การดูดจับโลหะหนักในน้ำทะเลโดยใช้ตัวดูดจับเอมิดอกซิมที่เตรียมโดยเทคนิคการฉายรังสีแกมมา

นายอภิชาติ ชาติภูวภัทร

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บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
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ADSORPTION OF HEAVY METALS IN SEAWATER USING AMIDOXIME ADSORBENT PREPARED BY GAMMA IRRADIATION TECHNIQUE

Mr. Apichart Chartpuwapat

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A Thesis Submitted in Partial Fulfillment of the Requirements
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อภิชาติ ชาติภูวภัทร : การดูดจับโลหะหนักในน้ำทะเลโดยใช้ตัวดูดจับเอมิดอกซิมที่เตรียมโดยเทคนิคการฉายรังสีแกมมา (ADSORPTION OF HEAVY METALS IN SEAWATER USING AMIDOXIME ADSORBENT PREPARED BY GAMMA IRRADIATION TECHNIQUE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ดุลยพงศ์ วงศ์แสวง, 57 หน้า.

สำหรับวัตถุประสงค์ของการป้องกันและความปลอดภัย โดยใช้เส้นใยเอมิดอกซิมตรวจสอบความสามารถในการดูดซับโลหะหนักในน้ำทะเล และสามารถสังเคราะห์เส้นใยเอมิดอกซิมได้สำเร็จโดยใช้เทคนิคการต่อกิ่งแบบเหนี่ยวนำด้วยการฉายรังสีแกมมาที่อุณหภูมิต่ำ โดยใช้โคบอลต์-60 เป็นต้นกำเนิดรังสี ระดับของการต่อกิ่งของอะคริโลไนไตรล์ (Acrylonitrile, AN) และเมทตะคริลิคแอซิด (Methacrylic acid, MAA) บนเส้นใยพอลิเอทิลีนความหนาแน่นต่ำที่ปริมาณรังสี 40 กิโลเกรย์ คำนวณได้ประมาณ 52 เปอร์เซ็นต์ และเส้นใยแสดงความสามารถในการดูดซับตะกั่ว, สารหนู, ปรอท และยูเรเนียม ในน้ำทะเล ภายใต้เงื่อนไขของการศึกษาสำหรับตะกั่วสามารถดูดซับได้ 5.33-33.50 กรัม-ตะกั่ว/กิโลกรัม-ตัวดูดซับ และสำหรับสารหนูสามารถดูดซับได้ 0.25-0.77 กรัม-สารหนู/กิโลกรัม-ตัวดูดซับ และสำหรับปรอทสามารถดูดซับได้ 0.0001 – 0.0075 กรัม-ปรอท/กิโลกรัม-ตัวดูดซับ และสำหรับยูเรเนียมสามารถดูดซับได้ 0.0005-0.0057 กรัม-ยูเรเนียม/กิโลกรัม-ตัวดูดซับ การดูดซับยังลดลงจากเวลาในการจุ่ม ดังนั้นเส้นใยเอมิดอกซิมสามารถนำมาใช้ได้อย่างมีประสิทธิภาพในการดูดซับสำหรับตะกั่ว, สารหนู, ปรอท และยูเรเนียม ในน้ำทะเล สำหรับการจุ่มที่ระยะเวลาสั้นๆ 3 วัน

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For safety and safeguards purposes, amidoxime fibers were investigated for the ability to adsorb heavy metals from seawater. Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit the ability to adsorb Pb, As, Hg and uranium form seawater. Under the studied conditions, for the case of Pb, the adsorption capability was 5.33 – 33.50 g-Pb/kg-adsorbent. For the case of As, the adsorption capability was approximately 0.25 – 0.77 g-As/kg-adsorbent. For the case of Hg, the adsorption capability was approximately 0.0001 – 0.0075 g-Hg/kg-adsorbent. For the case of U, the adsorption capability was approximately 0.0005 – 0.0057 g-U/kg-adsorbent.The adsorption also reduced with submerging time. Thus, the amidoxime fibers can be used as a very effective detector for Pb, As, Hg and uranium in seawater for the submerging time as short as 3 days.

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CHAPTER 1

Introduction

1.1 Introduction

Throughout history and in the present time, chemical and biological weapons have been used to cause harmful and sometimes fatal effects to people. One of such cases was the terrorist attack in Tokyo on March 20,1995, where the sarin nerve gas was released in the Tokyo subway, killing 13 people and some 5,500 others were injured to varying degrees [18]. In the First World War, arsenic was applied in chemical weapons. In the Vietnam War, dimethyl arsenic acid was applied for the destruction of rice cultures [20].

Protective measures can be taken in situations with related threat from CBRN weapons. There is an institution established for management of this problem, which is Chemical, biological, radiological and nuclear centres of excellence (CBRN CoE) for the mitigation of and preparedness against risks related to CBRN material and agents. The origin of these risks can be criminal (proliferation, theft, sabotage and illicit trafficking), accidental (industrial catastrophes, in particular chemical or nuclear, waste treatment and transport) or natural (mainly pandemics but also the consequence of natural hazards on CBRN material and facilities). The CBRN CoE Initiative seeks to boost cooperation at national, regional and international levels, and to develop a common and coherent CBRN risk mitigation policy at national and regional level. Risk mitigation comprises prevention, preparedness and post-crisis management [19].

With the rapid development of global industry and the advent of new technologies, environmental contamination has presented a great threat to human health; especially with significantly the amounts of heavy metal ions in wastewater.

Various methods such as chemical precipitation, oxidation, reduction, ion exchange, reverse osmosis, membrane separation, filtration, electrolysis and adsorption have been used to remove and recover toxic contaminants from industrial effluents. For example, radiation-induced grafting of cellulose has been used for adsorption of hazardous water pollutants [11] and grafting of acrylonitrile onto chitin has been used for adsorption of arsenic in water [12].

Currently, there are a number of industrial factories which use chemicals in manufacturing processes which are located near rivers and sea. Sometimes, they intentionally release wastewater to rivers and sea. Therefore, for safety and safeguard purposes, wastewater must be measured every time. The amidoxime chelating functional groups may have the ability to adsorb heavy metals in seawater besides uranium. Therefore, the purpose of this research work is to detect heavy metals in seawater using the amidoxime adsorbent.

1.2 Objective

To adsorb heavy metals in seawater using amidoxime adsorbent prepared by gamma irradiation technique

1.3 Scope of research

1. Synthesize amidoxime adsorbent using gamma radiation
2. Collect seawater sample from the Andaman Sea
3. Study adsorption of 3 heavy metals and uranium in seawater
4. For each heavy metal, study 3 concentrations in seawater
5. Recover adsorbed heavy metals and uranium from the amidoxime fibers

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1.4 Methodology

1. Collect seawater sample from the Andaman Sea
2. Synthesize amidoxime fibers by irradiation-induced graft polymerization technique using gamma ray
3. Submerge amidoxime adsorbent into the collected Andaman Sea water
4. Recover adsorbed heavy metals and uranium from the amidoxime fibers
5. Analyze results and discussion.

1.5 Outcome

1. Gain knowledge on detection of heavy metals in seawater using amidoxime adsorbent.
2. Gain knowledge on the preparation of amidoxime fibers.

1.6 research background

S. Choi et. al. (2003) [6]: In order to recover uranium ions from seawater, chelate-type resins with amidoxime and amidoxime/carboxylic acid groups were prepared by radiation-induced polymerization of acrylonitrile (AN) and AN/acrylic acid and by subsequent amidoximation of cyano group of poly(AN), respectively. The resins were characterized by FT–IR, FT–Raman, solid-state 13C-NMR, SEM, and elemental analysis, respectively. The adsorption rates of uranium ion by resins with the amidoxime/carboxylic acid group were higher than that of resins with the amidoxime group. The adsorption of uranium ions in artificial seawater by chelate-type resins was also examined.

T. Kawai et. al. (2000) [5]: To improve the adsorption rate of uranium from seawater, hydrophilic amidoxime (AO) fibers were prepared by cografting of methacrylic acid (MAA) with acrylonitrile (AN) onto polypropylene fibers and subsequent conversion of the produced cyano group to an amidoxime group by reaction with hydroxylamine. An optimum amidoximation time of 0.75 h was selected at a weight ratio of AN to MAA (x/y) of 80/20. By varying x/y in the monomer mixture, cografted polymers were prepared. The value of x/y governed the AO group density and water content of the resultant fibrous adsorbents. As x/y increased, the AO group density of the fiber increased and its water content decreased. The AO/MAA adsorbent, based on the PP fibers prepared by cografting at an x/y of 60/40 and subsequent amidoximation, exhibited the highest uranium adsorption rate in the flow-through mode.

A. Zhang et. al. (2005) [4]: The influence of pH value on the adsorption of U(VI) onto macroporous fibrous polymeric adsorbent containing amidoxime chelating functional group (MFPA) was studied. U(VI) showed no adsorption below pH 1.0 and low adsorption in a pH range of 2.0 to 7.0, respectively. The adsorption of U(VI) onto MFPA increased significantly from pH 7.0 to 8.0 and then decreased evidently when the pH was in excess of 8.0. The optimum pH value in experiment was determined to be 8.0, which is close to that of seawater.

M. R. Lutfor et. al. (2011) [7]: Synthesis of poly(hydroxamic acid)-poly(amidoxime) chelating ligands was carried out from poly(methylacrylate-co-acrylonitrile) grafted sago starch and hydroxylamine in alkaline medium. The binding property of metal ions was performed and maximum sorption capacity of the copper was 3.20 mmol/ g and the rate of exchange of some metals was faster, i.e. $t_{1/2} \approx 7$ min (average). Two types of wastewater containing chromium, zinc, nickel, copper and iron, etc. were used and the heavy metal recovery was found to be highly efficient, about 99% of the metals could be removed from the metal plating wastewater.

Fenglin Huang et. al. (2013) [10]: Polyacrylonitrile (PAN) nanofibers were prepared by electrospinning and they were modified with hydroxylamine to synthesize amidoxime polyacrylonitrile (AOPAN) chelating nanofibers, which were applied to adsorb copper and iron ions. The conversion of the nitrile group in PAN was calculated by the gravimetric method. The structure and surface morphology of the AOPAN nanofiber were characterized by a Fourier transform infrared spectrometer (FT-IR) and a scanning electron microscope (SEM), respectively. The adsorption abilities of Cu^{2+} and Fe^{3+} ions onto the AOPAN nanofiber mats were evaluated. FT-IR spectra showed nitrile groups in the PAN were partly converted into amidoxime groups. SEM examination demonstrated that there were no serious cracks or sign of degradation on the surface of the PAN nanofibers after chemical modification. The adsorption capacities of both copper and iron ions onto the AOPAN nanofiber mats were higher than those into the raw PAN nanofiber mats. The adsorption data of Cu^{2+} and Fe^{3+} ions fitted particularly well with the Langmuir isotherm. The maximal adsorption capacities of Cu^{2+} and Fe^{3+} ions were 215.18 and 221.37 mg/g, respectively.

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A. Nilchi et. al. (2008) [8]: In this study, the acrylonitrile (AN)–divinylbenzene (DVB)–methylacrylate (MA) resin was synthesized via suspension polymerization in the presence of toluene as diluent, and benzoylperoxide (BPO) as initiator. The effects of MA as a hydrophilic agent and toluene as a diluent on the anion and cation exchange capacity of the synthesized amidoxime resins were investigated before and after alkaline treatment. The results showed that the anion exchange capacity decreased with an increase in the amount of MA while alkaline treatment had no significant effect. Also, the cation exchange capacity increased with an increase in the amount of hydrophilic agent and reached a maximum point. The sorption equilibrium was achieved relatively fast within 40 min, and the resin exhibited affinity towards lead (II), copper (II) and in particular U(VI), and the order of adsorption affinity were $UO_2^{2+} > Pb^{2+} >> Co^{2+} > Cu^{2+} >> Cd^{2+}$. The adsorption of uranium was directly depended up on the pH value. Furthermore, the macroreticular chelating resin, containing amidoxime group had higher adsorption of uranium (VI) than other metal ions studied. Finally, the alkaline treatment enhanced the potential for much faster adsorption and the highly porous chelating resin provided a more favorable pore structure for the rapid rate of diffusion of metal ions.

Jie Chen et. al. (2012) [9]: Two types of silica gel supported amidoxime (SG-HE-AO and SG-HO-AO) adsorbents were prepared via the reactions of silica gel supported acrylonitrile functional group (SG-AN) with hydroxylamine under alkaline conditions. The SG-AN was obtained by so-called ‘‘heterogeneous’’ and ‘‘homogeneous’’ methods and named SG-HE-AN and SG-HO-AN, respectively. All the structures of adsorbents and intermediate were characterized by FT-IR, SEM, porous structure analysis and elemental analysis. The amidoxime group content of SG-HE-AO and SG-HO-AO were 1.28 and 0.77 mmol g_1, respectively, indicating that the heterogeneous method is more effective than the homogeneous method to anchored functional groups onto the surface of silica gel in this study. In terms of Hg(II) adsorption, SG-HE-AO exhibited better capability than SG-HO-AO. The adsorption kinetics of the two adsorbents followed the pseudo secondorder process in the temperature range of 5–35 ^{o}C. Increased temperature was beneficial to adsorption. Langmuir and Freundlich isotherm models were both applied to experimental data analysis, and the former proved to be a better fit. Finally, in Hg(II)–Pb(II), Hg(II)–Ag(I), Hg(II)–Cu(II) and Hg(II)–Ni(II) binary systems, both SG-HE-AO and SG-HO-AO exhibited excellent adsorption selectivity for Hg(II).

Truong Thi Hanh et. al. (2015) [12]: Radiation-induced grafting is an effective technique for preparation of novel materials. In this study, partially deacetylated chitin with deacetylation degree (DDA) of about 40% was graft-copolymerized with acrylonitrile (AN) by a γ-ray pre-irradiation method. The maximal grafting degree of AN onto preirradiated chitin at 2571.2 kGy was 114% for AN concentration in dimethylformamide of 40% (v/v) at 70 ^{o}C for 8 h. The mixture ratio of 0.1 N NH_2OH HCl to 0.1 N NaOH was selected to be 7:3 (v/v) for amidoxime conversion of cyano-groups on grafted chitin (Chi-g-AN). The characteristics of modified chitin were depicted by the FT-IR spectra, BET area and SEM images. Adsorption equilibrium of As(III) onto Chi-g-AN converted amidoxime (Chi-g-AN-C) fits with the Langmuir model and the maximal adsorption capacity was 19.724 mg/g. The break-through times of As(III) on Chi-g-AN-C in column adsorption experiments increased with the increase in bed depths.

Vareeporn Ratnitsai et. al. (2015) [14]: Enhancement of uranium extraction from seawater using chromic-acid-treated amidoxime adsorbent was studied. Chromic-acid-treated amidoxime fibers were synthesized based on the simultaneous irradiation grafting method at a low temperature. Low-density polyethylene (LDPE) fibers were treated with chromic acid for up to 90 minutes. After the treatment, the fibers were submerged in 60:40 acrylonitrile:methacrylic acid monomer by volume and irradiated with 40 kGy γ-ray. When submerged in shallow seawater with an average temperature of 30 °C for 4 weeks, the amidoxime adsorbent exhibited the adsorption capacity of 2.06 g-U/kg-adsorbent. Uranium concentrations in Thailand's seawater collected at various depths and locations were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) to be about 3 ppb everywhere.

CHAPTER 2
LITERATURE REVIEWS

2.1 Arsenic

Arsenic is a chemical element with symbol As and atomic number 33. Arsenic is a metalloid, which basically means that it has the properties of both metal and non-metal. Arsenic can be found in natural in 2 types: organic and inorganic. The inorganic form is more toxic than organic.

Arsenic can be found in seawater (2-4 ppb), and in rivers (0.5-2 ppb). Half of the arsenic present is bound to particles. Freshwater and sea algae contain about 1-250 ppm of arsenic, freshwater mycrophytes contain 2-1450 ppm, marine molluscs contain 1-70 ppm, marine crustaceans contain 0.5-69 ppm, and fishes contain 0.2-320 ppm (all values are based on dry mass). In some marine organisms, such as algae and shrimp, arsenic can be found in organic compounds. The legal limit for arsenic in water applied by the World Health Organization (WHO) is 10 µg/L.

2.1.1 Into the body

Arsenic can enter the body via exposed skin, breathing, eating food and drinking water contaminated with arsenic. When arsenic gets inside the body, it will be removed very quickly from the body. Research study found that approximately 80-90% of arsenic into the body will be removed from body by urine within 2 days.

2.1.2 Health effects

Arsenic occurs in inorganic and organic forms. Inorganic arsenic compounds (such as those found in water) are highly toxic while organic arsenic compounds (such as those found in seafood) are less harmful to health.

2.1.2.1 Acute effects

The immediate symptoms of acute arsenic poisoning include vomiting, abdominal pain and diarrhoea. These are followed by numbness and tingling of the extremities, muscle cramping and death, in extreme cases.

2.1.2.2 Long-term effects

The first symptoms of long-term exposure to high levels of inorganic arsenic (e.g., through drinking-water and food) are usually observed in the skin, and include pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (hyperkeratosis). These occur after a minimum exposure of approximately five years and may be a precursor to skin cancer.

2.2 Lead

Lead is a chemical element with symbol Pb and atomic number 82. Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements.

Seawater contains trace amounts of lead (2-30 ppt). On average, rivers contain between 3 and 30 ppb. Phytoplankton contains approximately 5-10 ppm lead (dry mass), freshwater fish contains approximately 0.5-1000 ppb, and oyster contains approximately 500 ppb.

The World Health Organization (WHO) stated a legal limit of 50 ppb for lead in 1995, which is decreased to 10 ppb in 2010.

2.2.1 Into the body

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%).

Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead.

Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes.

2.2.2 Health effects

For as far as we know, lead fulfils no essential function in the human body. It can merely do harm after uptake from food, air or water.

Lead can cause several unwanted effects, such as:

- Disruption of the biosynthesis of haemoglobin and anaemia
- A rise in blood pressure
- Kidney damage
- Miscarriages and subtle abortions
- Disruption of nervous systems
- Brain damage
- Declined fertility of men through sperm damage
- Diminished learning abilities of children
- Behavioural disruptions of children, such as aggression, impulsive behavior and hyperactivity

Lead can enter a foetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children.

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2.3 Mercury

Mercury is a chemical element with symbol Hg and atomic number 80. Mercury is the only common metal which is liquid at ordinary temperatures. Mercury is sometimes called quicksilver. It is a heavy, silvery-white liquid metal. It is a rather poor conductor of heat if compared with other metals but it is a fair conductor of electricity. It alloys easily with many metals, such as gold, silver, and tin. These alloys are called amalgams.

2.3.1 Into the body

Mercury is not naturally found in foodstuffs, but it may turn up in food as it can be spread within food chains by smaller organisms that are consumed by humans, for instance through fish. Mercury concentrations in fish usually greatly exceed the concentrations in the water they live in. Cattle breeding products can also contain eminent quantities of mercury. Mercury is not commonly found in plant products, but it can enter human bodies through vegetables and other crops, when sprays that contain mercury are applied in agriculture.

2.3.2 Health effects

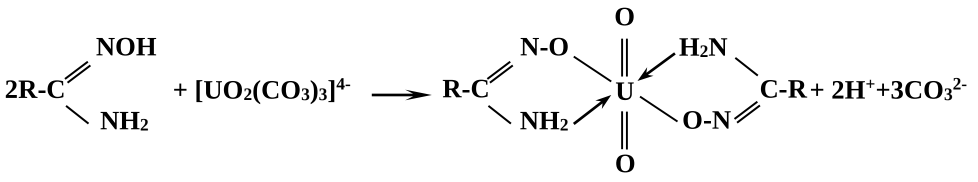
Elemental and methylmercury are toxic to the central and peripheral nervous systems. The inhalation of mercury vapour can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys, and may be fatal. The inorganic salts of mercury are corrosive to the skin, eyes and gastrointestinal tract, and may induce kidney toxicity if ingested.

Neurological and behavioural disorders may be observed after inhalation, ingestion or dermal exposure of different mercury compounds. Symptoms include tremors, insomnia, memory loss, neuromuscular effects, headaches and cognitive and motor dysfunction. Mild, subclinical signs of central nervous system toxicity can be seen in workers exposed to an elemental mercury level in the air of 20 $\mu g/m^3$ or more for several years. Kidney effects have been reported, ranging from increased protein in the urine to kidney failure.

2.4 Uranium

Uranium is a chemical element with symbol U and atomic number 92. It is a silvery-white metal in the actinide series of the periodic table. In nature, uranium is found as uranium-238 (99.3%) and uranium-235 (0.7%). In seawater contains about 4.5 billion tons of dissolved uranium. Uranium is dissolved in seawater at a concentration of about 3 mg/m^3 in the ionic form of uranyl tricarbonate ions.

For the adsorption of uranium in seawater, the functional group of the adsorbent must be able to create uranyl complex at the pH and temperature of natural seawater. For the case of amidoxime functional group, UO_2^{2+} ions will be adsorbed through the reaction shown in Equation (1):



(1)

2.5 Polymer

Polymers are substances containing a large number of structural units joined by the same type of linkage. These substances often form into a chain-like structure. Polymers in the natural world have been around since the beginning of time. Starch, cellulose, and rubber all possess polymeric properties.

2.5.1 The Structure of Polymers

Many common classes of polymers are composed of hydrocarbons, compounds of carbon and hydrogen. These polymers are specifically made of carbon atoms bonded together, one to the next, into long chains that are called the backbone of the polymer. Because of the nature of carbon, one or more other atoms can be attached to each carbon atom in the backbone. There are polymers that contain only carbon and hydrogen atoms. Polyethylene, polypropylene, polybutylene, polystyrene and polymethylpentene are examples of these. Polyvinyl chloride (PVC) has chlorine attached to the all-carbon backbone. Teflon has fluorine attached to the all-carbon backbone.

2.5.1.1 Classification based on structure of polymers, there a four types of molecular structures.

1. Linear chain polymers
2. Branched chain polymers
3. Crossed linked polymers.
4. Network Polymer

1. Linear chain polymers

In a Linear Polymer the mer units are joined together end-to-end in single chains. Van der Waal bonding exist between chains and are not very significant. They have very good chain packing efficiency thus they can easily crystallize. Linear polymers are high density polymers. For example, polythene, nylon and polyesters are linear chain polymers.

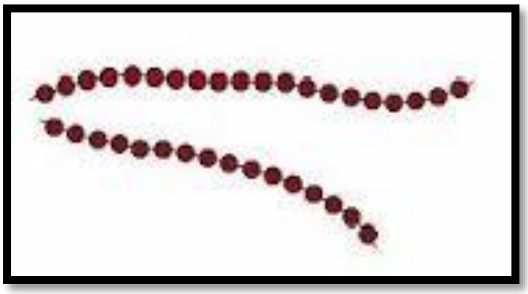


Figure 1. Linear chain polymers
(source: http://www.kazuli.com/UW/4A/ME534/asgn1.htm)

2. Branched chain polymers

In Branched Polymers side branch chains are connected to the main chains. The branches, considered to be part of the main chain molecule results from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches which, in turn, lowers the polymer density. Branched polymers are typically stronger than liner polymers, since the chains resist motion For example, low density polyethene , glycogens etc.

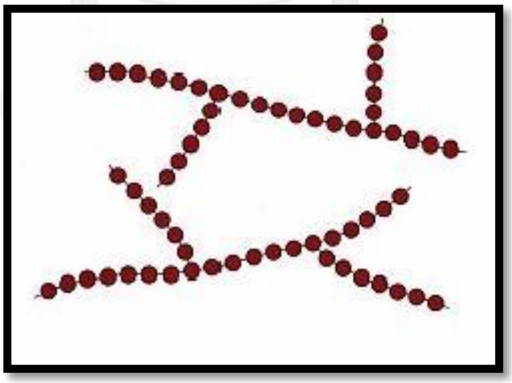


Figure 2. Branched chain polymers
(source: http://www.kazuli.com/UW/4A/ME534/asgn1.htm)

3. Cross-linked polymers

In a Cross Linked Polymer adjacent linear chains are joined to one to another at various positions by covalent bonds. The process of cross linking is achieved either during syntheses or by a non-reversible chemical reactions that occurs at high temperatures. Cross linking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Cross-linked polymers are stronger than branched polymers, but are also more brittle. For example melamine formaldehyde resin bakelite etc.

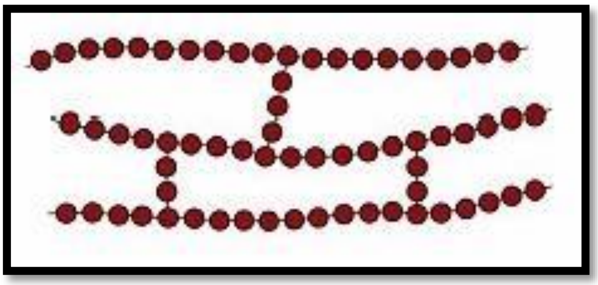


Figure 3. Cross-linked polymers
(source: http://www.kazuli.com/UW/4A/ME534/asgn1.htm)

4. Network Polymer

In a Network Polymer tri-functional mer units, having three active covalent bonds form three dimensional networks. These materials creates distinctive mechanical and thermal properties.

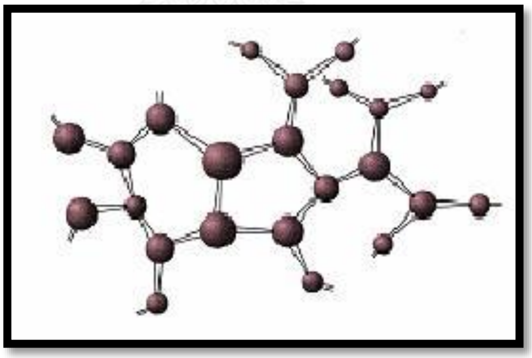


Figure 4. Network Polymer
(source: http://www.kazuli.com/UW/4A/ME534/asgn1.htm)

2.5.1.2 Copolymers

Copolymers are polymer which consist of two different mer units. They are linear addition chains composed of two or more types of molecules. There are four types of copolymers as seen in the figure below; (a) alternating monomers, (b) random monomers, (c) block copolymers and (d) grafted copolymers. In the figure open blocks represent one type of monomer and solid blocks represent a second type of monomer.

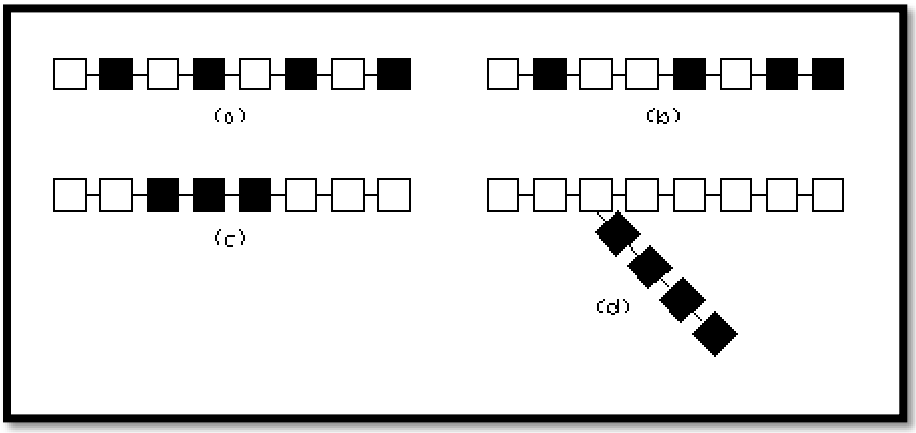


Figure 5. Copolymers
(source: http://www.kazuli.com/UW/4A/ME534/asgn1.htm)

2.5.2 Polyethylene (PE)

Polyethylene (PE) - The term polyethylene describes a huge family of resins obtained by polymerizing ethylene gas, $H_2C=CH_2$, and it is by far the largest volume commercial polymer. This thermoplastic is available in a range of flexibilities and other properties depending on the production process, with high density materials being the most rigid. Polyethylene can be formed by a wide variety of thermoplastic processing methods and is particularly useful where moisture resistance and low cost are required. Low density polyethylene typically has a density value ranging from 0.91 to 0.925 g/cm³, linear low density polyethylene is in the range of 0.918 to 0.94 g/cm³, while high density polyethylene ranges from 0.935 to 0.96 g/cm³ and above.

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2.5.2.1 Low density polyethylene (LDPE)

LDPE has a high degree of short- and long-chain branching. Natural color is milky color, translucent with high impact strength

2.5.2.2 Linear low density polyethylene (LLDPE)

LLDPE is a substantially linear polymer with significant numbers of short branches. Natural color is milky color, translucent with high impact strength.

2.5.2.3 High density polyethylene (HDPE)

HDPE has a low degree of branching. Natural color is milky white, semi-translucent depending on density.

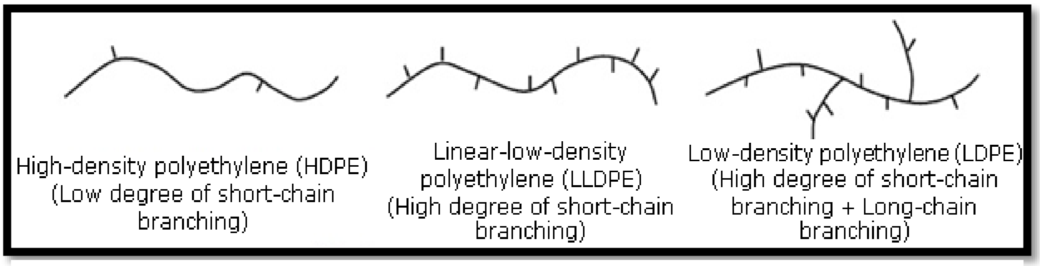

Figure 6. Schematic model of the structure of polyethylene
(source: http://www.toyo-heisei.co.jp/tec_info_1_2_e.html)

2.5.3 Carboxyl group

The carboxyl group is an organic functional group consisting of a carbon atom double bonded to an oxygen atom and single bonded to a hydroxyl group.

The carboxyl group is commonly written as -C(=O)OH or -COOH.

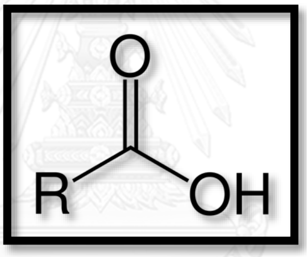

Figure 7. Carboxyl function group
(source: http://chemistry.about.com/od/chemistryglossary/g/Carboxyl-Group-Definition.htm)

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2.6 Interaction of gamma rays

Gamma ray is an electromagnetic wave. When it enters matter, many interactions will occur. The three important types are photoelectric effect, Compton scattering and pair production.

2.6.1 Photoelectric effect

Photoelectric effect occurs when gamma photon interacts with matter and transfers all energy to an electron. The electron is ejected from the atom, which is called photoelectron. The kinetic energy of the ejected electron (E_e) is equal to the difference between energy of the incoming photon (hv) and the binding energy (B.E.) as shown in Equation (2):

$$\mathrm{E_e} = \mathrm{hv} - \mathrm{B.E.} \tag{2}$$

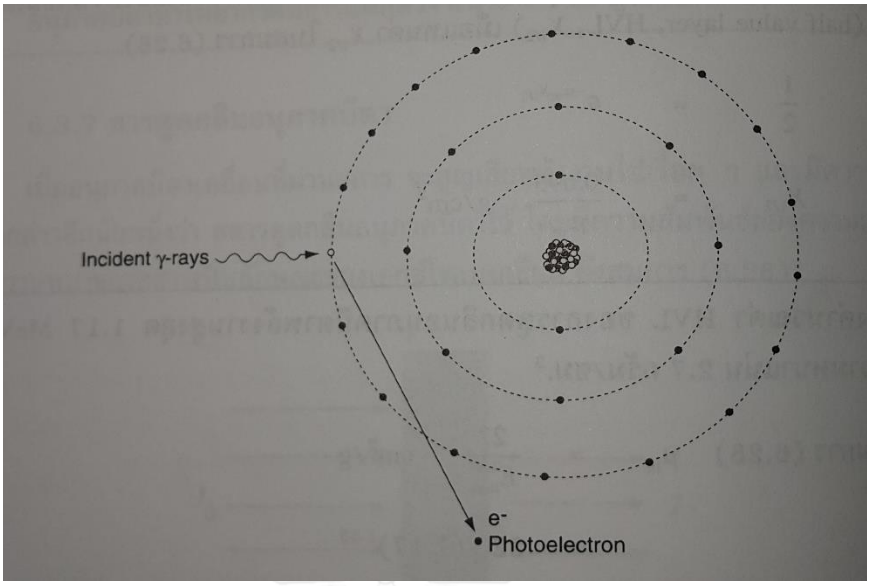

Figure 8. Photoelectric effect

2.6.2 Compton scattering

Compton scattering occurs when gamma photon interacts with an electron in the atom. The photon losses some energy to the electron and the ejected Compton electron leaves the orbit with an angle (Φ) to the original direction. The photon with lower energy changes direction through an angle (θ) with the original direction, having longer wavelength. The energy of the scattered photon (hv') can be calculated from the initial photon energy (hv) according to Equation (3):

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$$\mathrm{hv}' = \frac{\mathrm{hv}}{1+(\mathrm{hv}/\mathrm{mc}^2)(1-\cos\theta)} \tag{3}$$

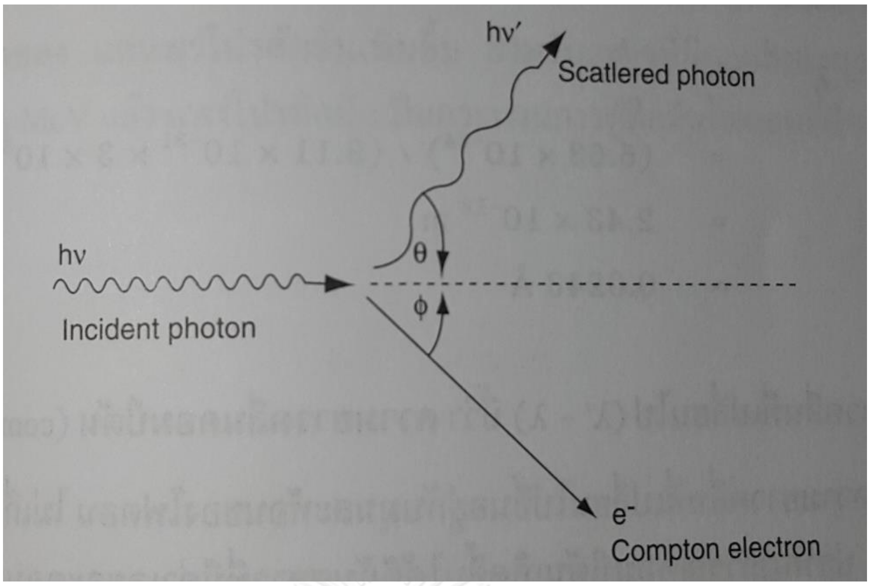

Figure 9. Compton effect

2.6.3 Pair production

Pair production occurs with gamma photon having energy of at least 1.022 MeV. The photon moves to near the nucleus of an atom and the photon disappears. The energy of the photon is used to create a pair of electron and positron (thus, the name “pair production”).

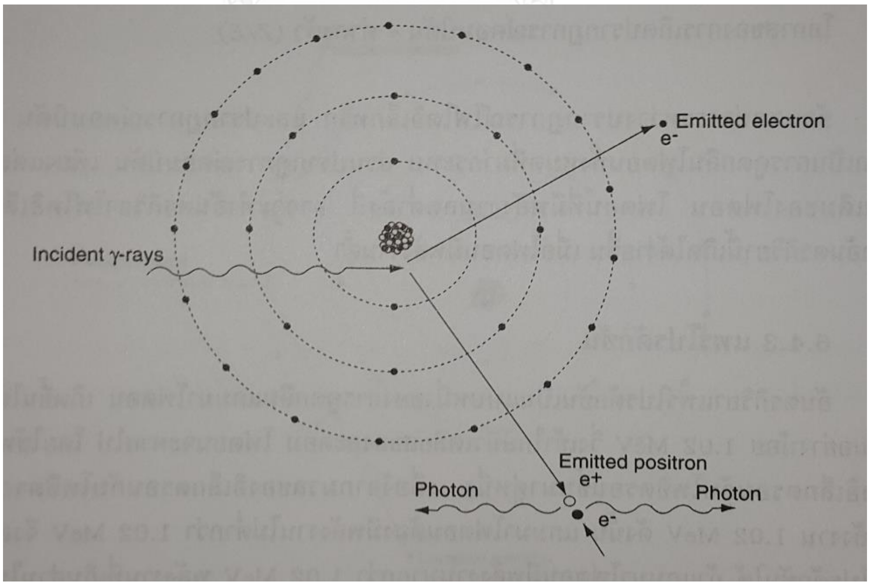

Figure 10. Pair production

2.7 Polymer irradiation

Energy from a radiation source can destroy bonds and arrange atoms, resulting in new structures. Many types of interactions will occur when irradiating polymers, which can be categorized as follows:

2.7.1 Damage by radiation

The destruction of covalent bonds by radiation is called Scission. Separation of carbon-to-carbon bond reduces the polymer's molecular weight. For example, the long chains of polytetrafluorethylene can be broken into short ones. The plastic loses strength and causes a rupture in the end.

2.7.2 Improvement by radiation

Some types of polymer is damaged by radiation. But if the radiation dose is controlled well, it can provide positive benefits. For example, radiation causes bonding of polyethylene to become broken and causes arrangement of new molecular structure of branches with polyethylene. The structure of this branch makes polyethylene exhibit a higher boiling point than that of water. On the contrary, excessive radiation dose will break apart chains of polyethylene.

2.7.3 Polymerization by radiation

When a monomer is irradiated, polymerization is initiated by a reactive species produced from a certain compound called an initiator. The reactive species can be a cation, anion, or free radical added to a monomer molecule. The process is repeated as monomer molecules are added to the polymerized chain.

2.7.4 Grafting by radiation

The use high-energy radiation for preparation of grafted and crosslinked polymers occurred since 1960. Main radiation sources are such as high-energy gamma rays and ion beams. The following three main methods have been used.

2.7.4.1 Preirradiation Technique

In this method, polymeric backbone will be irradiated first, usually by irradiation in vacuum or under inert gas to produce relatively-stable free radicals. The irradiated polymer is then reacted with the monomer.

2.7.4.2 Peroxidation Technique

This technique is similar to the preirradiation technique, however, the polymer will be irradiated in the presence of air or oxygen. This procedure produces hydroperoxide or diperoxide, depending on the nature of the polymer type and condition of irradiation.

2.7.4.3 Simultaneous Method

The polymer will be irradiated simultaneously with monomer. Monomer may be in the form of vapor, liquid or solution. Active sites will occur on both monomer and polymer.

2.8 Preparation of amidoxime functional group

Adsorption of heavy metals from seawater can be achieved using a polymer material with the amidoxime functional group. Synthesis of the amidoxime fibers consists of 2 step:

1. Irradiation-induced graft polymerization

Gamma ray is used to attack to C-H bond within polyethylene (PE). A reaction with acrylonitrile monomer mixed with methacylic acid is induced. Under a suitable condition, grafting of the cyano group and the carboxylic group on the surface of polyethylene occurs.

2. Amidoximation

NH_2OH is used under a suitable condition to convert the cyano group into the amidoxime functional group as shown in the Figure.

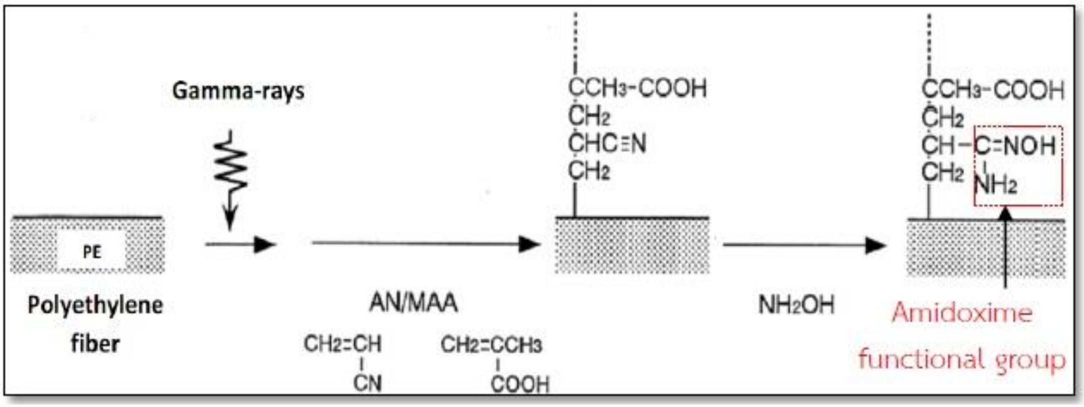

Figure 11. Preparation of amidoxime fibers

2.9 Water Quality standards

Table 1. Water Quality standards [1]

Industrial Effluent Standards		
Parameters	**Standard Values**	**Method for Examination**
1. pH value	5.5-9.0	pH Meter
2.Temperature	not more than 40°C	Thermometer during the sampling
3.Heavy metals		
1. Zinc (Zn)	not more than 5.0 mg/l	Atomic Absorption Spectro Photometry; Direct Aspiration or Plasma Emission Spectroscopy ; Inductively Coupled Plama : ICP
2. Chromium (Hexavalent)	not more than 0.25 mg/l	
3. Chromium (Trivalent)	not more than 0.75 mg/l	
4. Copper (Cu)	not more than 2.0 mg/l	
5. Cadmium (Cd)	not more than 0.03 mg/l	
6. Barium (Ba)	not more than 1.0 mg/l	
7. Lead (Pb)	not more than 0.2 mg/l	
8. Nickel (Ni)	not more than 1.0 mg/l	
9. Manganese (Mn)	not more than 5.0 mg/l	

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10. Arsenic (As)	not more than 0.25 mg/l	Atomic Absorption Spectrophotometry; Hydride Generation, or Plasma Emission Spectroscopy; Inductively Coupled Plasma : ICP
11. Selenium (Se)	not more than 0.02 mg/l	
12. Mercury (Hg)	not more than 0.005 mg/l	Atomic Absorption Cold Vapour Technique

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CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Low-density polyethylene (LDPE) fiber
3.1.2 Acrylonitrile (AN)
3.1.3 Methacrylic acid (MAA)
3.1.4 Dimethyl sulfoxide (DMSO)
3.1.5 N,N-dimethylformamide (DMF)
3.1.6 Hydroxylamine hydrochloride (NH2OH•HCl)
3.1.7 Methanol
3.1.8 Potassium hydroxide (KOH)
3.1.9 Sodium hydroxide (NaOH)
3.1.10 Sulfuric acid (H2SO4)
3.1.11 Hydrochloric acid (HCl)
3.1.12 Nitric acid (HNO3)
3.1.13 Lead (II) nitrate
3.1.14 Arsenic trioxide
3.1.15 Mercury (II) Chloride
3.1.16 Tricarbonate uranylate solution
3.1.17 Deionized water (DI water)
3.1.18 Seawater sample
3.1.19 Plastic sieve
3.1.20 Filter paper
3.1.21 Gamma Irradiator
3.1.22 Fourier Transform Infrared Spectrometer
3.1.23 Scanning Electron Microscope, JSM model 6400
3.1.24 Inductively Coupled Plasma Mass Spectrometry

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3.2 Location of seawater collection

Seawater sample was collected from the Andaman Sea at Phuket Marine Biological Center.

Figure 12. Phuket Marine Biological Center at Phuket province

Figure 13. Collected seawater

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3.3 Synthesis

3.3.1 Preparation of amidoxime fibers

3.3.1.1 Irradiation-induced cograft polymerization

To prepare LDPE fibers for cograft polymerization, LDPE fibers were washed with deionized water (DI) and dried in a forced-convection oven at 50°C for 24 hours to obtain a constant weight. The weight of LDPE fibers was recorded.

The fibers were immersed in a container containing two monomers with a mixing ratio of 60:40 [acrylonitrile (AN) : methacrylic acid (MAA)] by volume. The presence of MAA enhanced the hydrophilicity of the fibers, and this optimized mixing ratio was adopted from Kawai's work [5]. The mixture of the two monomers was diluted in 50 (w/w)% DMSO as a solvent.

The simultaneous irradiation cografting method at low temperature was achieved by putting ice cubes around the container for irradiation. The container was irradiated with gamma-ray from Co-60 at 40 kGy [13].

(a) Ice cubes around the container (b) Gamma-ray radiator

Figure 14. Ice cubes around the container for irradiation and gamma-ray radiator

After irradiation, the fibers were removed from the container and were thoroughly washed with DMF several times to completely remove homopolymer formation. The fibers were washed with deionized water (DI) and dried in a forced-convection oven at 50°C for 24 hours to obtain a constant weight. The weight of cografted fibers was recorded. The degree of cografting was calculated from the weight gain using Equation (4):

$$\text{Degree of cografting} = \frac{(W_1 - W_0)}{W_0} \text{x} 100 \tag{4}$$

where W_0 is the weight of the starting fibers and W_1 is the weight of the cografted fibers. Then, the cografted fibers were investigated for the characteristic band of the cyano group by Fourier Transform Infrared (FTIR) Spectroscopy technique.

3.3.1.2 Amidoximation of cyano group

The cyano groups of the cografted fibers were converted into the amidoxime groups by immersing the cografted fibers in 3 (w/v)% $NH_2OH{\bullet}HCl$ solution at 77 ^{o}C for 1.5 hours. The fibers were subsequently washed with 50 : 50 (v/v)% methanol : DI water and immersed in 1 M HCl solution for 15 minutes. The amidoxime fibers were washed DI and dried in a forced-convection oven at 50 ^{o}C for 48 hours to obtain a constant weight. The weight of the amidoxime fibers was recorded. Alkaline treatment of fibers was performed by submerging in a potassium hydroxide (KOH) solution at 80 ^{o}C for 1 hour. Then, the amidoxime fibers were repeatedly washed with DI water until pH of 9 of the rinse was obtained. Finally, the fibers were dried in a forced-convection oven at 50^{o}C for 48 hours to obtain a constant weight. The weight of the amidoxime fibers was recorded and the amidoxime group density was calculated from the weight gain using Equation (5):

$$\text{Amidoxime group density (mol/kg)} = \frac{(W_2 - W_1)}{69.5W_2} \text{x} 1000 \qquad (5)$$

where W_2 is the weight of the amidoxime fibers and the number 69.5 represents the molecular weight of hydroxylamine hydrochloride, $NH_2OH{\bullet}HCl$ (Saito K. et. al., 1987). Then, the amidoxime fibers were investigated for the characteristic bands of the amidoxime group using the FTIR technique. The amidoxime fibers were placed in bags constructed of loosely-woven plastic fibers. The lose surfaces of the plastic bags ensured no obstruction to the flow of seawater.

Figure 15. Plastic bag containing amidoxime fibers

3.3.2 Submerging of amidoxime adsorbent into the collected Andaman seawater

To test heavy metal adsorption efficiencies of amidoxime fibers, the fibers in the plastic bags were submerged in a sample of seawater in a 50-L plastic container in a laboratory at room temperature. The seawater sample was collected from Phuket Province, Thailand. For the study of Pb adsorption, 3 concentrations in seawater were studied: 0.2, 1 and 2 g/L. For the study of As adsorption, 3 concentrations in seawater were studied: 0.25, 0.625 and 1.25 g/L. For the study of Hg adsorption, 3 concentrations in seawater were studied: 0.005, 0.025 and 0.05 g/L. For the study of U adsorption, 1 concentrations in seawater were studied: 150 ppb. The submerging time was 1, 2, 3 and 4 weeks.

(a) System before addition of heavy metals

(b) System after addition of heavy metals

Figure 16. 50-L plastic container for the study

3.3.3 Recovery of adsorbed heavy metals and uranium from the amidoxime fibers

Amidoxime fibers were removed from the seawater sample, washed with DI water and dried in a forced-convection oven at 50°C for 1 hour. They were then immersed in 1 M HCl at 50 °C for 1 hour in order to elude adsorbed metals. The HCl solution with eluents was dried and added with 30 mL 1% nitric acid solution to prepare for an analysis by inductively coupled plasma mass spectrometry (ICP-MS).

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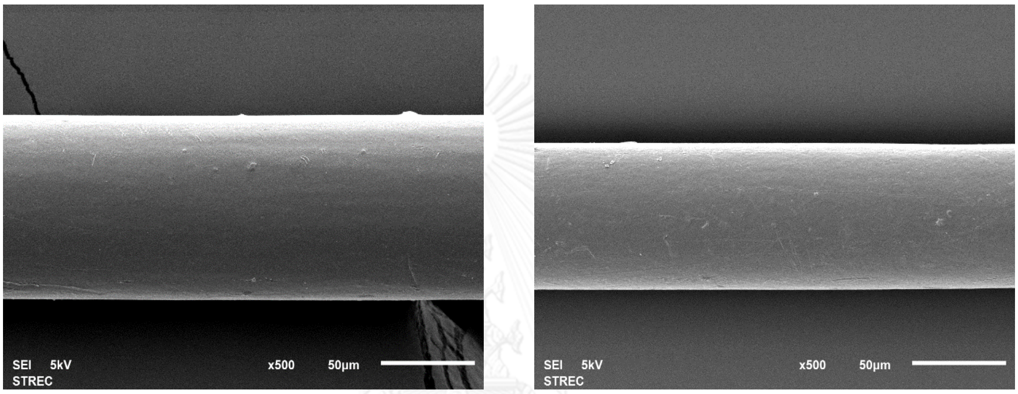
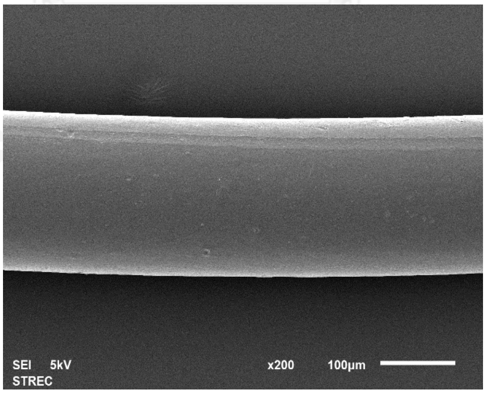
CHAPTER 4
RESULTS

4.1 SEM analysis of fiber surfaces

Fiber surfaces were observed by scanning electron microscope (SEM). Figure 17(a) shows the smooth surface of LDPE fiber. Figure 17(b) shows the surface of the cografted LDPE fiber which is rougher than LDPE fiber. Figure 17(c) show the surface of the amidoxime fiber.



(a) LDPE fiber **(b) Cografted LDPE fiber**



(c) Amidoxime fiber

Figure 17. SEM micrographs of the adsorbent under different states of preparation

4.2 FTIR analysis of functional groups

Characteristic absorption bands of functional groups were investigated by the FTIR technique. For the FTIR spectra of the LDPE fiber shown in Figure 18, the characteristic absorption bands of polyethylene at wave numbers 2849 and 1463 cm^{-1} due to C-H alkyl stretch and C-H, respectively, are clearly present. In fact, as expected, these two absorption bands are present in all spectra. The characteristic absorption bands of cografted AN/MAA appear at wave numbers 2243 and 1712 cm^{-1} due to C≡N of poly(acrylonitrile) and C=O of poly(methacrylic acid), respectively, as shown in Figure 19. After the amidoxime group conversion, the C≡N band at wave number 2243 cm^{-1} disappears, and the N-H stretch band of the amidoxime group at wave number 3360 cm^{-1} as well as the C=O band of the amidoxime group at wave number 1657 cm^{-1} become present, as shown in Figure 20.

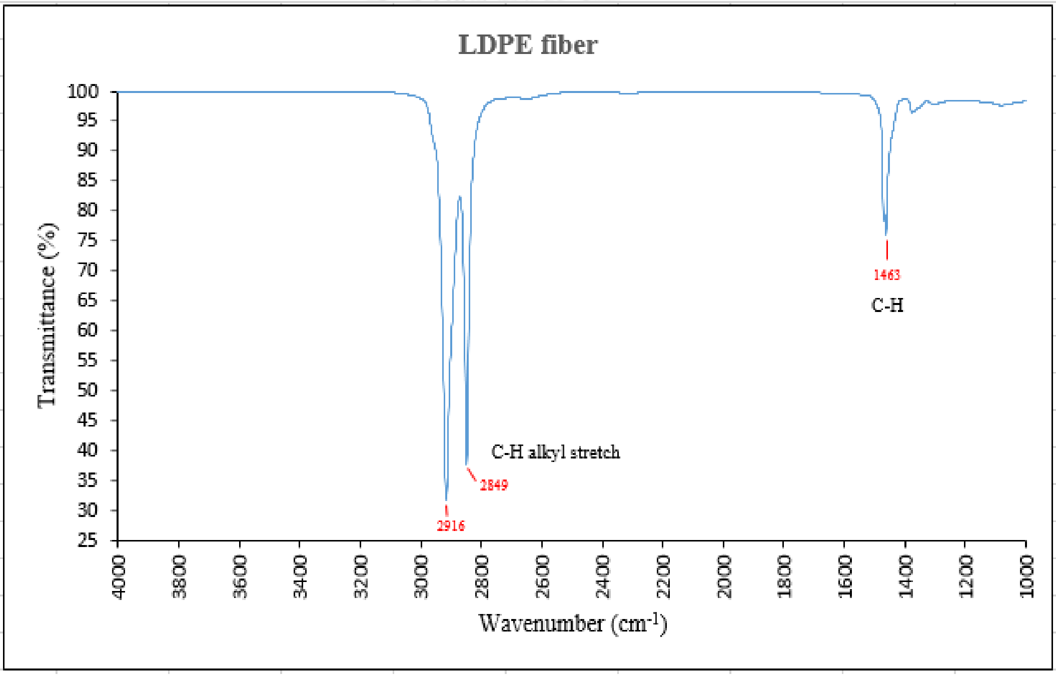


Figure 18. FTIR spectra of LDPE fiber

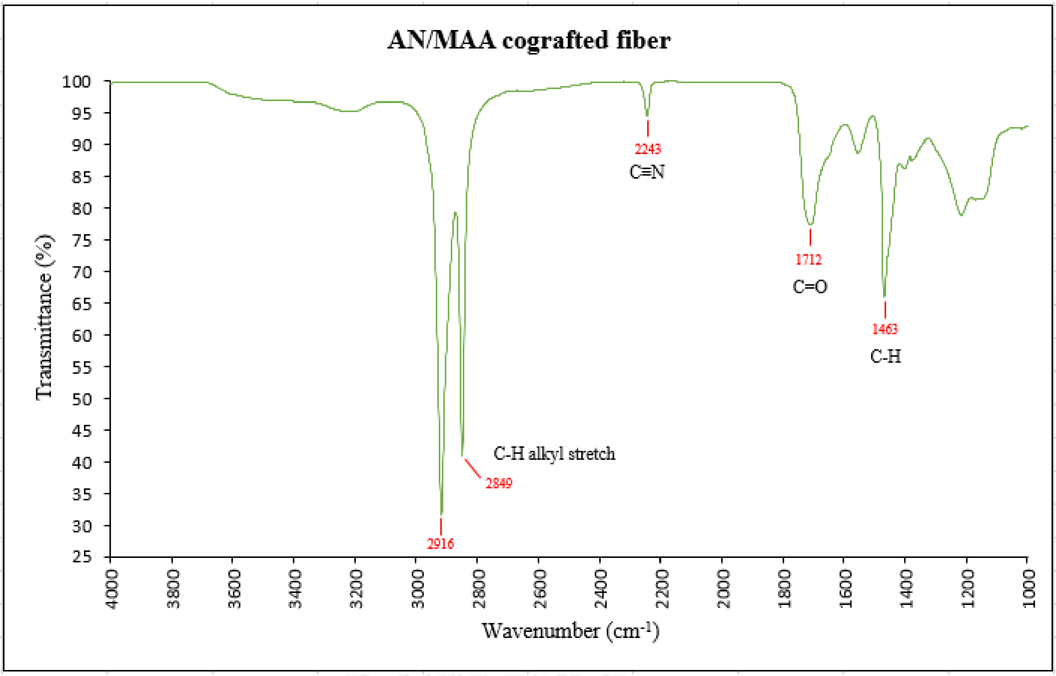


Figure 19. FTIR spectra of AN/MAA cografted fiber

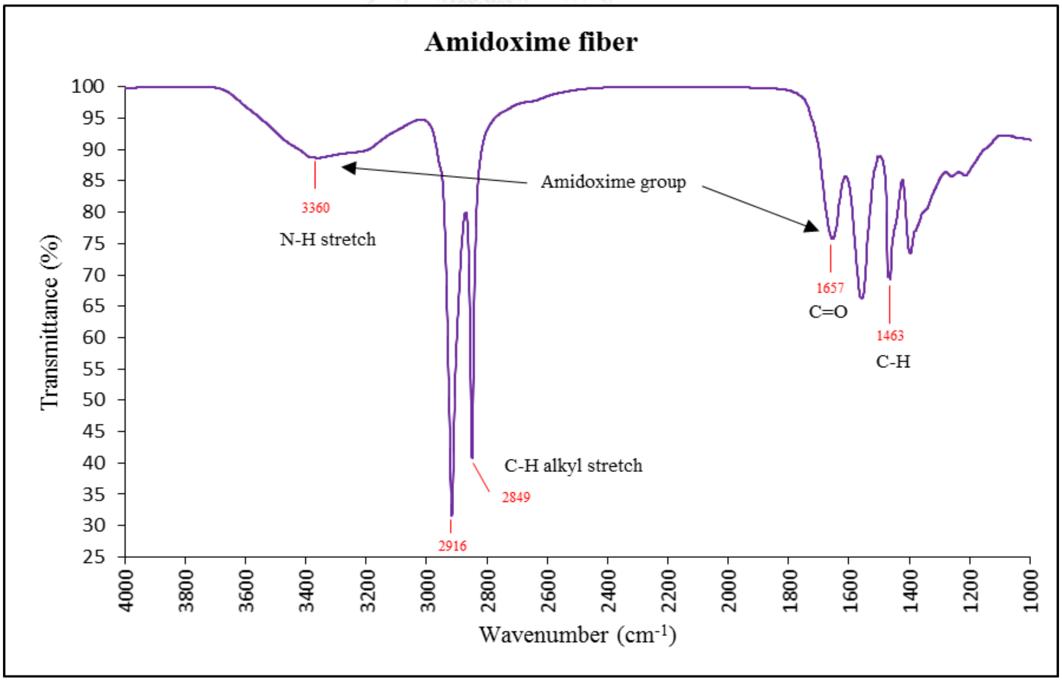


Figure 20. FTIR spectra of amidoxime fiber

4.3 Heavy metals and uranium extraction from seawater

4.3.1 Pb adsorption efficiency of amidoxime fibers

Results from ICP-MS analysis are shown Table 2 and plotted in Figure 21 in order to show the trends. For concentration 1, the adsorption efficiencies for Pb for the submerging time of 0.43, 1, 2, 3 and 4 weeks were 26.0017, 18.6132, 13.0232, 10.8492 and 10.3790 g-Pb/kg-adsorbent, respectively. For concentration 2, the adsorption efficiencies for Pb were 31.6170, 33.4965, 13.5412, 9.4919 and 7.5622 g-Pb/kg-adsorbent, respectively. For concentration 3, the adsorption efficiencies for Pb was 7.9123, 17.1148, 10.8818, 5.3325 and 9.0186 g-Pb/kg-adsorbent, respectively. The adsorption efficiency for Pb was substantially higher than that of As, Hg and U.

Moreover, the adsorption reduced with submerging time. This behavior can be explained as follows. When the adsorbent was initially submerged in the seawater, heavy metals were adsorbed rapidly, reaching full capacity of the adsorbent in a short time. With continued submersion, heavy metals in the seawater bind with the adsorbed heavy metals and results in de-adsorption. This behavior was also observed in the study on Cu(II) ion absorption by chitosan [15].

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Table 2. Results of Pb adsorption of the amidoxime fibers

Plastic container	**Concentration of Pb (g/L)**	**Submersion duration (weeks)**	**Elements**
			Pb (g-Pb/kg-adsorbent)
1	0.2	0.43	26.0017
		1	18.6132
		2	13.0232
		3	10.8492
		4	10.3790
2	1	0.43	31.6170
		1	33.4965
		2	13.5412
		3	9.4919
		4	7.5622
3	2	0.43	7.9123
		1	17.1148
		2	10.8818
		3	5.3325
		4	9.0186

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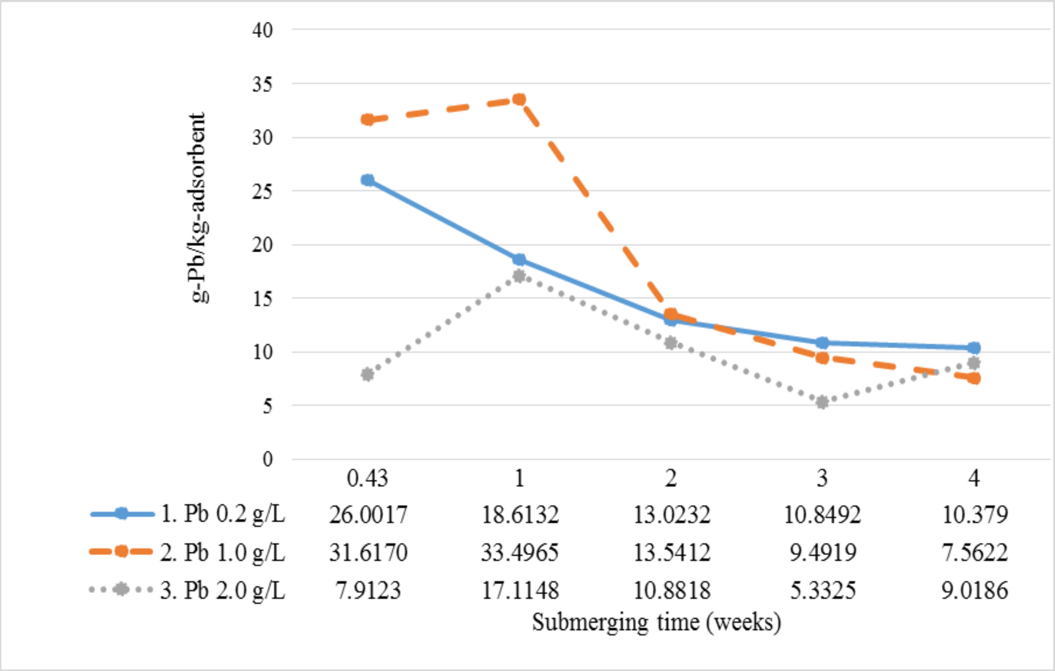

Figure 21. Results of Pb adsorption of the amidoxime fibers (Results from Table 2)

4.3.2 As adsorption efficiency of amidoxime fibers

Results from ICP-MS analysis are shown Table 3 and plotted in Figure 22 in order to show the trends. For concentration 1, the adsorption efficiencies for As for the submerging time of 0.43, 1, 2, 3 and 4 weeks were 0.7757, 0.5938, 0.5708, 0.3842 and 0.3970 g-As/kg-adsorbent, respectively. For concentration 2, the adsorption efficiencies for As were 0.6725, 0.7704, 0.4647, 0.3094 and 0.3147 g-As/kg-adsorbent, respectively. For concentration 3, the adsorption efficiencies for As was 0.7454, 0.5107, 0.4706, 0.2484 and 0.2780 g-As/kg-adsorbent, respectively. Moreover, the adsorption reduced with submerging time and did not appear to be significantly affected by the concentrations of heavy metals in seawater under the studied conditions.

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Table 3. Results of As adsorption of the amidoxime fibers

Plastic container	**Concentration of As (g/L)**	**Submersion duration (weeks)**	**Elements**
			As (g-As/kg-adsorbent)
1	0.25	0.43	0.7757
		1	0.5938
		2	0.5708
		3	0.3842
		4	0.3970
2	0.625	0.43	0.6725
		1	0.7704
		2	0.4647
		3	0.3094
		4	0.3147
3	1.25	0.43	0.7454
		1	0.5107
		2	0.4706
		3	0.2484
		4	0.2780

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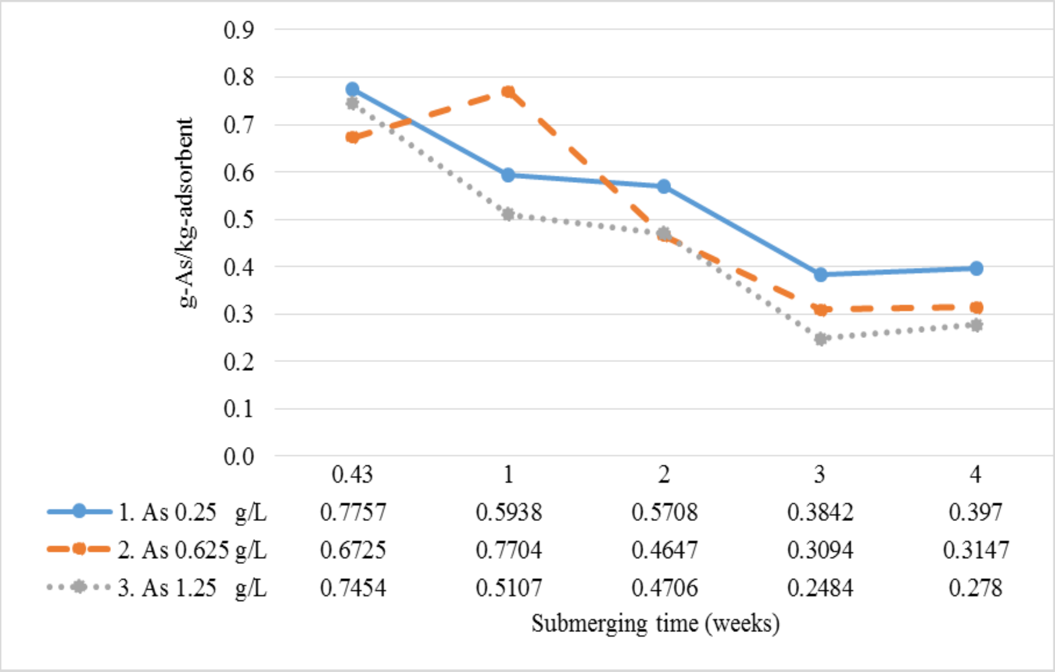

Figure 22. Results of As adsorption of the amidoxime fibers (Results from Table 3)

4.3.3 Hg adsorption efficiency of amidoxime fibers

Results from ICP-MS analysis are shown Table 4 and plotted in Figure 23 in order to show the trends. For concentration 1, the adsorption efficiencies for As for the submerging time of 0.43, 1, 2, 3 and 4 weeks were 0.0075, 0.0034, 0.0014, 0.0013 and 0.0018 g-Hg/kg-adsorbent, respectively. For concentration 2, the adsorption efficiencies for As were 0.0064, 0.0064, 0.0047, 0.0009 and 0.0001 g-Hg/kg-adsorbent, respectively. For concentration 3, the adsorption efficiencies for As was 0.0029, 0.0028, 0.0039, 0.0007 and 0.0031 g-Hg/kg-adsorbent, respectively. The adsorption efficiency was very low compared to the cases of Pb and As, and the overall adsorption trend reduced with submerging time.

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Table 4. Results of Hg adsorption of the amidoxime fibers

Plastic container	**Concentration of Hg (g/L)**	**Submersion duration (weeks)**	**Elements**
			Hg (g-Hg/kg-adsorbent)
1	0.005	0.43	0.0075
		1	0.0034
		2	0.0014
		3	0.0013
		4	0.0018
2	0.025	0.43	0.0064
		1	0.0064
		2	0.0047
		3	0.0009
		4	0.0001
3	0.05	0.43	0.0029
		1	0.0028
		2	0.0039
		3	0.0007
		4	0.0031

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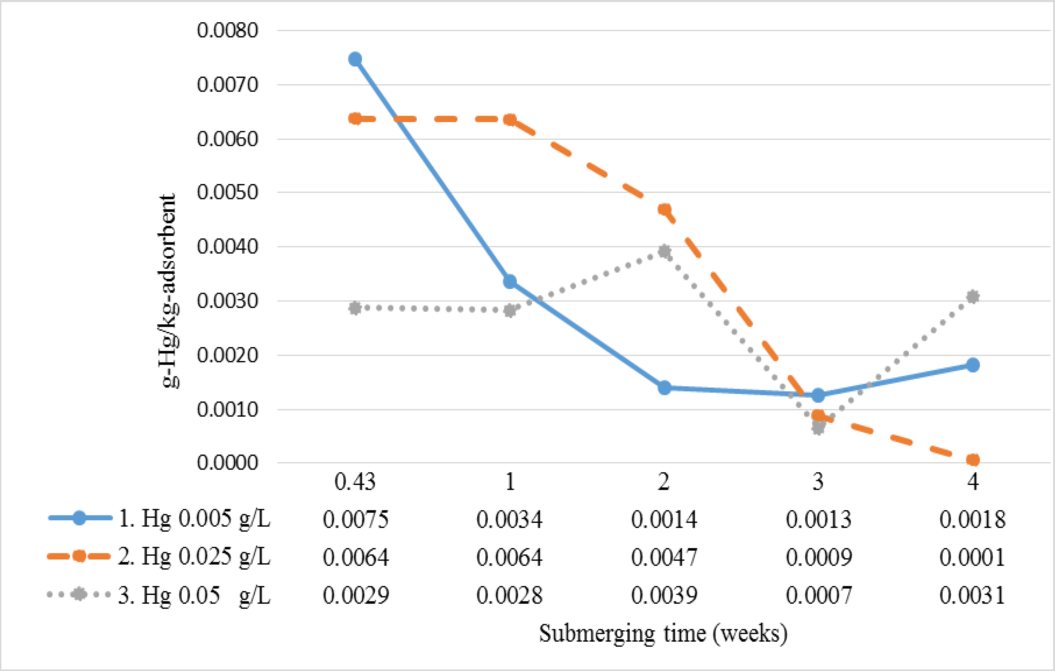

Figure 23. Results of Hg adsorption of the amidoxime fibers (Results from Table 4)

4.3.4 Uranium adsorption efficiency of amidoxime fibers

Results from ICP-MS analysis are shown Table 5 and plotted in Figure 24 in order to show the trends. For concentration 1, the adsorption efficiencies for U for the submerging time of 0.43, 1, 2, 3 and 4 weeks were 0.0053, 0.0057, 0.0038, 0.0038 and 0.0025 g-U/kg-adsorbent, respectively. For concentration 2, the adsorption efficiencies for U were 0.0029, 0.0037, 0.0013, 0.0010 and 0.0005 g-U/kg-adsorbent, respectively. For concentration 3, the adsorption efficiencies for U was 0.0017, 0.0015, 0.0007, 0.0008 and 0.0007 g-U/kg-adsorbent, respectively.

It can be observed that higher Pb, As and Hg concentrations in the seawater cause the uranium adsorption capability to decrease. This is because heavy metals in the seawater bind with the surface of amidoxime fibers and prevent uranium from being adsorbed. This, higher heavy metal concentrations causes more inhibition of uranium adsorption.

Table 5. Results of Uranium adsorption of the amidoxime fibers

Plastic container	**Concentration of U (ppb)**	**Submersion duration (weeks)**	**Elements** U (g-U/kg-adsorbent)
1	150	0.43	0.0053
		1	0.0057
		2	0.0038
		3	0.0038
		4	0.0025
2	150	0.43	0.0029
		1	0.0037
		2	0.0013
		3	0.0010
		4	0.0005
3	150	0.43	0.0017
		1	0.0015
		2	0.0007
		3	0.0008
		4	0.0007

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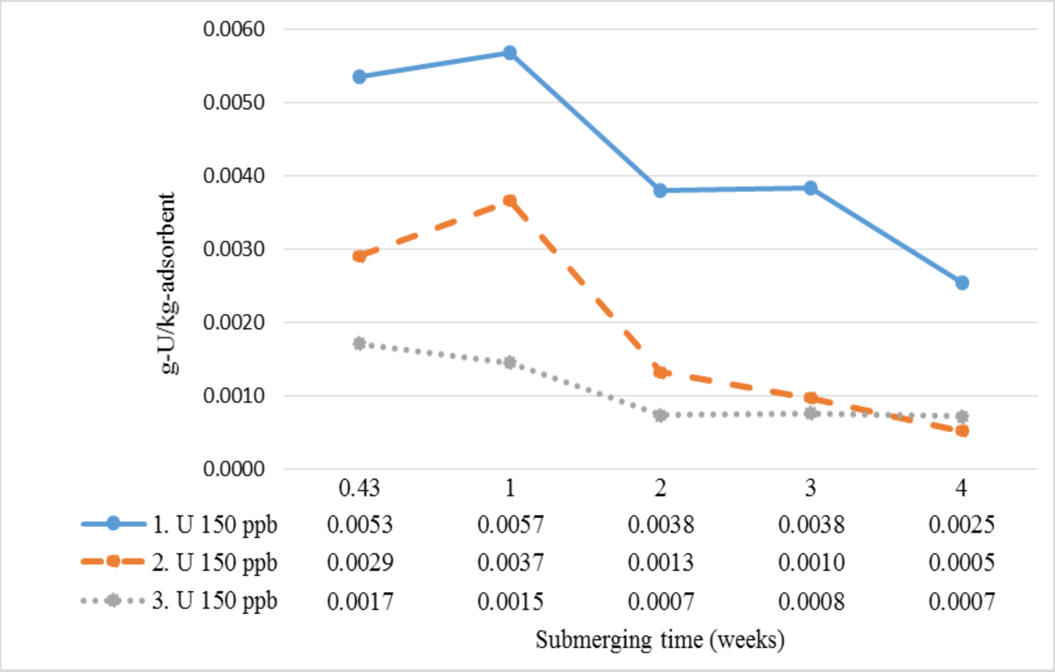

	0.43	1	2	3	4
1. U 150 ppb	0.0053	0.0057	0.0038	0.0038	0.0025
2. U 150 ppb	0.0029	0.0037	0.0013	0.0010	0.0005
3. U 150 ppb	0.0017	0.0015	0.0007	0.0008	0.0007

Figure 24. Results of Uranium adsorption of the amidoxime fibers (Results from Table 5)

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CHAPTER 5

CONCLUSIONS

5.1 SEM analysis of fiber surfaces

Observation of the surface by scanning electron microscope (SEM) finds that cografted LDPE fiber is rougher than LDPE fiber, so AN/MAA was cografted onto the fiber.

5.2 FTIR analysis of functional groups

FTIR spectra of the LDPE and cografted fibers showed the absorption bands of polyethylene and the absorption bands of cografted AN/MAA, respectively. After amidoximation, the N-H stretch and the carboxyl peaks appeared. Thus, from FTIR analysis, it was confirmed that the synthesized polymer contained the amidoxime functional group on the surface.

5.3 Heavy metal and uranium extraction from seawater

5.3.1 Pb adsorption efficiency of amidoxime fibers

Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit the ability to adsorb Pb form seawater. Under the studied conditions, for the case of Pb, the adsorption capability was approximately 5.33 – 33.50 g-Pb/kg-adsorbent. The adsorption also reduced with submerging time because of de-adsorption. Thus, the amidoxime fibers can be used as a very effective detector for Pb in seawater for the submerging time as short as 3 days.

5.3.2 As adsorption efficiency of amidoxime fibers

Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit the ability to adsorb As form seawater. Under the studied conditions, for the case of As, the adsorption capability was approximately 0.25 – 0.77 g-As/kg-adsorbent. The adsorption also reduced with submerging time because of de-adsorption. Thus, the amidoxime fibers can be used as a very effective detector for As in seawater for the submerging time as short as 3 days.

5.3.3 Hg adsorption efficiency of amidoxime fibers

Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit a very low ability to adsorb Hg form seawater. Under the studied conditions, for the case of Hg, the adsorption capability was approximately 0.0001 – 0.0075 g-Hg/kg-adsorbent, and the adsorption also reduced with submerging time because of de-adsorption. Thus, the amidoxime fiber can be used as an effective detector for Hg in seawater for the submerging time as short as 3 days.

5.3.4 Uranium adsorption efficiency of amidoxime fibers

Amidoxime fibers were successfully synthesized by the simultaneous irradiation grafting technique at low temperature using Co-60 as the gamma ray source. The degree of cografting of AN/MAA onto LDPE fibers at the total dose of 40 kGy was calculated to be approximately 52%. The fibers exhibit the ability to adsorb U form seawater. Under the studied conditions, for the case of U, the adsorption capability was approximately 0.0005 – 0.0057 g-U/kg-adsorbent. The adsorption also reduced with submerging time. Thus, the amidoxime fibers can be used as an effective detector for U in seawater for the submerging time as short as 3 days.

5.4 Suggestions for future work

1. Study the absorption of heavy metals in river water.
2. Study the effects of pH and temperature on heavy metal absorption
3. Study factors that can inhibit the absorption of amidoxime fibers

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APPENDIX

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APPENDIX A

Calculation of the degree of cografting

Equation (4) is used:

$$\text{Degree of cografting} = \frac{(W_1 - W_0)}{W_0} x100$$

where W_0 is the weight of the starting fibers.
W_1 is the weight of the cografted fibers.

Table A1 Weigh of LDPE fibers and cografted fibers

	Weight of the starting fibers (g)	Weight of the cografted fibers (g)	Degree of cografting (%)
1	19.1541	29.3353	53.1542
2	19.5596	29.7583	52.1417
3	19.8453	30.3283	52.8236

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APPENDIX B

Calculation of the amidoxime group density

Equation (5) is used:

$$\text{Amidoxime group density (mol/kg)} = \frac{(W_2 - W_1)}{69.5W_2} \text{x1000}$$

where W_1 is the weight of the cografted fibers.

W_2 is the weight of the amidoxime fibers.

The number 69.5 represents the molecular weight of hydroxylamine hydrochloride.

Table B1 Weigh of cografted and amidoxime fibers

	Weight of the cografted fibers (g)	Weight of the amidoxime fibers (g)	Amidoxime group density (mol/kg)
1	29.3353	29.3353	53.1542
2	29.7583	29.7583	52.1417
3	30.3283	30.3283	52.8236

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APPENDIX C

Calculation of the Pb concentration

1. Concentration of 0.2 g/L
Lead (II) nitrate ($Pb(No_3)_2$) was used
Molecular weight of Pb is 207.19

Pb	207.19 g	weight of $Pb(No_3)_2$	331.2 g
Pb	0.2 g	weight of $Pb(No_3)_2$	0.3197 g

Calculate from the equation:

$$\mathrm{Pb} = \frac{0.2\ \mathrm{g} \times 331.2\ \mathrm{g}}{207.19\ \mathrm{g}}$$

$$\mathrm{Pb} = 0.3197\ \mathrm{g}$$

water 1 L	use Pb	0.3197 g
water 20 L	use Pb	6.394 g

Calculate from the equation:

$$\mathrm{pb} = \frac{20\ \mathrm{L} \times 0.3197\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{Pb} = 6.394\ \mathrm{g}$$

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2. Concentration of 1 g/L

Lead (II) nitrate ($Pb(No_3)_2$) was used

Molecular weight of Pb is 207.19

Pb	207.19 g	weight of $Pb(No_3)_2$	331.2 g
Pb	1 g	weight of $Pb(No_3)_2$	1.5985 g

Calculate from the equation:

$$\text{Pb} = \frac{1\ \text{g} \times 331.2\ \text{g}}{207.19\ \text{g}}$$

$$\text{Pb} = 1.5985\ \text{g}$$

water 1 L	use Pb	1.5985 g
water 20 L	use Pb	31.97 g

Calculate from the equation:

$$\text{Pb} = \frac{20\ \text{L} \times 1.5985\ \text{g}}{1\ \text{L}}$$

$$\text{Pb} = 31.97\ \text{g}$$

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3. Concentration of 2 g/L
Lead (II) nitrate ($Pb(No_3)_2$) was used
Molecular weight of Pb is 207.19

Pb	207.19 g	weight of $Pb(No_3)_2$	331.2 g
Pb	2 g	weight of $Pb(No_3)_2$	3.1971 g

Calculate from the equation:

$$\mathrm{Pb} = \frac{2\ \mathrm{g} \times 331.2\ \mathrm{g}}{207.19\ \mathrm{g}}$$

$$\mathrm{Pb} = 3.1971\ \mathrm{g}$$

water	1 L	use Pb	3.1971 g
water	20 L	use Pb	63.942 g

Calculate from the equation:

$$\mathrm{Pb} = \frac{20\ \mathrm{L} \times 3.1971\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{Pb} = 63.942\ \mathrm{g}$$

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APPENDIX D

Calculation of the As concentration

1. Concentration of 0.25 g/L
Arsenic trioxide (As_2O_3) was used
Molecular weight of As is 74.9216

As	74.9216 g	weight of As_2O_3	197.84 g
As	0.25 g	weight of As_2O_3	0.6602 g

Calculate from the equation:

$$\mathrm{As} = \frac{0.25\ \mathrm{g} \times 197.84\ \mathrm{g}}{74.9216\ \mathrm{g}}$$

$$\mathrm{As} = 0.6602\ \mathrm{g}$$

water 1 L	use As	0.6602 g
water 20 L	use As	13.204 g

Calculate from the equation:

$$\mathrm{As} = \frac{20\ \mathrm{L} \times 0.6602\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{As} = 13.204\ \mathrm{g}$$

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2. Concentration of 0.625 g/L
Arsenic trioxide (As_2O_3) was used
Molecular weight of As is 74.9216

As	74.9216 g	weight of As_2O_3	197.84 g
As	0.625 g	weight of As_2O_3	1.6504 g

Calculate from the equation:

$$\mathrm{As} = \frac{0.625\ \mathrm{g} \times 197.84\ \mathrm{g}}{74.9216\ \mathrm{g}}$$

$$\mathrm{As} = 1.6504\ \mathrm{g}$$

water 1 L	use As	1.6504 g
water 20 L	use As	33.008 g

Calculate from the equation:

$$\mathrm{As} = \frac{20\ \mathrm{L} \times 1.6504\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{As} = 33.008\ \mathrm{g}$$

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3. Concentration of 1.25 g/L
Arsenic trioxide (As_2O_3) was used
Molecular weight of As is 74.9216

As	74.9216 g	weight of As_2O_3	197.84 g
As	1.25 g	weight of As_2O_3	3.3008 g

Calculate from the equation:

$$\mathrm{As} = \frac{1.25\ \mathrm{g} \times 197.84\ \mathrm{g}}{74.9216\ \mathrm{g}}$$

$$\mathrm{As} = 3.3008\ \mathrm{g}$$

water 1 L	use As	3.3008 g
water 20 L	use As	66.016 g

Calculate from the equation:

$$\mathrm{As} = \frac{20\ \mathrm{L} \times 3.3008\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{As} = 66.016\ \mathrm{g}$$

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APPENDIX E

Calculation of the Hg concentration

1. Concentration of 0.005 g/L
Mercury (II) chloride ($HgCl_2$) was used
Molecular weight of Hg 200.59

Hg	200.59 g	weight of $HgCl_2$	271.50 g
Hg	0.005 g	weight of $HgCl_2$	0.0068 g

Calculate from the equation:

$$\mathrm{Hg} = \frac{0.005\ \mathrm{g} \times 271.50\ \mathrm{g}}{200.59\ \mathrm{g}}$$

$$\mathrm{Hg} = 0.0068\ \mathrm{g}$$

water	1 L	use Hg	0.0068 g
water	20 L	use Hg	0.136 g

Calculate from the equation:

$$\mathrm{Hg} = \frac{20\ \mathrm{L} \times 0.0068\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{Hg} = 0.136\ \mathrm{g}$$

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2. Concentration of 0.025 g/L
Mercury (II) chloride ($HgCl_2$) was used
Molecular weight of Hg 200.59

Hg	200.59 g	weight of $HgCl_2$	271.50 g
Hg	0.025 g	weight of $HgCl_2$	0.0338 g

Calculate from the equation:

$$\mathrm{Hg} = \frac{0.025\ \mathrm{g} \times 271.50\ \mathrm{g}}{200.59\ \mathrm{g}}$$

$$\mathrm{Hg} = 0.0338\ \mathrm{g}$$

water 1 L	use Hg	0.0338 g
water 20 L	use Hg	0.676 g

Calculate from the equation:

$$\mathrm{Hg} = \frac{20\ \mathrm{L} \times 0.0068\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{Hg} = 0.676\ \mathrm{g}$$

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3. Concentration of 0.05 g/L
Mercury (II) chloride ($HgCl_2$) was used
Molecular weight of Hg 200.59

Hg	200.59 g	weight of $HgCl_2$	271.50 g
Hg	0.05 g	weight of $HgCl_2$	0.0676 g

Calculate from the equation:

$$\mathrm{Hg} = \frac{0.05\ \mathrm{g} \times 271.50\ \mathrm{g}}{200.59\ \mathrm{g}}$$

$$\mathrm{Hg} = 0.0676\ \mathrm{g}$$

water	1 L	use Hg	0.0676 g
water	20 L	use Hg	1.352 g

Calculate from the equation:

$$\mathrm{Hg} = \frac{20\ \mathrm{L} \times 0.0676\ \mathrm{g}}{1\ \mathrm{L}}$$

$$\mathrm{Hg} = 1.352\ \mathrm{g}$$

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