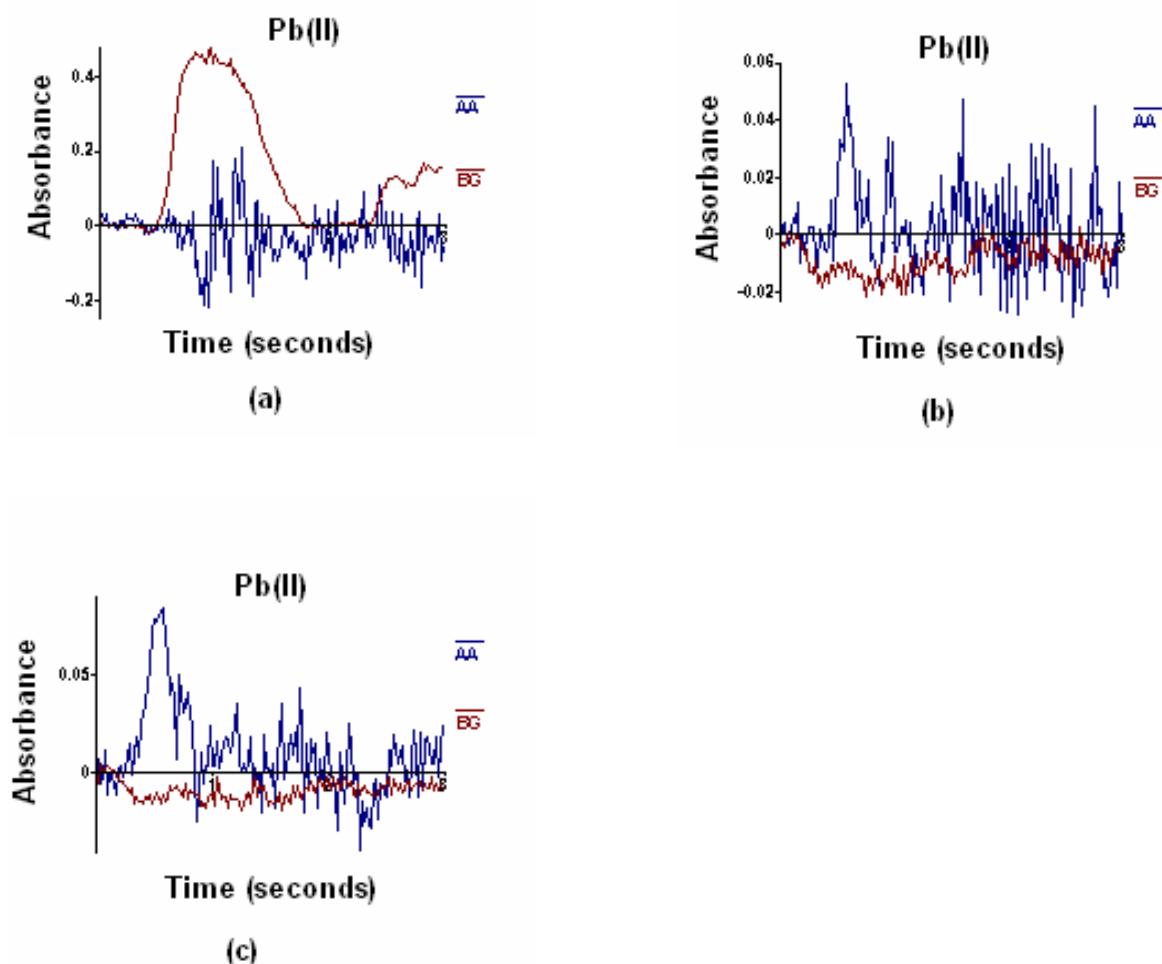


Figure 4.18. Atomization signal curves of the Pb(II) ions in the sea water. (a) directly measured. (b) After 1:1 adsorption-desorption cycle applied. (c) After 50:1 (50-fold pre-concentration) adsorption-desorption cycle applied.

The results obtained from sea water samples showed that lead ion concentration could be determined when the samples contained high amount of interferences. This pre-concentration method give an advantage for the determination of the lead ions in the medium separated from the matrices.

The same behavior in the case of costal natural sea water was observed for the certified sea water samples which were given in Figure 4.19 (a) and (b).

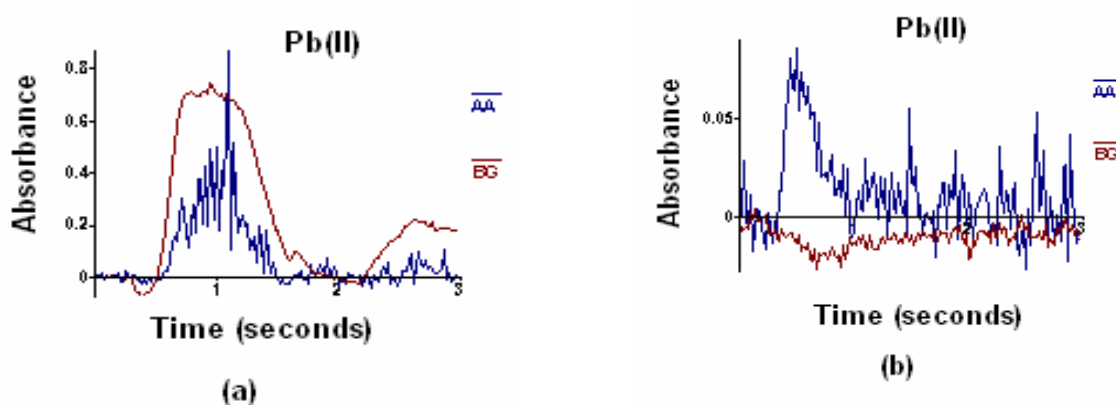


Figure 4.19. Atomization signal curves of Pb(II) ions. (a) Directly measured from certified sea water. (b) After 1:1 adsorption-desorption cycle applied to the certified sea water.

4.3.9. Recovery of Pb(II) ions from standard aqueous and certified sea water samples

The effect of the medium on the recovery of lead ion was tested by using standard lead ion solution containing no inorganic and organic matrices and also international standard sea water containing high amount of matrices. Discovered method was applied to two samples under the same conditions. Finally, Pb(II) ion desorption ratios for two samples were calculated by measuring the initial and final concentration of lead ions by GF-AAS after the method was applied.

Desorption ratios are given in Figure 4.20. As seen from Figure 4.20, there were no critical difference on the desorption ratios of Pb(II) ions obtained in different media containing different amount of interferences. This result showed that matrix elimination could be done well by using the poly(NHMMA-15-crown-5) hydrogels for the determination of the Pb(II) ions in different aqueous media.

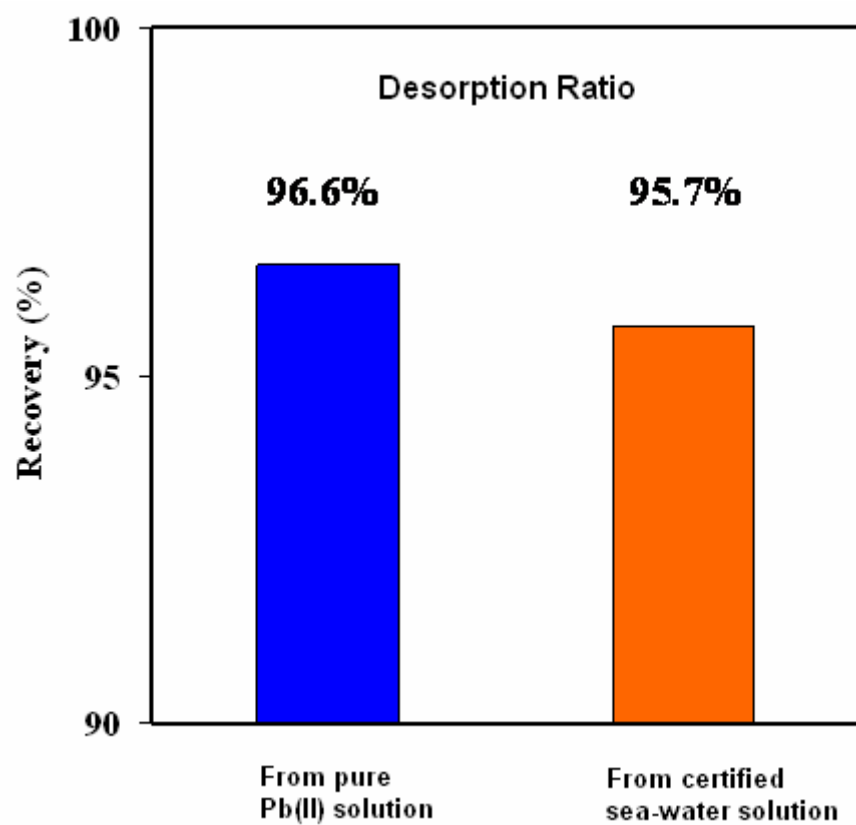


Figure 4.20. Desorption ratio of Pb(II) ions from two aqueous samples containing no interferences and containing high amount of interferences was applied by a technique that poly(NHMMMA-15-crown-5) hydrogels were used .

5. CONCLUSION

In this study, the hydrogels containing hexacyclene and lead ionophore were synthesized successfully using N-(Hydroxymethyl)methacrylamide monomer for the specific removal, pre-concentration and recovery of Au(III) and Pb(II) ions from different samples containing high amount of interference effects.

Hexacyclene and lead ionophore content in the modified hydrogels were found to be 9% for the poly(NHMMA-hexacyclene) and 11.6% for the poly(NHMMA-15-crown-5) hydrogels. These amounts of specific ligand for Au(III) and Pb(II) ions are more suitable for the applications.

There was no critical change on the swelling ratio of the poly(NHMMA-15-crown-5) hydrogels that were examined in different pH solutions.

Swelling ratio of the poly(NHMMA-hexacyclene) hydrogels decreased with the increasing irradiation dose rates. The decrease in the equilibrium swelling ratio of the hydrogels synthesized at high dose rates is because of the high decrease of crosslinking occurring inside the hydrogels.

0.8 kGy irradiation dose was used for the production of hydrogels. This is the optimum high dose to introduce maximum specific ligand in the structure of the hydrogels.

Percentage swelling of poly(NHMMA-hexacyclene) hydrogels was found to be 2.5-fold more than poly(NHMMA-15-crown-5) hydrogels. This is because of the more hydrophilic character of the hexacyclene than the lead ionophore.

FT-IR spectra of the synthesized hydrogels have been showed that hydrogels were synthesized successfully from N-(Hydroxymethyl)methacrylamide and the specific ligands at low irradiation doses.

Gold ion adsorption onto the poly(NHMMA-hexacyclene) hydrogels was performed at low pHs between pH 1.0 and pH 2.0. This is really important to remove all interferences resulting from other transition and toxic metals in the natural samples on the removal, pre-concentration and recovery of trace amount of Au(III) ions.

Gold adsorption capacity of the poly(NHMMA-hexacyclene) hydrogels was found to be 1138 mg gold/g dry gels. This amount of Au(III) ion adsorption capacity is really feasible to recover Au(III) ions from the samples efficiently.

Adsorption equilibrium time for the Au(III) ion adsorption onto the poly(NHMMA-hexacyclene) hydrogels is really short (about 10 h) and it was feasible in the application processes.

0.8 M Thiourea in 3M HCl solution was a suitable desorption agent to desorb gold ions from the poly(NHMMA-hexacyclene) hydrogels in a short time (about 10 h).

Repeated use experiments were showed that the same hydrogels could be used more than 5 times for the adsorption-desorption of Au(III) ions with less than 3% loss on the adsorption capacity of the hydrogels.

Back-ground and atomic signals of Au(III) ions in GF-AAS spectrometry showed that high amount of matrices can be eliminated for Au(III) ion determination in the solubilized anode slime sample using the poly(NHMMA-hexacyclene) hydrogels after the adsorption-desorption cycle.

Recovery and pre-concentration experiments showed that pre-concentration factor could be at least 500-fold and recovery of the Au(III) ions could be more than 91.7% for the pre-concentration and the recovery of the Au(III) ion onto the poly(NHMMA-hexacyclene) hydrogels.

Discovered method was tested using an anode slime sample solution after adding known amount of standard gold ion into anode slime sample solution. After applying the method discovered in this study, it was observed that the method was working efficiently.

In the anode slime sample solution all metal ion concentrations and Au(III) ion concentration were measured before and after the method applied. Only Au(III) ion concentration was reduced from 1 ppm to 0.05 ppm (about 95% adsorption). Concentrations of the other transition and toxic metal ions were not changed because of the less adsorption capacity of these ions at low pHs (less than pH 2.0).

The adsorption capacity of the Pb(II) ions onto the poly(NHMMA-15-crown-5) hydrogels was found very high at all pH regions (between 1 and 8). But its maximum value was found at pH 4.0. This may be resulted from the suitable hydrated ionic size of the lead ion at this pH.

Adsorption capacity of the Pb(II) ions was found about 594 mg/g dry gels when the poly(NHMMA-15-crown-5) hydrogels were used. This adsorbed Au(III) ions value is really high, and the process seems to be very feasible for the real applications.

Adsorption equilibrium time of Pb(II) ion on the poly(NHMMA-15-crown-5) hydrogels is really short (about 2h) and this short time is really suitable for the time consumed and low-cost applications.

The best suitable desorbing agent to desorb Pb(II) ions from poly(NHMMA-15-crown-5) hydrogels was found to be 3M HNO₃.

Selectivity of the Pb(II) ion adsorption onto the poly(NHMMA-15-crown-5) hydrogels was tested mixing Cu(II), Ni(II), Co(II), Ag(I), Cr(III), Cd(II), Fe(III) and Zn(II) ions into the standard lead solution at different pHs and different lead ion concentrations. It was found that only iron showed interference effects at high pHs. But at pH 2.0, no interference effect was seen on the adsorption of Pb(II) ions onto the poly(NHMMA-15-crown-5) hydrogels.

When 100-fold less Pb(II) ion was used in the mixture (at pH 2.0), compared to the concentration of the other metal ions, it could not be observed interference effects resulted from the other metal ions.

Method validation for the recovery of Pb(II) ions was tested on the international sea-water standard. It was concluded that method working perfectly if a sample containing high amount of inorganic interferences was used and analyzed with discovered method in this study.

For four different samples such as drinking water, tap water, well water and sea water, Pb(II) ion concentration in the samples were measured by GF-AAS before and after the discovered method was applied. For the direct measurements, Pb(II) ion concentrations could be measured with high standard deviations and lead ion concentrations could not be measured in some cases because of the trace lead

ion concentrations especially in drinking water and tap water. When the discovered method was applied, standard deviation on the results were reduced dramatically due to the elimination of the matrices and detection limits could be improved applying pre-concentration during the method application.

Recovery of the lead was not changed when the standard lead solution and standard sea-water solution were used. In the case of standard lead solution, recovery was found to be 96.6% and in the case of standard sea-water, recovery was found to be 95.7%. These recovery values showed that method was really suitable to remove interference effects from the lead analysis solutions.

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