การสกัดยูเรเนียมจากน้ำทะเลโดยใช้เส้นใยพอลิ(อะคริโลไนไตรล์)เอมีดอกซิมที่ผ่านการปรับปรุงด้วยกรดโครมิค

นางสาววีรภรณ์ รัตนิสสัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
สาขาวิชาวิศวกรรมนิวเคลียร์ ภาควิชาวิศวกรรมนิวเคลียร์
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

URANIUM EXTRACTION FROM SEAWATER USING CHROMIC ACID PRE-TREATED POLY(ACRYLONITRILE) AMIDOXIME FIBERS

Miss Vareeporn Ratnitsai

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Engineering Program in Nuclear Engineering
Department of Nuclear Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2014

Thesis Title	URANIUM EXTRACTION FROM SEAWATER USING CHROMIC ACID PRE-TREATED POLY(ACRYLONITRILE) AMIDOXIME FIBERS
By	Miss Vareeporn Ratnitsai
Field of Study	Nuclear Engineering
Thesis Advisor	Assistant Professor Doonyapong Wongsawaeng, Ph.D.
Thesis Co-Advisor	Associate Professor Nares Chankow, M.Eng

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

--Dean of the Faculty of Engineering
(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

--Chairman
(Associate Professor Supitcha Chanyotha, Ph.D.)
--Thesis Advisor
(Assistant Professor Doonyapong Wongsawaeng, Ph.D.)
--Thesis Co-Advisor
(Associate Professor Nares Chankow, M.Eng)
--Examiner
(Associate Professor Sunchai Nilsuwankosit, Ph.D.)
--Examiner
(Associate Professor Somyot Srisatit, M.Eng.)
--External Examiner
(Urith Archakositt, D.Eng.)

วรีภรณ์ รัตนิสสัย : การสกัดยูเรเนียมจากน้ำทะเลโดยใช้เส้นใยพอลิ(อะคริโลไนไตรล์)เอมีดอกซิมที่ผ่านการปรับปรุงด้วยกรดโครมิค (URANIUM EXTRACTION FROM SEAWATER USING CHROMIC ACID PRE-TREATED POLY(ACRYLONITRILE) AMIDOXIME FIBERS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดุลยพงศ์ วงศ์แสวง, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: นเรศร์ จันทน์ขาว, 94 หน้า.

ได้ศึกษาการสกัดยูเรเนียมจากน้ำทะเลโดยใช้ตัวดูดซับเอมีดอกซิมที่ผ่านการปรับปรุงด้วยกรดโครมิค ซึ่งสังเคราะห์โดยใช้วิธีการต่อกิ่งแบบเหนี่ยวนำด้วยการฉายรังสีแกมมาโดยตรงที่อุณหภูมิต่ำ การสังเคราะห์ทำโดยนำเส้นใยพอลิเอธิลีนชนิดความหนาแน่นต่ำมาปรับปรุงด้วยกรดโครมิคที่เวลาต่างๆ จนถึง 90 นาที หลังจากนั้นนำเส้นใยแช่ในมอนอเมอร์ผสมระหว่างอะคริโลไนไตรล์กับกรดเมทาคริลิคในอัตราส่วน 60 : 40 โดยปริมาตร แล้วฉายรังสีแกมมาจากโคบอลต์-60 ที่ความแรงรังสีรวม 40 กิโลเกรย์ พบว่าประสิทธิภาพการต่อกิ่งที่มากที่สุดคือประมาณ 90% ซึ่งเป็นเส้นใยที่ผ่านการปรับปรุงโดยกรดโครมิคนาน 20 นาที ประสิทธิภาพการต่อกิ่งที่ได้นี้มีค่าสูงกว่าค่าในรายงานจากวารสารอื่นอยู่ถึง 30% ต่อจากนั้นนำเส้นใยที่ต่อกิ่งแล้วมาเปลี่ยนให้เป็นเส้นใยเอมีดอกซิมโดยการแช่เส้นใยในสารละลายไฮดรอกซิลามีนไฮโดรคลอไรด์เป็นเวลานาน 75 นาที ได้ความหนาแน่นของกลุ่มเอมีดอกซิมเป็น 2.65 โมลต่อกิโลกรัม เมื่อทดลองนำเส้นใยเอมีดอกซิมที่ผ่านการปรับปรุงด้วยกรดโครมิคแช่ในน้ำทะเลที่ฝั่งอันดามันที่อุณหภูมิเฉลี่ย 30 องศาเซลเซียส เป็นเวลานาน 4 สัปดาห์ ได้ค่าการดูดซับยูเรเนียมเท่ากับ 2.06 กรัมยูเรเนียมต่อกิโลกรัมตัวดูดซับ ซึ่งมีค่าสูงกว่าค่าในรายงานจากวารสารอื่นอยู่ถึง 37% ประสิทธิภาพการต่อกิ่งและการดูดซับยูเรเนียมที่สูงขึ้นอย่างมากนี้ เป็นผลเนื่องมาจากการเพิ่มขึ้นของพื้นที่ผิวเส้นใยพอลิเอธิลีนชนิดความหนาแน่นต่ำที่ผ่านการปรับปรุงด้วยกรดโครมิคอย่างเหมาะสม การศึกษาการใช้ซ้ำของเส้นใยเอมีดอกซิมที่ผ่านการปรับปรุงด้วยกรดโครมิค พบว่าการดูดซับยูเรเนียมมีค่าลดลงเหลือประมาณ 65% หลังจากใช้ซ้ำเป็นจำนวน 8 ครั้ง การวิเคราะห์ค่าความเข้มข้นของยูเรเนียมในน้ำทะเลประเทศไทย พบว่ามีค่าประมาณ 3 ส่วนในพันล้านส่วน โดยไม่ขึ้นอยู่กับตำแหน่งและความลึกของน้ำทะเล

ภาควิชา วิศวกรรมนิวเคลียร์
สาขาวิชา วิศวกรรมนิวเคลียร์
ปีการศึกษา 2557

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5271825721 : MAJOR NUCLEAR ENGINEERING
KEYWORDS: URANIUM EXTRACTION / URANIUM RECOVERY / SEAWATER / AMIDOXIME FUNCTIONAL GROUP / IRRADIATION GRAFTING / CHROMIC ACID

VAREEPORN RATNITSAI: URANIUM EXTRACTION FROM SEAWATER USING CHROMIC ACID PRE-TREATED POLY(ACRYLONITRILE) AMIDOXIME FIBERS. ADVISOR: ASST. PROF. DOONYAPONG WONGSAWAENG, Ph.D., CO-ADVISOR: ASSOC. PROF. NARES CHANKOW, M.Eng, 94 pp.

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 low temperature. Low-density polyethylene (LDPE) fibers were treated with chromic acid for up to 90 minutes. After the treatment, fibers were submerged in 60 : 40 acrylonitrile : methacrylic acid monomer by volume and irradiated with gamma ray from Co-60 for a total dose of 40 kGy. The maximum grafting efficiency of about 90% occurred at 20 minutes of chromic acid treatment time, which was as much as 30% higher than literature-reported values. Cografted fibers were converted into amidoxime fibers by reaction with hydroxylamine hydrochloride solution for 75 minutes, obtaining the amidoxime group density of 2.65 mol/kg. Chromic acid pre-treated amidoxime fibers submerged in Andaman seawater with the average temperature of 30^{o}C for 4 weeks exhibited the uranium adsorption capacity of 2.06 g-U/kg-adsorbent, which was 37% higher than literature-reported values. These significantly-increased grafting and adsorption efficiencies were attributed to the increased surface area of LDPE fibers appropriately treated with chromic acid. Study on the usage repeatability of chromic-acid-treated amidoxime fibers revealed that the adsorption capacity reduced to about 65% after 8 cycles of repeated usage. Uranium concentration in Thailand's seawater was analyzed to be around 3 ppb, regardless of location and depth of seawater.

Department:	Nuclear Engineering	Student's Signature	
Field of Study:	Nuclear Engineering	Advisor's Signature	
Academic Year:	2014	Co-Advisor's Signature	

ACKNOWLEDGEMENTS

I would like to express my profound gratitude to Asst. Prof. Dr. Doonyapong Wongsawaeng, my advisor, for valuable advices, continued suggestions, caring, patience, and for his excellent guidance which help me all the time of research and writing of this dissertation. I would like to express my sincere appreciation to my co-advisor, Assoc. Prof. Nares Chankow, who lets me experience the research and supports the dissertation.

I take this opportunity to express my sincere gratitude and deep regards to my guide, Assoc. Prof. Chyagrit Siri-Upathum, for the starting idea to conduct my research and for his exemplary guidance and constant encouragement in the course of this dissertation.

Besides my advisor and my co-advisor, I would like to thank the rest of my dissertation committee: Assoc. Prof. Dr. Supitcha Chanyotha, Assoc. Prof. Dr. Sunchai Nilsuwankosit, Assoc. Prof. Somyot Srisatit, and Dr. Urith Archakositt for their kindness during the defense examination of my dissertation and for all of their insightful comments and suggestions.

I offer my sincere appreciation for the learning opportunities, kind support and valuable advices provided by all lecturers and staff members at the Nuclear Engineering Department, Faculty of Engineering, Chulalongkorn University.

I would like to thank the Ministry of Science and Technology, the Electricity Generating Authority of Thailand, and the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) for the funding support of my Ph.D. study and research work.

I would like to thank the Faculty of Science and Technology, Rajamangala University of Technology Tawan-Ok, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Office of Atoms for Peace and Thailand Institute of Nuclear Technology for the equipment supports.

Finally, I thank tremendously my family and friends for their invaluable help and constant encouragement during the full course of my study.

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1
INTRODUCTION

1.1 Background and rationale

Energy-producing natural resources such as oil, natural gas and coal have become dwindled in quantities in recent years because of their limited quantities. They are consumed after use and cannot be re-created, or it would take thousands of years for nature to replenish the diminishing quantities. Therefore, we must find alternative energy resources. One of the options is to use nuclear energy, and the nuclear fuel is uranium.

Uranium is a natural resource that can be found in earth's crust and seawater, albeit a miniscule concentration present in all the oceans. Although the amount of uranium resource in the earth's crust may be limited, there are about 4,500 million tons of uranium dissolved in the oceans (1) and this enormous quantity can be said to be unlimited. If only half of this quantity can be extracted, it can plentifully provide fuel for nuclear power plants worldwide for several thousands of years. Because of the topography of Thailand that has very long coastlines, it is of interest to study the recovery of uranium from seawater to be used as nuclear fuel for Thailand's future nuclear power program.

The concentration of uranium in seawater is about 3 mg/m^3 (2), and does not appear to vary significantly from oceans to oceans. Uranium predominantly exists in seawater in the form of uranyl tricabonate ion, $UO_2(CO_3)_3^{4-}$ (2, 3). There are several methods to chemically synthesize polymers suitable for adsorbing uranium from seawater. For instance, amidoxime chelating functional groups (1, 4, 5) have the ability to displace the carbonate ions at the pH of natural seawater. One of the ways to synthesize amidoxime-group-containing polymers is by bombarding a polyethylene film with an energetic electron beam. Then, it is grafted with acrylonitrile under nitrogen atmosphere to obtain acrylonitrile-grafted film. Afterwards, it is soaked in hydroxylamine hydrochloride solution to obtain HCl-conditioned amidoxime membrane. A method by K. Saito (2) to produce amidoxime membranes yields an amidoxime group density of about 1.8 mol/kg. Later, A. Zhang (5) developed a chemical process to enable a direct use of poly(acrylonitrile) with amidoxime groups in the structure. This yields an amidoxime membrane with an amidoxime group density of about 2.61 mol/kg, which can absorb more quantities of uranium.

The available surface area of polyethylene has a direct relationship with the grafting percentage. Surface modification of polyethylene by increasing the surface area (or, equivalently, surface roughness) is desirable in order to enhance uranium adsorption (6). This can be achieved by chemical modification such as chromic acid treatment (7-10). However, the preparation conditions for amidoxime adsorbents such as fiber types, total gamma ray dose of irradiation-induced cograft polymerization process, amidoximation time, temperature and reaction time for uranium elution have not been optimized for obtaining a higher efficiency of uranium extraction from seawater.

The purpose of this dissertation is to enhance the adsorption of uranium from seawater by increasing the available surface area of polyethylene fibers by chromic acid treatment, resulting in the increased grafting of acrylonitrile and methacrylic acid.

1.2 Research objective

1.2.1 To study and perform enhancement of uranium extraction from seawater using chromic acid pre-treated poly(acrylonitrile) amidoxime fibers.

1.3 Scope of dissertation

1.3.1 Pre-treat the polyethylene fiber surface by chromic acid.

1.3.2 Prepare the amidoxime fibers by irradiation-induced cograft polymerization technique.

1.3.3 Test the amidoxime fibers with seawater samples collected from Gulf of Thailand and Andaman Sea.

1.3.4 Recover adsorbed uranium from the amidoxime fibers and compare extraction efficiency with other techniques.

CHAPTER 2
LITERATURE REVIEWS

2.1 Uranium

2.1.1 Uranium in seawater

Seawater represents an almost inexhaustible resource of materials. About 80 elements could be detected in seawater. However, the chemistry of seawater is dominated only by the presence of the following six ions: CI^{-}, Na^{+}, Mg^{2+}, Ca^{2+}, K^{+}, and SO_4^{2-}, which constitute more than 99.5% of the dissolved materials. Metal ions of the elements dissolved in seawater, together with their concentrations, are shown in Table 2.1.

Table 2.1 Concentrations and chemical species of metal ions dissolved in seawater (1)

Metal	**Concentration**		**Main chemical species**
	[mol/l]	[mg/l]	
Li	2.5×10^{-5}	0.173	Li^{+}
Be	6.3×10^{-10}	5.6×10^{-6}	$Be(OH)^{+}$
Na	0.468	10.77×10^{3}	Na^{+}
Mg	5.32×10^{-2}	12.9×10^{2}	Mg^{2+}
Al	3.7×10^{-8}	1.0×10^{-3}	$[Al(OH)_4]^{-}$
K	1.02×10^{-2}	3.8×10^{2}	K^{+}
Ca	1.02×10^{-2}	4.12×10^{2}	Ca^{2+}
Sc	1.3×10^{-11}	6×10^{-7}	$Sc(OH)_3$
Ti	2×10^{-8}	1×10^{-3}	$Ti(OH)_4$
V	3.7×10^{-8}	1.9×10^{-3}	$H_2VO_4^{-}$, HVO_4^{2-}
Cr	1.54×10^{-9}	8.0×10^{-5}	$Cr(OH)_3$, CrO_4^{2-}
Mn	3.6×10^{-9}	2.0×10^{-4}	Mn^{2+}, $MnCl^{+}$
Fe	2.3×10^{-8}	1.3×10^{-3}	$[Fe(OH)_2]^{+}$, $[Fe(OH)_4]^{-}$
Co	6.8×10^{-10}	4.0×10^{-5}	Co^{2+}
Ni	3.4×10^{-9}	2.0×10^{-4}	Ni^{2+}
Cu	1.6×10^{-9}	1.0×10^{-4}	$CuCO_3$, $Cu(OH)^{+}$
Zn	1.5×10^{-10}	1.0×10^{-5}	$Zn(OH)^{+}$, Zn^{2+}, $ZnCO_3$
Ga	4.3×10^{-10}	3×10^{-5}	$[Ga(OH)_4]^{-}$
Ge	6.9×10^{-10}	5×10^{-5}	$Ge(OH)_4$
Rb	1.4×10^{-6}	0.120	Rb^{+}
Sr	9.2×10^{-5}	8.1	Sr^{2+}
Y	1.5×10^{-11}	1.3×10^{-6}	$Y(OH)_3$

Table 2.1 Concentrations and chemical species of metal ions dissolved in seawater

Metal	**Concentration**		**Main chemical species**
	[mol/l]	[mg/l]	
Zr	3.3×10^{-10}	3×10^{-5}	$Zr(OH)_4$
Nb	1×10^{-10}	1×10^{-5}	-
Mo	1.0×10^{-7}	1.0×10^{-2}	MoO_4^{2-}
Ag	9.3×10^{-11}	1.0×10^{-5}	$[AgCl_2]^-$
Cd	8.9×10^{-11}	1.0×10^{-5}	$CdCl_2$
In	0.8×10^{-12}	1×10^{-5}	$In(OH)_2^+$
Sn	8.4×10^{-11}	1×10^{-5}	$[SnO(OH)_3]^-$
Sb	1.7×10^{-9}	2.1×10^{-5}	$[Sb(OH)_6]^-$
Cs	3×10^{-9}	4.0×10^{-5}	Cs^+
Ce	1×10^{-10}	1×10^{-5}	$Ce(OH)_3$
Pr	4×10^{-12}	6×10^{-5}	$Pr(OH)_3$
Nd	1.9×10^{-11}	3×10^{-5}	$Nd(OH)_3$
Sm	3×10^{-12}	5×10^{-5}	$Sm(OH)_3$
Eu	9×10^{-13}	1×10^{-8}	$Eu(OH)_3$
Gd	4×10^{-12}	4×10^{-7}	$Gd(OH)_3$
Tb	9×10^{-13}	1×10^{-7}	$Tb(OH)_3$
Dy	6×10^{-12}	9×10^{-7}	$Dy(OH)_3$
Ho	1×10^{-12}	2×10^{-7}	$Ho(OH)_3$
Er	4×10^{-12}	8×10^{-7}	$Er(OH)_3$
Tm	8×10^{-13}	2×10^{-7}	$Tm(OH)_3$
Yb	5×10^{-12}	8×10^{-7}	$Yb(OH)_3$
Lu	9×10^{-13}	2×10^{-7}	$Lu(OH)_3$
Pb	7.2×10^{-11}	1.5×10^{-5}	$PbCO_3$, $[Pb(CO_3)_2]^{2-}$
Bi	1×10^{-10}	2×10^{-5}	BiO^+, $Bi(OH)_2^+$
Ra	3×10^{-16}	7×10^{-11}	Ra^{2+}
Th	4×10^{-11}	1×10^{-5}	$Th(OH)_4$
Pa	2×10^{-16}	5×10^{-11}	-
U	1.4×10^{-8}	3.3×10^{-3}	$[UO_2(CO_3)_3]^{4-}$

Seawater contains about 4.5 billion tons of dissolved uranium. The average concentration of uranium in seawater is about 3.3 µg/l. Table 2.2 gives uranium compounds expected to be found dissolved in typical seawater and their concentrations.

Table 2.2 Concentrations of uranium compounds dissolved in natural seawater at 25 °C and at pH of 8.1 (1)

Compound	**Concentration [mol/l]**	**Weight fraction [wt% of U]**
UO_2^{2+}	$1.53x10^{-17}$	$0.01x10^{-5}$
$UO_2(OH)_2$	$1.53x10^{-12}$	0.01
$[UO_2(CO_3)_2]^{2-}$	$5.46x10^{-11}$	0.39
$[UO_2(OH)_3]^-$	$2.43x10^{-10}$	1.75
$[UO_2(CO_3)_3]^{4-}$	$1.37x10^{-8}$	98.82

As can be seen in Table 2.2, uranium appears mainly in seawater as the tricarbonate uranylate anion, $[UO_2(CO_3)_3]^{4-}$, having the highest weight fraction of uranium compounds dissolved in natural seawater. The structure of the tricarbonate uranylate complex is shown in Figure 2.1.

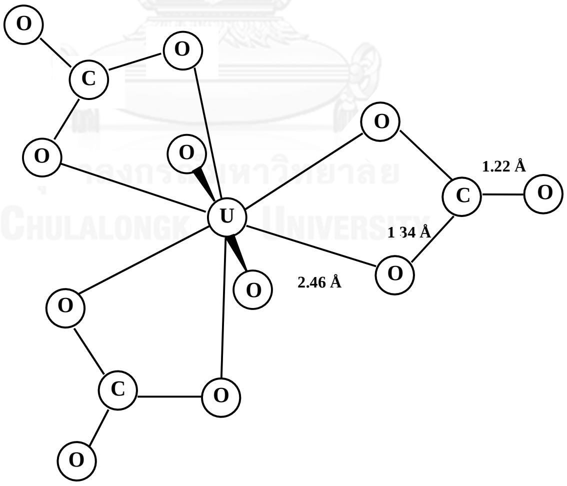


Figure 2.1 Structure of the tricarbonate uranylate anion (1)

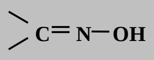
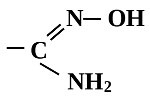
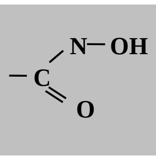
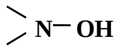
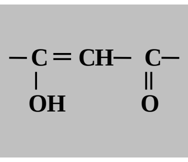
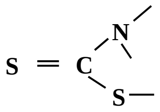
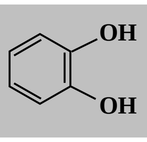
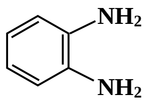
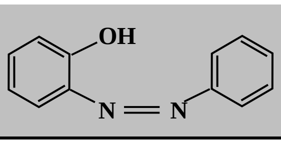
2.1.2 Uranium recovery from seawater

Methods for the extraction of uranium from natural seawater have been achieved by solid adsorbents, solvent extraction, ion flotation and electrolysis. However, for a large-scale uranium recovery, only the adsorptive accumulation by utilizing a suitable solid adsorbent appears to be feasible with regard to economic reasons and environmental impacts. The solid adsorbent should be almost insoluble in seawater and eluents, and should be highly stable against physical, chemical, and biological degradation in order to allow for long-term recycling and to avoid contamination of the ocean. In addition, since most of the uranium is adsorbed only on the surface of the adsorbent, any loss due to friction would mean a serious loss of uranium.

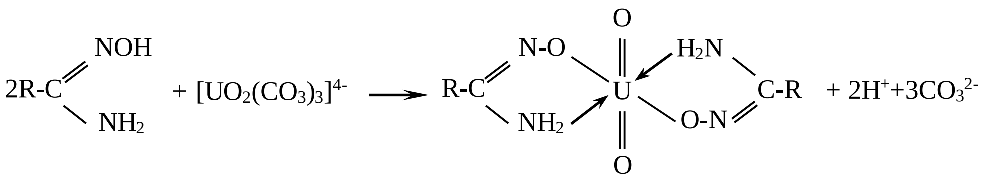
It is assumed that for any adsorbent to bind uranium present in natural seawater, the functional group of the adsorbent must form a stable uranyl complex at the pH and temperature of natural seawater. Generally, the binding mechanism proceeds via a direct carbonate substitution by the functional group.

Uranium-binding functional groups have been chosen in accordance with their capability to displace the carbonate ions in $[UO_2(CO_3)_3]^{4-}$ at the pH of natural seawater. This type of functional groups is summarized in Table 2.3.

Table 2.3 Functional groups exhibiting the ability to adsorb uranium by displacing carbonate ions in $[UO_2(CO_3)_3]^{4-}$ (1)

Functional group	Structure
Oximes	
Amidoximes	
Hydroxamic acids	
Hydroxylamines	
1, 3-Diketones	 $-C(OH)=CH-C(=O)-$
Dithiocarbaminates	
o-Dihydroxyaromatics	
o-Diaminoaromatics	
o-Hydroxyazoaromatics	

The uranium adsorption mechanism by the amidoxime functional group can be represented in Eq. (1).



(1)

Metal ions binding with the amidoxime functional group is graphically illustrated in Figure 2.2.

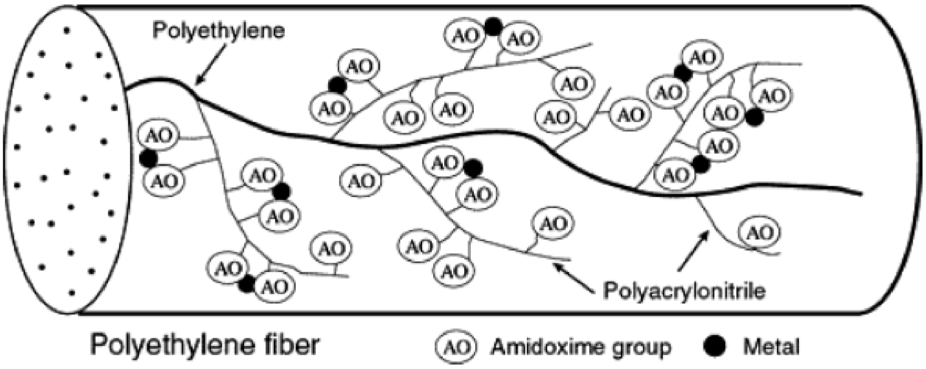


Figure 2.2 Graphic representation of metal ions binding with the amidoxime functional group (11)

2.1.3 Uranium elution

The process of recovery of uranium from seawater includes the elution of uranium from the adsorbent. Elution should proceed quickly with high efficiency, measurable by the concentration of uranium in the eluent compared to the initial concentration in seawater. A further increase in the concentration of uranium in the eluent up to the precipitability in the form of yellow cake can be achieved by ion exchange. In addition, one of the important attributes of the elution process is a high selectivity.

In many eluent tests, only mineral acids and aqueous solutions of alkaline and ammonium carbonates yielded measurable elution efficiencies. However, the disadvantage of the acid elution is a small instability of the functional groups leading to a slight decrease in the uranium adsorption efficiency with repeated use and elution. Investigations on the stability of uranium-binding functional groups revealed that the amidoxime functional group is stable in dilute hydrochloric acid with an elution efficiency of about 90%. Moreover, the adsorbent is physically durable in the seawater environment and chemical eluents.

2.2 Polymer

Polymers are macromolecules built up by linking together large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are known as monomers, and the reactions by which they combine are termed polymerization. There may be hundreds, thousands, tens of thousands, or even more monomer molecules linked together in a polymer molecule.

Polymers can be classified in many different ways. The classifications can be based on the origin of the polymer, the polymer structure, or the polymerization mechanism (12, 13).

2.2.1 Polymer origin

In classifying polymer this way, there are two types of polymers: natural and synthetic. *Natural polymers* occur in nature and can be extracted. They are often water-based. Examples of naturally-occurring polymers are starch, natural rubber, silk, wool, DNA, cellulose and proteins. *Synthetic polymers* are chemically manufactured from separate materials, or are derived from petroleum oil, and made by scientists and engineers. Examples of synthetic polymers include fibers, nylon, polyethylene, polyester, Teflon, and epoxy.

2.2.2 Polymer structure

Classification of polymers by polymer structure takes the following types:

2.2.2.1 Linear, branched and cross-linked

A polymer is formed when a very large number of structural units (repeating units or monomers) are made to link up by covalent bonds under appropriate conditions. We should know the term “functionality” in order to understand the type of molecules that can form a polymer. The functionality of a molecule is simply its interlinking capacity, or the number of sites it has available for bonding with other molecules under the specific polymerization conditions.

The structural units resulting from the reaction of monomers may in principle be linked together in any understandable pattern. These monomers are joined end-to-end like links along a chain. A polymer with a simple *linear structure* is, for example, high-density polyethylene (HDPE). In some polymers shorter chains grow off the long chain at certain intervals so that a *branched structure* is formed, for example, low-density polyethylene (LDPE). In other polymers the branches become chemically linked to each other, resulting in a *cross-linked structure* as shown in Figure 2.3. In addition, *ladder polymers* have only condensed cyclic units in the chain; they are also commonly referred to as double-chain polymers.

(a). Linear (b). Branched

(c). Cross-linked (d). Ladder

Figure 2.3 Structure of polymers

2.2.2.2 Homopolymer or copolymer

Polymer may be either homopolymers or copolymers depending on the composition of polymer. Polymers consisting of repeated long chains of the same monomer unit in the polymer molecules are known as *homopolymer*. On the other hand, polymers consisting of two different repeating units in the polymer molecules are called *copolymers*. The repeating unit and the structural unit of a polymer are not necessarily the same.

The repeating units on the copolymer chain may be arranged in various degrees of order along the backbone. There are several types of copolymer systems:

- *Random copolymer*

Random copolymer is a polymer comprised of two or more different repeating units attached in a random order. If the repeating units are represented by A and B, the random copolymer might have the structure shown below:

—AABBABABBAAABAABBA—

- *Alternating copolymer*

If there is an ordered arrangement of the two repeating units along the polymer chain, the alternating copolymer might have the structure shown below:

—ABABABABABABABABAB—

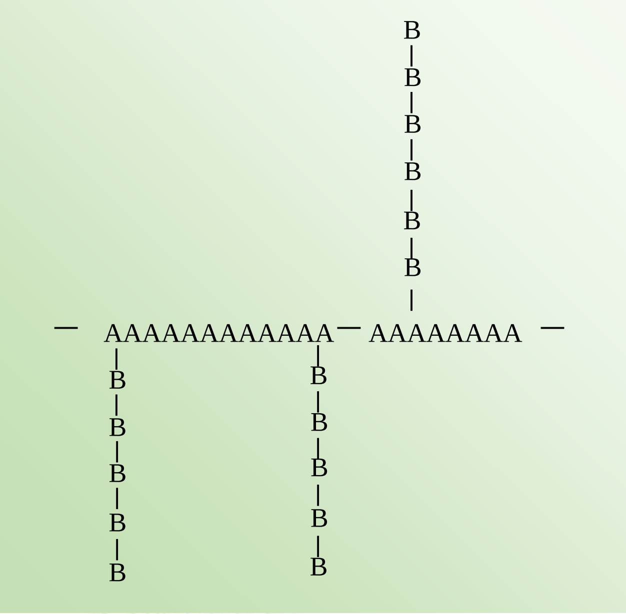
- *Block copolymer*

A block copolymer is a polymer consisting of long sequences of the same monomer alternating in series with different monomer blocks, which is shown below. The blocks are covalently bounded to each repeating unit.

– AAAAA – BBBBB – AAAAA – BBBBB –

- *Graft copolymer*

A graft copolymer forms when sequences of one monomer are grafted onto a backbone of another monomer type. The graft copolymer might have the structure shown below:



2.2.3 Polymerization mechanism

Polymers may be classified widely as condensation, addition, or ring-opening polymers, depending on the variety of polymerization reactions involved in their formation. *Condensation polymers* are any kind of polymers formed through a condensation reaction, releasing small molecules as by-products. *Addition polymers* are produced by reactions in which monomers are added one after another to a rapidly growing chain. The growing polymer in addition polymerization proceeds via a chain mechanism. Like all chain reactions, three fundamental steps are concerned: initiation, propagation, and termination. Furthermore, ring-opening polymerization polymers are acquired from the separation and then polymerization of cyclic compounds having high molecular weights.

Consequently, this classification has been replaced by the terms step-reaction (condensation) and chain-reaction (addition) polymerization. These terms focus more on the manner in which the monomers are linked together during polymerization.

In this dissertation, the chain reaction polymerization is considered. Chain polymerization is initiated by a reactive species (I*) produced from some compound termed an initiator (I) shown in the Equation (2).

$$I \longrightarrow I^* \qquad (2)$$

The reactive species may be a cation, anion, or free radical added to a monomer molecule, and then the process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center as shown in Equation (3).

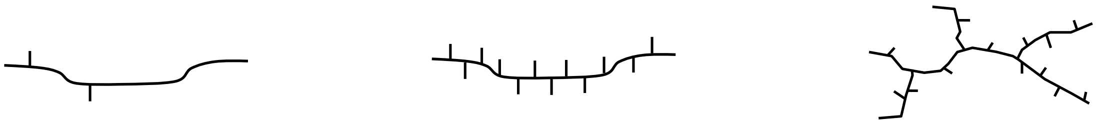
$$I^* + M \longrightarrow I\text{-}M^* \xrightarrow{M} I\text{-}M\text{-}M^* \longrightarrow \text{etc.} \qquad (3)$$

Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the reaction conditions, which is shown in Equation (4).

$$I\text{-}(M)_j\text{-}M^* + I\text{-}(M)_k\text{-}M^* \longrightarrow I\text{-}(M)_n\text{-}I \qquad (4)$$

2.3 Polyethylene

Ethylene may be polymerized by a number of processes to produce different varieties of polyethylene. The most important type of polyethylene includes high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and low-density polyethylene (LDPE). The main difference among these polymers is their chain as shown in Figure 2.4. HDPE is a linear polymer with almost no branches, LLDPE is a linear polymer with a varying amount of short branches, and LDPE is a branched polymer (0.5-3 long branches per 1000 carbons in the backbone) with a large amount of short branches (30 short branches per 1000 carbons in the backbone).



(a). HDPE (b). LLDPE (c). LDPE

Figure 2.4 Polyethylene chain architectures (14)

Melted linear polyethylene chains crystallize upon cooling yielding a semi-crystalline polymer (about 60 % crystallinity). The crystalline fraction decreases as branching increases, and LDPE and LLDPE are amorphous polymers. The names of these polymers come from the effect of crystallization on the density of the polymer; the higher the degree of crystallization the higher the density. The properties of high density and low density polyethylene are shown in Table 2.4.

Table 2.4 Properties of polyethylene (14)

Property	**Polyethylene**	
	HDPE	LDPE
Specific gravity	0.941-0.965	0.912-0.94
Crystallinity (%)	80-95	50-70
Melting temperature (^{o}C)	127-135	98-120
Tensile strength (MPa)	17.9-33.1	15.2-78.6
Tensile modulus (MPa)	413-1034	55.1-172
Elongation at break (%)	20-130	150-600
Impact strength (ft-lb/in. notch)	0.8-14	716
Heat deflection temperature (^{o}C at 66 psi)	60-88	38-49

2.4 Radiation characteristics

The radiation used in a particular application is determined largely by the characteristic of the objects to be irradiated and the penetration required, since the various types of radiation give different depth-dose profiles. For example, irradiation of bulk liquid or solid samples generally requires one of the more penetrating radiations such as gamma or x radiation. The less-penetrating radiations are used if reaction is to be restricted to the surface layers of a solid sample.

Neutrons and heavier charged-particle radiations can be used to dislocate atoms in solids. However, neutron irradiation may induce radioactivity in the material and is therefore generally avoided. Radioactivity can also be induced by other radiations if their energy is sufficiently high, for example, by electromagnetic and electron radiation at energies above 10-20 MeV (The actual energy depends upon the material being irradiated.). The energy of electron and x-ray beams employed commercially may be limited to several MeVs to avoid nuclear reactions that could induce significant radioactivity in the irradiated product. The main characteristics of gamma-rays involved with this dissertation are as follows:

2.4.1 Linear energy transfer

Irradiating materials with different types of high-energy and ionizing radiations produces similar chemical changes, even though the relative proportions of the chemical products formed may differ. One of the factors in the differences that are observed is described as the linear energy transfer (LET) of the radiation. The LET is the energy transferred to material as an ionizing radiation travels through it. The LET is closely related to the stopping power, the energy loss per unit distance, dE/dx. When an ionizing radiation passes through a material, it ionizes and excites nearby molecules. The charged particles may act as the primary radiation itself, as in the case of positive ion and electron irradiation, secondary electrons in the case of x and γ irradiation, or protons or other ionizing particles in the case of neutron irradiation. As for the LET of the radiation, it is referred to as the linear rate at which a particle loses energy and is generally given in units of keV/µm. (15)

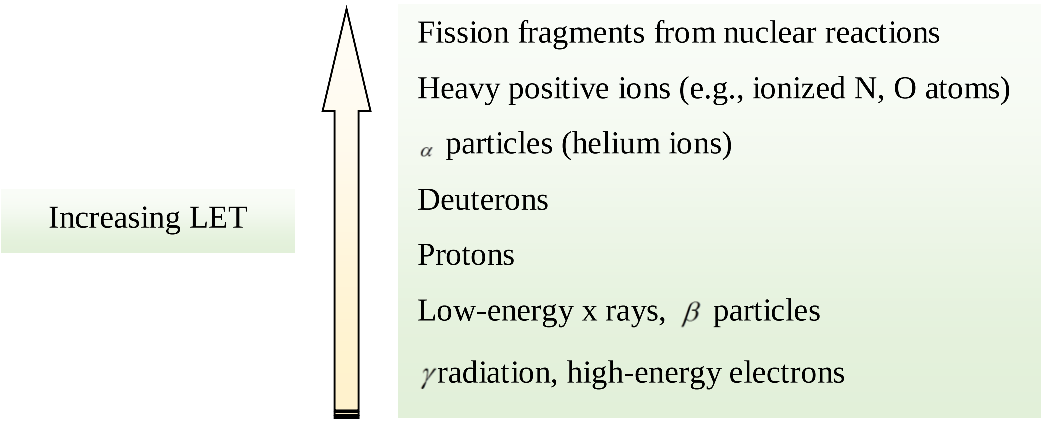


Figure 2.5 Relative linear energy transfers of different radiations (15)

The penetration of electromagnetic, electron, and other charged-particle radiations in a material is inversely related to their linear energy transfers. Particles with lower linear energy transfers penetrate to a greater depth in a material than higher linear energy transfer particles of comparable energy.

2.4.2 Interaction of gamma rays

Gamma rays are usually reserved for radiation emitted by radionuclides, which are electromagnetic radiation. Gamma rays can interact with matters in several ways, but only three important types are taken into consideration in radiation processing. These are the photoelectric effect, Compton scattering, and pair production (16).

2.4.2.1 Photoelectric effect

In the principal interaction process of the photoelectric effect, it occurs predominantly with low-energy photons. The incident photon interacts with an entire atom in which the photon completely disappears, and one of atomic electrons is ejected by the atom from one of its bound shells, which is known as a *photoelectron*. Energy and momentum are conserved throughout the process. 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 of the photoelectron in the atom (E_b). Thus, the kinetic energy of an emitted photoelectron is given by:

$$E_{e^-} = h\nu - E_b \tag{5}$$

The photoelectric process is the predominant interaction for gamma rays (or X-rays) of low energy. Thus, the probability of photoelectric effect per atom decreases rapidly with increasing incident photon energy (E_γ). This process is also highly probable for materials with high atomic numbers (Z).

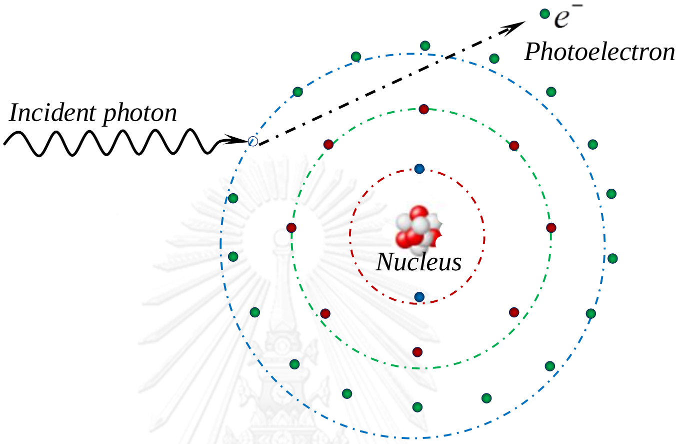


Figure 2.6 Illustration of photoelectric effect

2.4.2.2 Compton scattering

The interaction process of Compton scattering occurs when a photon interacts with an electron, and the incident photon is deflected through an angle (θ) with respect to its original direction, which is now called a *scattered photon*. The energy of the photon transferred to the electron, called *a recoil electron*, can be calculated from conservation of energy and momentum. The scattered photon energy ($h\nu'$) is given by:

$$h\nu' = \frac{h\nu}{1+\frac{h\nu}{m_0c^2}\left(1-\cos\theta\right)} \tag{6}$$

where m_0c^2 represents the rest mass energy of the electron (0.511 MeV). The probability of Compton scattering per atom of the material depends on the number of electrons of scattering targets and hence increases linearly with the atomic number.

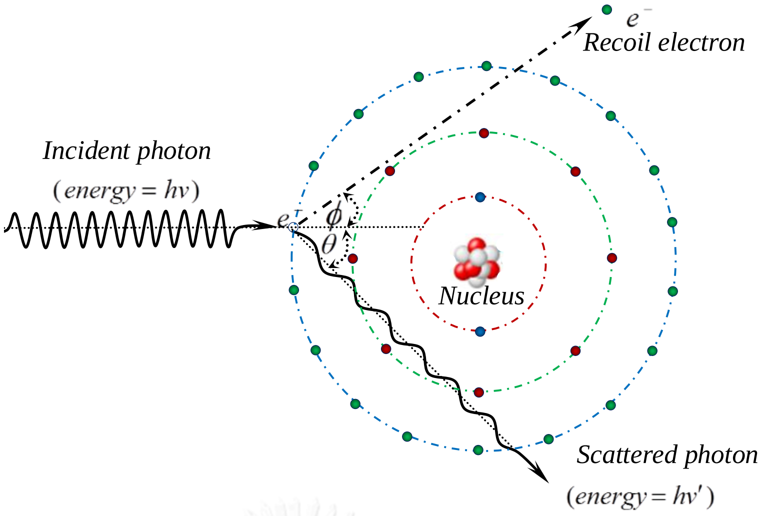


Figure 2.7 Illustration of Compton scattering

2.4.2.3 Pair production

In this process, in the presence of an atomic nucleus, a gamma ray energy of at least 1.022 MeV disappears with a formation of a positron and an electron. The kinetic energy of each particle is half of the energy of the incident photon above 1.022 MeV, as it takes 0.511 MeV of photon energy to create each particle. The positron is slowed down in the material and finally annihilates with an orbital electron to form two gamma rays emitted in opposite directions with equal energies of at least 0.511 MeV. These gamma rays are called annihilation radiation. Thus, two gamma rays are usually produced as secondary products of the interaction. The probability of pair production per nucleus increases steadily with increasing incident photon energy.

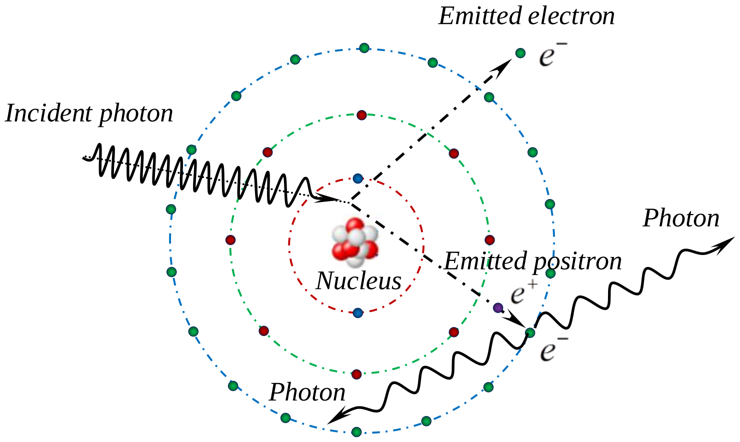


Figure 2.8 Illustration of pair production

2.5 Radiation processing

High-energy radiation for initiation of polymerization can be particle radiation or electromagnetic radiation, for example, electrons and gamma rays. The interactions of these radiations with matters are complicated. The chemical effects of different types of radiation are the same qualitatively, but they are different quantitatively. The basis of radiation processing occurs when a material is irradiated. The energy of high energy radiation (gamma rays, x-rays or electron beam) is transferred to atoms or molecules of that material and so ionization and excitation occur. Moreover, the material undergoes certain physical and chemical changes, depending on types of radiation and the absorbed dose. The result of high energy radiation is to produce reactive ions, free radicals, and excited states collectively known as active species in materials as shown in Equation (7).

$$\text{Substrate} \xrightarrow[\text{Gamma-ray}]{\text{Electron beam}} \text{cations + anions + free radicals} \qquad (7)$$

The effects of radiation on materials may also depend on the types of radiation, radiation dose, linear energy transfer and irradiation method. The roles of reactive ions, free radicals, and excited states in the applications of radiation processing of polymeric materials include polymerization, grafting, cross-linking, and degradation of synthetic polymers.

Monomers that can be polymerized by reactive ions or free radical mechanisms are shown in Table 2.5. They can be polymerized by exposure to high energy radiation.

Table 2.5 Polymerization mechanisms for selected monomers (17)

Monomer	**Mechanisms**		
	Radical	Cationic	Anionic
Ethylene	+	+	-
Isobutylene	-	+	-
Dienes	+	-	+
Styrene	+	+	+
Vinyl chloride	+	-	-
Vinylidene chloride	+	-	+
Acrylates	+	-	+

+, high molecular weight polymer formed; -, no reaction or oligomer only.

The method of irradiating polymer to generate free radicals that may be capable of initiating polymerization of monomers in contact with the original polymer is called the *simultaneous irradiation method*. The method in which the irradiated polymer is subsequently immersed in a monomer is called the *pre-irradiation method*. Under appropriate conditions, it is possible to graft a second polymer onto the original polymer. A wide variety of monomers have been successfully grafted onto surfaces of both natural and synthetic fibers or other polymer surfaces. Polymer surface modification by grafting is one of the principal ways to improve surface properties, for example, to become adsorbents or ion-exchange resins.

Advantages of radiation initiation over other chemical alternatives include the following:

1) Radiation-induced reactions can be carried out at low temperatures, resulting in less danger of fire or explosion, and lower energy cost.
2) Radiation processing can be systematized and controlled easily.
3) Radiation processing can be controlled from the outside.
4) Radiation-induced reactions do not require a catalyst.
5) Radiation initiation does not produce residues of the initiator or catalyst chemicals in the products.

6) Gamma radiation can be used to irradiate huge solid materials with acceptably uniform dose.

Disadvantages of radiation initiation include the following:

1) Initial capital cost of radiation processing is higher than that of the chemical process because of expensive radiation sources and related system and equipment.

2) If chemical yields of products are low, then the reaction cannot sustain a chain reaction.

3) Safety anxiety of the general public must be satisfied. In some countries, this may be a lengthy and expensive process when sources of ionizing radiation are involved.

2.6 Radiation-induced grafting method

Grafting of a wide variety of monomers onto substrates has been accomplished by using various techniques, for example, radiation, corona discharge, low-temperature plasma, UV treatment and thermal treatment to accelerate the polymerization. Substrates such as films or fibers can be in contact with the grafting solution containing monomers. Recent researches in radiation grafting focus on the following three main methods: pre-irradiation, peroxidation, and simultaneous methods.

In pre-irradiation grafting, the substrate (PH) is first irradiated, usually in vacuum or in an inert gas, to produce relatively-stable free radicals, which are then reacted with a monomer (M) as shown in Equations (8) and (9), usually at elevated temperature.

$$PH \rightsquigarrow P^* + H^* \qquad (8)$$

$$P^* + M \longrightarrow PM^* \qquad (9)$$

For peroxidation grafting, it is the least often used of all the irradiation techniques. The substrate is irradiated in the presence of air or oxygen, leading to the formation of diperoxides and hyperoxides. Storage of the stable peroxy radicals is possible until combination with monomer is required. Monomer with or without solvent is then reacted with the activated peroxy trunk polymer in air or under vacuum at elevated temperature.

The simultaneous method is the one most generally used. The base polymer is irradiated while in direct contact with the monomer. The monomer may be present as vapor, liquid or solution. The grafting process can occur via a free radical mechanism as in Equations (8) and (9), and for homopolymer formation it is shown in Equations (10) and (11).

$$M \rightsquigarrow M^{*} \tag{10}$$

$$M^{*} + M \longrightarrow M^{*}_{n} \tag{11}$$

The advantage of the simultaneous method is that both monomer and substrate are exposed directly to the radiation source. In practice, the radiation doses required for complete grafting in the pre-irradiation and peroxidation grafting methods are higher than for the simultaneous method. In general, the simultaneous radiation grafting process is preferred with radiation-sensitive substrates. The factors affecting the optimization of grafting include the role of solvents, the effects of temperature, the radiation doses and dose rates, and methods for minimizing homopolymer formation.

Recent advances in surface grafting of polymers using irradiation method are shown in Table 2.6.

Table 2.6 Modification of polyethylene by radiation-initiated graft copolymerization(15)

Polymer	Grafted Monomer	Properties or Use of Product
Polyethylene	Acrylic acid	High adhesion to aluminum
	Acrylic acid, acrylonitrile, etc.	Ion-exchange properties
	Methacrylic acid	Highly hydrophilic
	N-Vinylpyrrolidone + acrylic acid	Highly hydrophilic
	Acenaphthene	Increased radiation resistance
	Phenylacetylene	High thermal resistance and electrical conductivity

2.7 Surface modification

Surface treatment is frequently employed as part of the conversion process to alter the surface characteristics of the specific material being used. There are two modification techniques as follows:

2.7.1 Chemical surface modification

Modification of the chemical composition of polymer surface by direct chemical reaction with a given solution is called wet treatment. Wet treatments can be used to improve surface properties of polymers. The chemical composition of the solution employed in the treatment is appropriately modified from general wet chemistry. In addition, specific solutions were developed in order to utilize specific liquid-polymer interaction, for example, chromic acid solution with high temperature is used to oxidize polymer surface. Since the chemical modification of surface properties also results in surface etching, this helps increase penetration of chemicals into pores, leading to both chemical and physical effects.

Chromic acid solution composes of sulfuric acid solution saturated with chromium trioxide. It can be used to treat polymer surface at temperature of about 70 ^{O}C to make it become very rough and full of crack, effectively increasing the surface area. Various functional groups can afterwards be grafted onto the modified surface of polyethylene.

2.7.2 Physical surface modification

The main purpose of physically modifying polymer surface is to adjust the surface layer. There are several ways to achieve this objective such as flame treatment, laser treatment and cold plasma treatment. An important side effect of surface treatment may be to also etch the surface.

Flame treatment is a method of chemically changing the surface molecular structure of a substrate. Usually, this is accomplished by having a polymer passing through a bank of flame jets at a given speed to provide the desired properties. In direct flame treatment, the high temperature is sufficient to dissociate nitrogen and oxygen molecules into active species including radicals, ions, and molecules in excited states. Also, exposure to the open flame oxidizes the polymer surface. Performing this treatment must ensure that there will be no thermal damage to sensitive materials such as thin-walled plastics or film substrates.

Laser is a photon source characterized by its high energy and phase coherence. Laser can be used to induce ablation or scission effects. The application involves essentially a sample moving below a photon source.

For low-temperature plasma treatment, an ionized region is formed inside a low-pressure plasma chamber. Plasma contains high energy photons, electrons, ions, radicals and excited species. Applications of cold plasmas are classified according to the type of feed gas, the product of surface reactions, and the intensity of ion bombardment. Exposure of polymer to a suitable plasma can cause chemical and physical changes to the surface or near-surface layers. Active sites on the surface can be created and, for instance, wetting properties can be improved by oxidation and formation of hydroxyl (OH) groups with oxygen or air plasma. Plasma polymerization of monomer onto polymer substrate can also be achieved when an appropriate monomer gas is fed into the plasma chamber. However, etching-induced damages can be a result of cold plasma treatment, as polymers are easy damaged by electron, ion, and excited atom bombardments. Surface bombardment can cause breakage of polymer bonds and crosslinking of polymer fragments, resulting in a formation of a brittle polymer surface layer.

CHAPTER 3
METHODOLOGY

3.1 Materials

3.1.1 Low-density polyethylene (LDPE) fiber
3.1.2 High-density polyethylene (HDPE) fiber
3.1.3 Polypropylene (PP) fiber
3.1.4 Acrylonitrile (AN)
3.1.5 Methacrylic acid (MAA)
3.1.6 Dimethyl sulfoxide (DMSO)
3.1.7 N,N-dimethylformamide (DMF)
3.1.8 Hydroxylamine hydrochloride ($NH_2OH{\bullet}HCl$)
3.1.9 Methanol
3.1.10 Potassium hydroxide (KOH)
3.1.11 Sodium hydroxide (NaOH)
3.1.12 Potassium dichromate ($K_2Cr_2O_7$)
3.1.13 Sulfuric acid (H_2SO_4)
3.1.14 Hydrochloric acid (HCl)
3.1.15 Nitric acid (HNO_3)
3.1.16 Deionized water (DI water)
3.1.17 Tricarbonate uranylate solution
3.1.18 Seawater sample
3.1.19 Gamma Irradiator, Gammacell 220 Excel
3.1.20 12-Liter Niskin Water Sampler
3.1.21 Plastic sieve
3.1.22 Plastic container
3.1.23 Fourier Transform Infrared Spectrometer
3.1.24 Inductively Coupled Plasma Atomic Emission Spectrometer
3.1.25 Scanning Electron Microscope, JSM model 6400
3.1.26 Energy dispersive X-ray spectrometer, JSM model 6400

3.2 Synthesis

3.2.1 Chromic-acid-treated LDPE fibers

A chromic acid solution, prepared by saturating 150 parts by weight (pbw) of H_2SO_4 solution with 7 pbw of $K_2Cr_2O_7$ and 12 pbw of DI water, was employed to modify the surface of LDPE fibers. LDPE fibers were produced from an extrusion machine (ThermoHake Polydrive; Single screw extruder) and the average diameter of the LDPE fibers was about 50-200 µm as illustrated in Figure 3.1. To synthesize chromic-acid-treated LDPE fibers, LDPE fibers were immersed in the chromic acid solution at 70°C. The duration of the chromic acid treatment varied from 2.5 to 90 minutes. After the treatment, the fibers were thoroughly washed with acetone and DI water successively, and finally dried in a forced-convection oven at 50°C for 24 hours.

Figure 3.1 LDPE fibers

3.2.2 Preparation of amidoxime fibers

The extraction of uranium from natural seawater can be accomplished by employing the polymeric adsorbent containing the amidoxime functional group for the ability to displace the carbonate ions in $[UO_2(CO_3)_3]^{4-}$ at the pH of natural seawater. This work follows Tamada's synthetic procedure of the adsorbent (18, 19) (except the chromic acid treatment), and the preparation scheme of amidoxime fibers consists of the following two steps, as summarized in Figure 3.2.

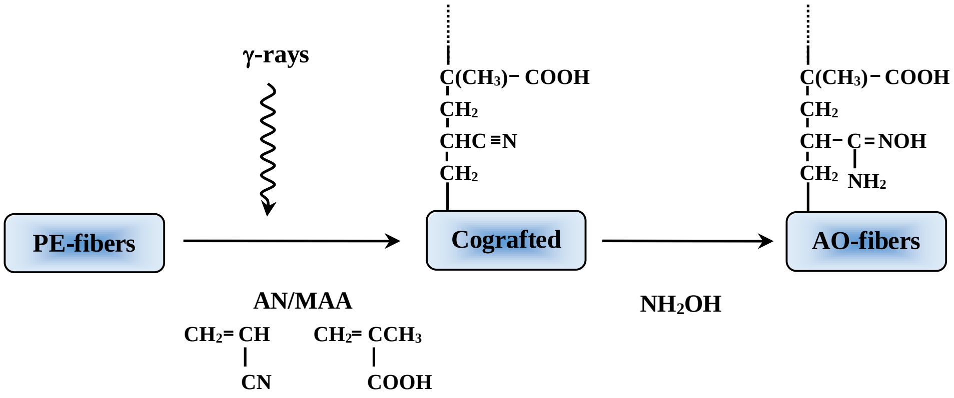


Figure 3.2 Synthesis schematic of amidoxime fibers

3.2.2.1 Irradiation-induced cograft polymerization

Radiation-induced cograft polymerization of a mixture of AN and MAA onto a polymeric adsorbent by the simultaneous irradiation cografting method was employed. Studied fibers for cografting were LDPE fibers, HDPE fibers and PP fibers (or chromic-acid-treated LDPE fibers). The fibers were immersed in a container containing two monomers with a mixing ratio of 60 : 40 (AN : MAA) by volume. The presence of MAA enhanced the hydrophilicity of the fibers, and this optimized mixing ratio was adopted from Kawai's work [3], who studied different mixing ratios and different chemicals and concluded that MAA with this mixing ratio was the most suitable one in terms of uranium uptake by the adsorbent. The mixture of the two monomers was diluted in 50 (w/w)% DMSO as a solvent as shown in Figure 3.3. The simultaneous irradiation cografting method at low temperature was achieved by putting ice cubes in water around the container for irradiation as shown in Figure 3.4. The container was irradiated with γ-ray from Co-60 (Gammacell 220 Excel at Office of Atoms for Peace in Bangkok, Thailand as shown in Figure 3.5) at the dose rate of 6.21 kGy/hr, and the total dose was varied from 5 - 50 kGy.

Figure 3.3 Immersed fibers in the solution of monomers*

(*Fibers shown in the Figure were from preliminary work. LDPE fibers were braided to assist in handling and weight control after irradiation. For real usage, it is not necessary that they be in the braided form.)

Figure 3.4 Ice cubes in water around the container for irradiation

Figure 3.5 Gamma-ray radiator (Gammacell 220 Excel)

After irradiation, the fibers were removed from the container and were thoroughly washed with DMF several times to completely remove residual AN and poly(acrylonitrile) homopolymer from the fiber surfaces. The cografted fibers were dried in a forced-convection oven at 50°C for 24 hours to obtain a constant weight, and the degree of cografting was calculated from the weight gain using the following formula:

$$\text{Degree of cografting (\%)} = \frac{(W_1 - W_0)}{W_0} \times 100 \qquad (12)$$

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.

3.2.2.2 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

(50 : 50 (v/v)% methanol : DI water and neutralized to pH of 7 by adding KOH solution) at 80°C for reaction times ranging from 15 to 120 minutes.

After the reaction, the fibers were rinsed with a methanol/DI water solution and immersed in 1 M HCl solution. Then, the fibers were repeatedly rinsed with DI water and dried in a forced-convection oven at 50°C for 24 hours to obtain a constant weight, and the amidoxime group density was calculated from the weight gain using the following formula:

$$\text{Amidoxime group density (mol/kg)} = \frac{(W_2 - W_1)}{69.5\,W_2} \times 1000 \qquad (13)$$

where W_2 is the weight of the amidoxime fibers and the number 69.5 represents the molecular weight of hydroxylamine hydrochloride, $NH_2OH{\bullet}HCl$ (2). Then, the amidoxime fibers were investigated for the characteristic bands of the amidoxime group using the FTIR technique. Finally, the fibers were immersed in 2.5 (w/v)% KOH solution at 80°C for 1 hour (5, 20, 21). Prior to uranium adsorption experiments, the fibers were repeatedly washed with DI water (3, 20). Then, the amidoxime fibers were packed in plastic sieves and placed in plastic containers for submerging in seawater as shown in Figures 3.6-3.7.

Figure 3.6 Plastic sieves containing amidoxime fibers

Figure 3.7 Plastic container for seawater submersion

3.3 Uranium concentrations in Thailand's seawater at various locations and depths

Seawater samples were collected at various locations in the Gulf of Thailand and the Andaman Sea as shown in Table 3.1. Figure 3.8 represents the map of seawater sampling points in Southern Thailand. For surface water sample collection, a plastic container was submerged into water just enough so that the opening was underneath the water surface. For water samples collected at 30 m and deeper, a commercial 12-Liter Niskin Water Sampler was used as illustrated in Figures 3.9-3.10. Collected seawater samples were sent to JFE Techno-Research Corporation Keihin Division in Japan for analysis of uranium concentrations using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) technique.

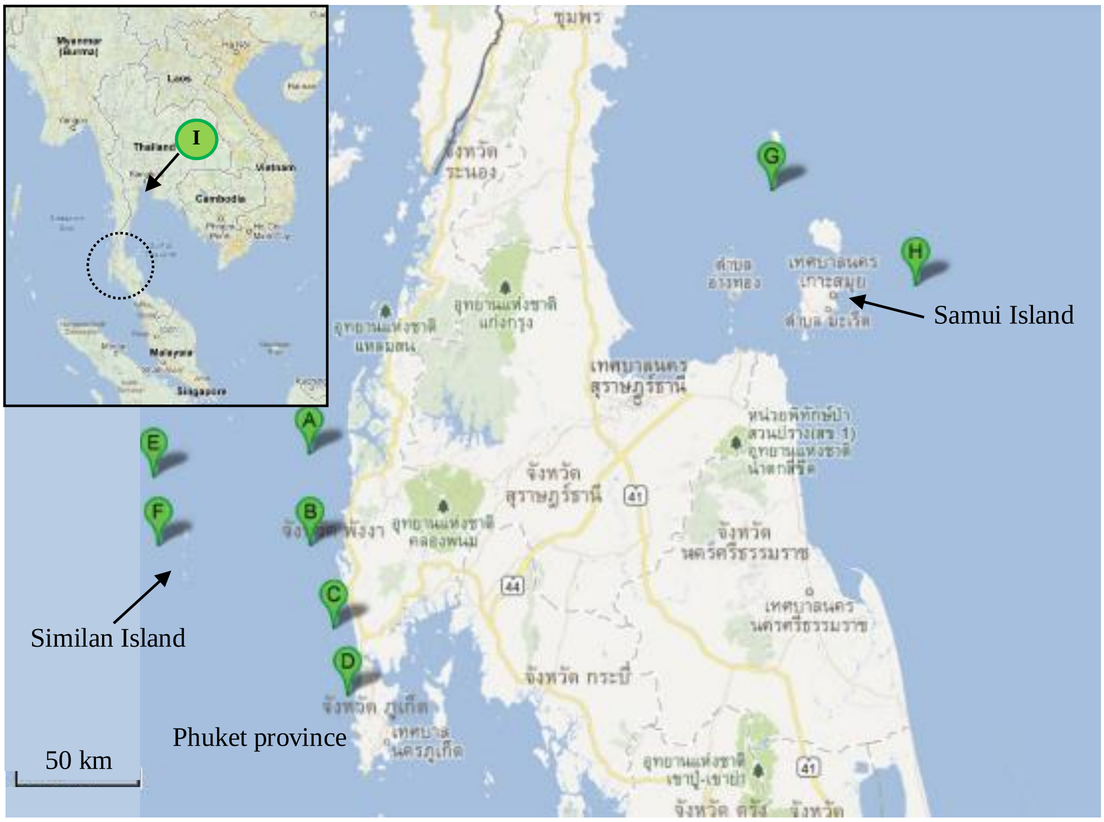


Figure 3.8 Map of seawater sampling points in Southern Thailand
(from Google Map)

Table 3.1 Location and time of seawater sampling

Region	Coordinate	Location	Date	Time
Andaman Sea	(A) 08°56.004' N 098°05.857' E	Koh Phra Thong Island, Phang Nga Province	10 Jan.2012	14.00 – 14.40
	(B) 08°35.992' N 098°06.264' E	Tublamu Pier, Phang Nga Province	10 Jan.2012	17.50 – 18.15
	(C) 08°17.701' N 098°11.267' E	Thai Mueang, Phang Nga Province	11 Jan.2012	18.00 – 18.45
	(D) 08°02.765' N 098°14.282' E	Bang Tao Beach, Phuket Province	11 Jan.2012	14.28 – 15.03
	(E) 08°51.096' N 097°31.207' E	Tachai Island, Phang Nga Province	7 Mar.2012	13.07 – 17.00
	(F) 08°35.731' N 097°32.268' E	Similan Island, Phang Nga Province	7 Mar.2012	9.30 – 11.30
Gulf of Thailand	(G) 09°54.360' N 099°48.830' E	Koh Tao, Surat Thani Province	16 May.2012	13.20 - 14.20
	(H) 09°33.069' N 100°21.002' E	Koh Samui, Surat Thani Province	17 May.2012	11.20 - 12.30
	(I) 12°55.715' N 100°51.769' E	Pattaya Beach, Chonburi Province	27 May.2012	11.20- 12.30

Figure 3.9 12-Liter Niskin Water Sampler

Figure 3.10 Seawater sampling and collection

3.4 Uranium extraction from seawater

3.4.1 Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers at various submerging durations in a laboratory setup

Four sets of non-chromic acid pre-treated amidoxime fibers, approximately 20 g each, 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 Tao Island, Surat Thani Province, Thailand. Synthesized $[UO_2(CO_3)_3]^{4-}$ was added to the seawater sample to increase the uranium concentration to about 250 ppb in order to have enough uranium for absorption of all fibers. The submerging time was 1, 2, 4 and 6 months.

3.4.2 Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers at various submerging durations in Kho Loy seawater

Twelve sets of non-chromic acid pre-treated amidoxime fibers, approximately 20 g each, were used in this part of the experiment. The non-chromic acid pre-treated amidoxime fibers were submerged in shallow seawater at the depth of 10 - 12 m at Kho Loy in Chonburi province, as shown in Figures 3.11. The submerging time was 0.5, 1, 1.5 and 2 months.

Figure 3.11 Kho Loy in Chonburi province (in the middle of the picture)

3.4.3 Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers at the SEA Laboratory on Redondo Beach in California, USA

Seventy grams of non-chromic acid pre-treated amidoxime fibers were submerged into circulated and continually refreshed seawater container at the SEA Laboratory on Redondo Beach in California, USA as shown in Figures 3.12-3.13. The average temperature of the seawater was 7°C. The submerging time was 10 days.

Figure 3.12 The SEA Laboratory on Redondo Beach in California, USA

Figure 3.13 Submerged non-chromic acid pre-treated amidoxime fibers in seawater container

3.4.4 Uranium adsorption efficiency of chromic acid pre-treated amidoxime fibers at various etching times in a laboratory setup

To modify the surface of LDPE fibers with chromic acid solution, LDPE fibers were immersed in the chromic acid solution at 70°C for 2.5 to 90 minutes. After the chromic acid treatment and the subsequent amidoximation, the fibers 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 Tao Island, Surat Thani Province, Thailand. Synthesized $[UO_2(CO_3)_3]^{4-}$ was added to the seawater sample to increase the uranium concentration to about 500 ppb in order to have enough uranium for absorption of all fibers. The submerging time was 30 days.

3.4.5 Uranium adsorption efficiency of chromic acid pre-treated amidoxime fibers at various submerging durations

Eighteen sets of chromic acid pre-treated amidoxime fibers, approximately 20 g each, were used in this part of the experiment. The chromic acid pre-treated amidoxime fibers were submerged in shallow seawater at the depth of ~ 5 - 8 m in front of Phuket Marine Biological Center in Phuket province, as shown in Figures 3.14-3.15. The average temperature of the seawater was 30°C. The submerging time was 1, 2, 3, 4, 6 and 8 weeks.

Figure 3.14 Equipment in front of Phuket Marine Biological Center in Phuket province

Figure 3.15 Submerged plastic containers containing fibers in front of Phuket Marine Biological Center

3.5 Uranium elution from amidoxime fibers

To elude adsorbed uranium, the fibers were removed from seawater, rinsed with DI water and immersed in 1 M HCl at 50°C for 1 hour, as shown in Figure 3.16. The uranium concentration in the eluent was analyzed by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

Figure 3.16 Eluent containing adsorbed metals

3.6 Usage repeatability

Because the PE fiber is insoluble in seawater and eluents, and is highly stable against physical, chemical, and biological degradation, it is desirable for the adsorbent to be capable of being reused several times. Thus, the ability of the adsorbent to be reused was evaluated by submerging the non-chromic acid pre-treated amidoxime fibers in seawater sample (with added $[UO_2(CO_3)_3]^{4-}$ in order to increase the uranium concentration to about 14.3 ppm) in a laboratory at room temperature. The seawater sample was collected from surface water of Tao Island, Surat Thani Province, Thailand. For every 3 days representing 1 cycle, the fibers were removed from seawater sample and the adsorbed metals were eluded using the same procedure discussed in Section 3.5. Prior to seawater submersion again, the fibers were conditioned by immersing in a

2.5 (w/v)% KOH solution for 1 hour at 80°C and repeatedly washed with deionized water as shown in Figure 3.17.

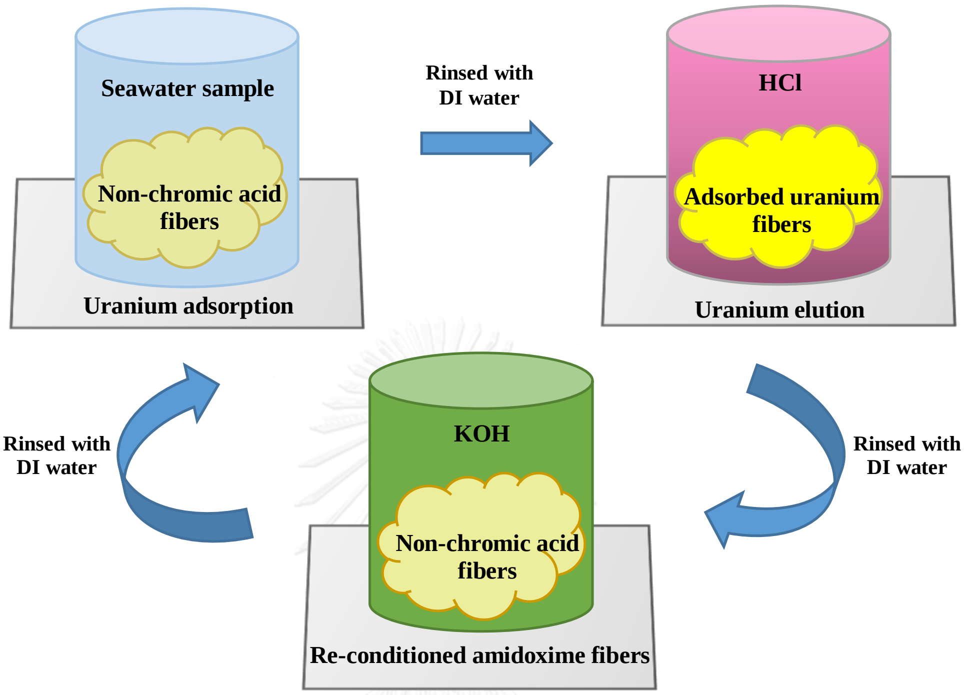


Figure 3.17 Procedure of the experiment on usage repeatability

3.7 Effect of pH and temperature on uranium extraction from seawater using non-chromic acid pre-treated amidoxime fibers

Thirty six sets of amidoxime fibers weighting approximately 2 g each were submerged in seawater samples in 5-L glass beakers as shown in Figure 3.18. Each beaker contains 4 sets of the non-chromic acid pre-treated amidoxime fibers. The seawater samples were collected from Tao Island, Surat Thani Province, Thailand. $[UO_2(CO_3)_3]^{4-}$ was added to the seawater samples to increase the uranium concentration to about 3.4 ppm in order to have enough uranium for absorption of all fibers. The pH value of $[UO_2(CO_3)_3]^{4-}$-containing seawater sample in each beaker was appropriately adjusted using dilute HCl and NaOH. The temperature in each beaker was controlled by a hot plate stirrer as represented in Figure 3.19. The experiment was carried out in an air-conditioned room in order to have the low temperature of 25°C. The submerging time was 0.5, 1, 1.5 and 2 months. The adsorbed metals were eluded using the same procedure discussed in Section 3.5.

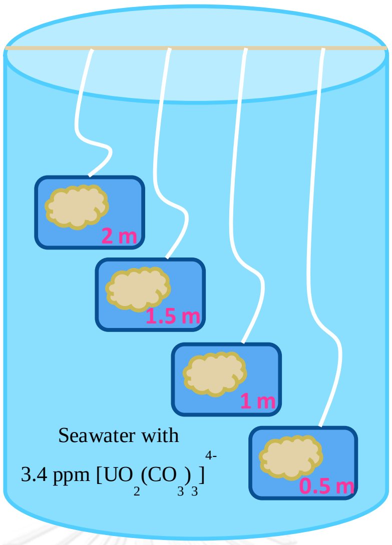


Figure 3.18 Drawing of the experiment on the effect of pH and temperature on uranium extraction from seawater using non-chromic acid pre-treated amidoxime fibers

Figure 3.19 Experiment on the effect of pH and temperature on uranium extraction from seawater using non-chromic acid pre-treated amidoxime fibers

CHAPTER 4
RESULTS

4.1 SEM analysis of fibers at various stages

Scanning electron microscope (SEM) was employed to observe the surface morphology of the fibers at various stages. Figure 4.1(a) illustrates the surface of the produced LDPE fiber with a very smooth appearance with some particles (or part of LDPE) on the surface. Figure 4.1(b) shows the surface of the cografted non-chromic-acid-treated LDPE fiber. Columns of grafted chemical chains were visible in the Figure. Figure 4.1(c) displays the surface of the non-chromic acid pre-treated amidoxime fibers. Columns of grafted chemical chains completely disappeared. The amidoxime function group must have completely filled in the spaces between the columns. Figures 4.1(d) – 4.1(k) show the surfaces of chromic-acid-etched LDPE fibers after the etching time of 2.5, 5, 10, 15, 20, 25, 30, and 60 minutes, respectively.

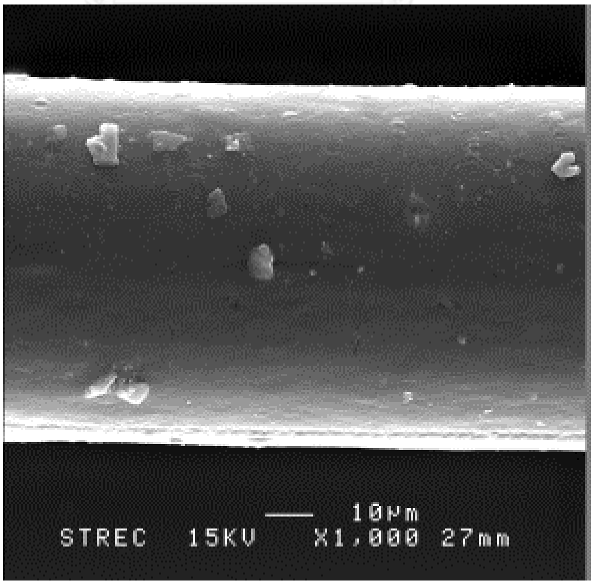


Figure 4.1(a) Starting LDPE fiber

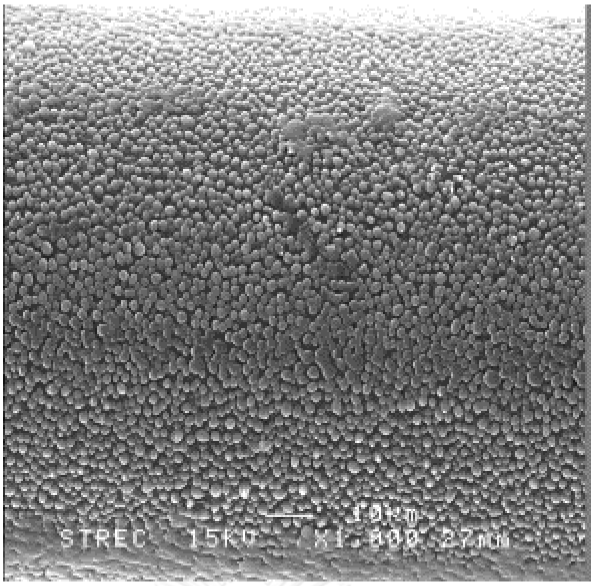


Figure 4.1(b) Cografted LDPE fiber

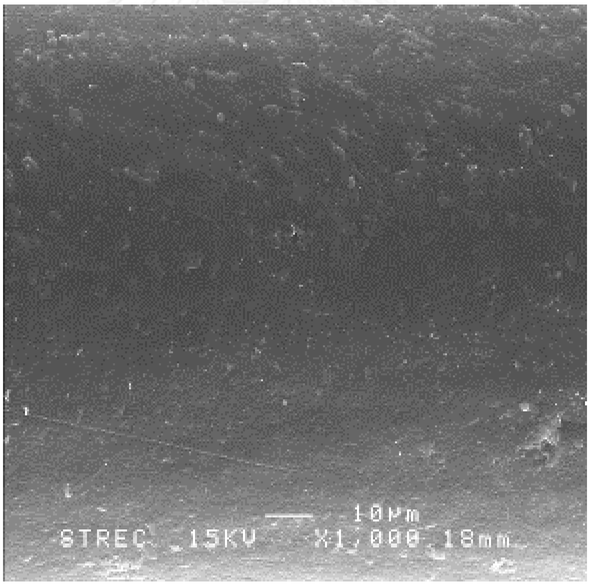


Figure 4.1(c) Amidoxime fiber

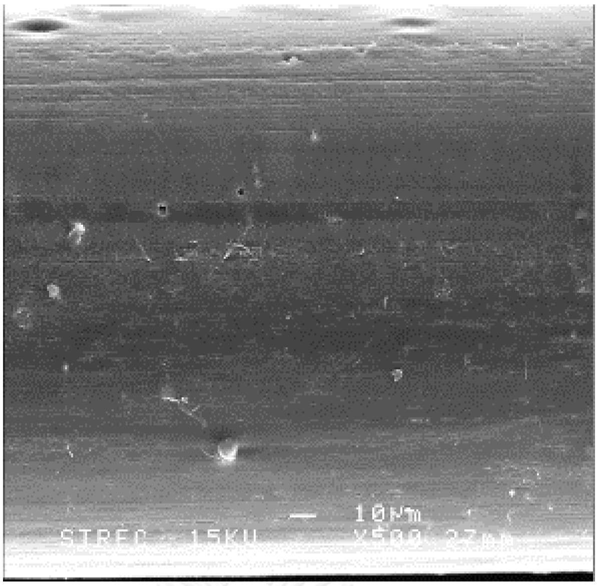


Figure 4.1(d) Chromic-acid-etched LDPE fiber after the etching time of 2.5 minutes

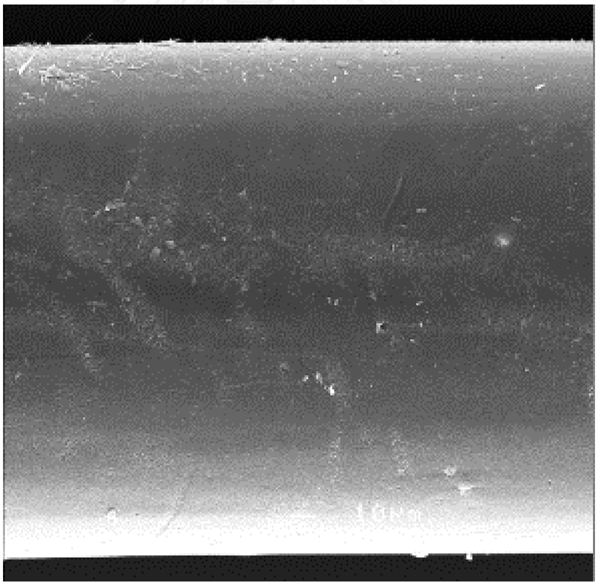


Figure 4.1(e) Chromic-acid-etched LDPE fiber after the etching time of 5 minutes

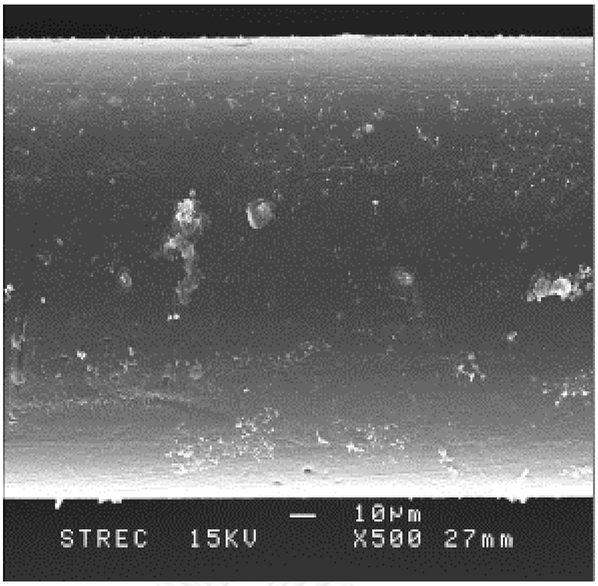


Figure 4.1(f) Chromic-acid-etched LDPE fiber after the etching time of 10 minutes

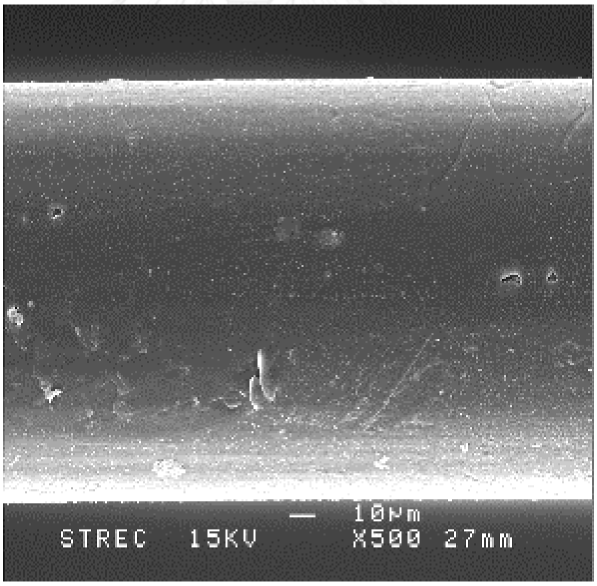


Figure 4.1(g) Chromic-acid-etched LDPE fiber after the etching time of 15 minutes

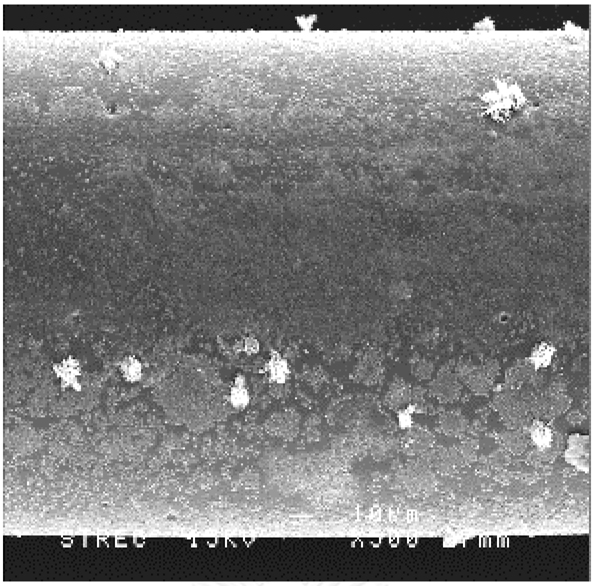


Figure 4.1(h) Chromic-acid-etched LDPE fiber after the etching time of 20 minutes

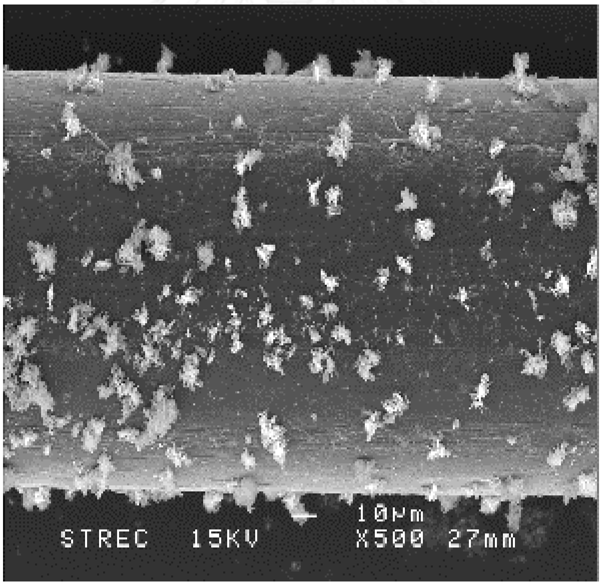


Figure 4.1(i) Chromic-acid-etched LDPE fiber after the etching time of 25 minutes

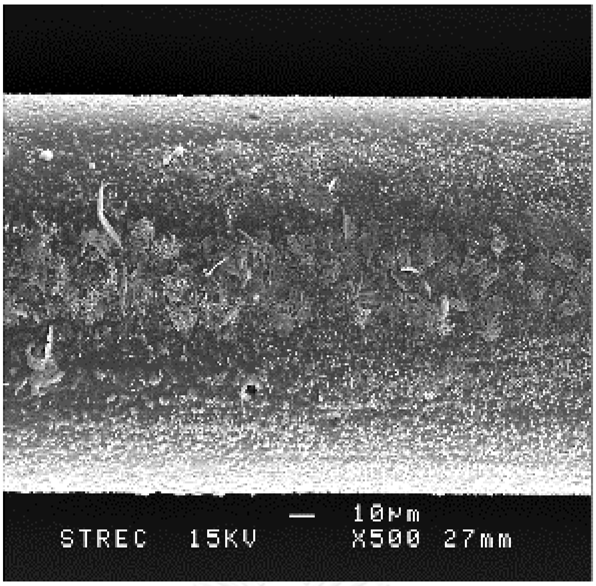


Figure 4.1(j) Chromic-acid-etched LDPE fiber after the etching time of 30 minutes

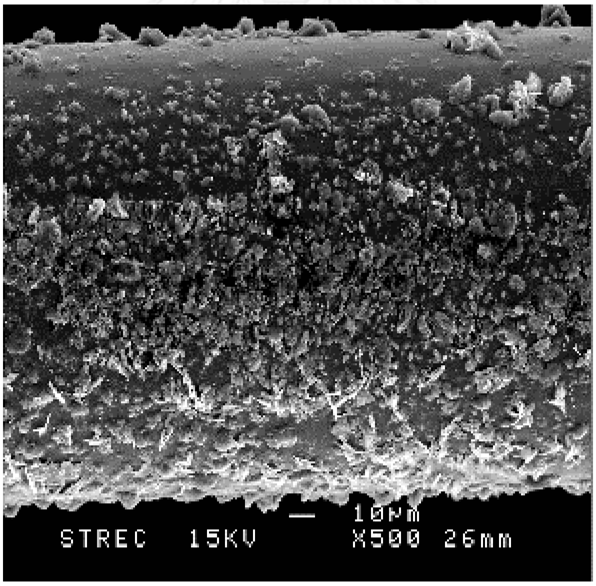


Figure 4.1(k) Chromic-acid-etched LDPE fiber after the etching time of 60 minutes

Figure 4.1 SEM images illustrating surface features of fibers at various stages

For the etching duration of 2.5-15 minutes, surface roughness increased only slightly, as the fiber appeared to be almost identical to that in Figure 4.1(a) (unetched). The slight increase in the surface roughness was responsible for the small increase in the grafting efficiency. For the etching time of 20 minutes, the surface roughness became much higher, so was the grafting efficiency. For the etching time of

25 minutes, the surface appeared quite smooth again, with a number of white “needle-like crystals” present. EDS analysis of these crystals indicated that they were composed mainly of sulfur with a small amount of chromium, indicating some left-over chromic acid. However, etched LDPE fibers shown in Figures 4.1(d) – 4.1(k) were prepared for the purpose of SEM observation only, so they were not thoroughly rinsed with acetone and DI water. Etched fibers that would undergo the amidoximation process would be thoroughly cleaned to ensure no left-over chromic acid. The surface smoothness was responsible for the decrease in the grafting efficiency from 20 to 25 minutes of etching time. For the etching times of 30 and 60 minutes, the surfaces appeared to be rough again, but this time on a macroscopic scale. This kind of surface roughness must not be suitable for grafting of monomers, as the cografting efficiency became abruptly reduced at the etching time of 30 minutes and more, as evident in Figure 4.7.

4.2 Preparation of amidoxime fibers

4.2.1 Degree of cografting of AN/MAA onto LDPE fibers

A mixture of AN and MAA monomers with 60:40 mixing ratio (the total concentration of the two monomers was set at 50 (w/w)% in dimethyl sulfoxide as the solvent) was cografted onto the fibers by the simultaneous irradiation cografting method. The irradiation was performed at low temperature by putting ice cubes in water around the container for irradiation, and the container was irradiated with γ-ray from Co-60 at a dose rate of 6.21 kGy/hr. The total dose was varied from 5 - 50 kGy. Figure 4.2(a) represents the starting LDPE fibers submerged into the AN/MAA solution and Figure 4.2(b) shows the cografted LDPE fibers with AN/MAA at a total dose of 40 kGy.

(a) Starting LDPE fibers (b) Cografted LDPE fibers

Figure 4.2 Radiation grafting of LDPE fibers with AN/MAA at total dose of 40 kGy

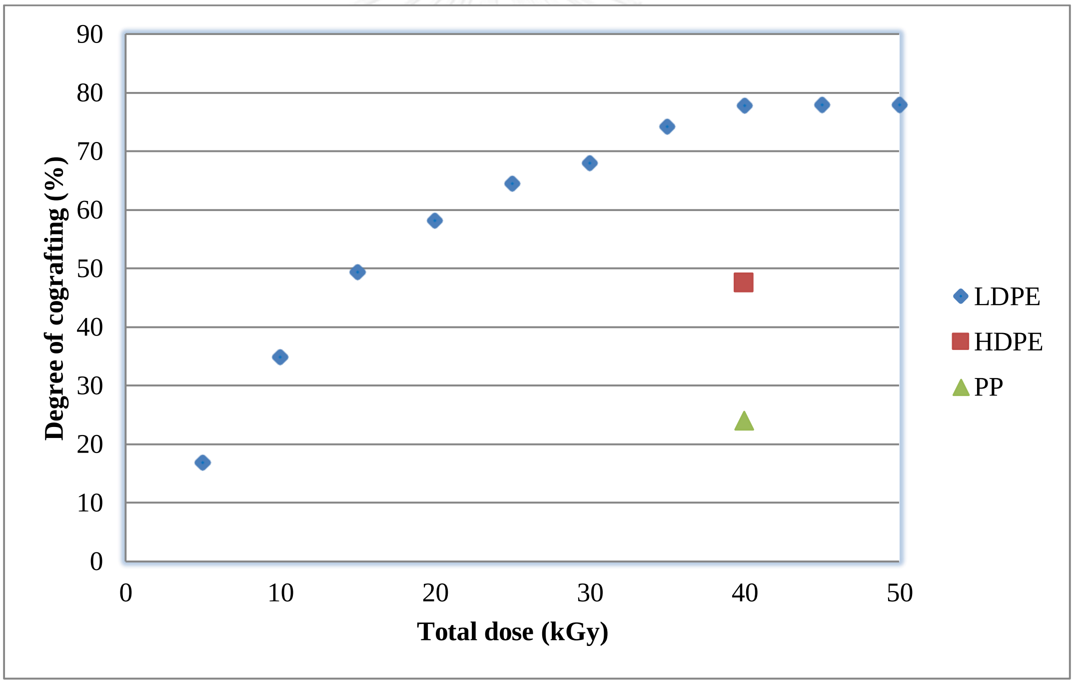


Figure 4.3 Degree of cografting of AN/MAA onto different types of fibers

Results of the degree of cografting of AN/MAA onto LDPE fibers vs. gamma ray dose are shown in Figure 4.3. It was obvious that as the total dose increased, the degree of cografting increased. At the total dose of 40 kGy, the degree of cografting became saturated at approximately 78%. Therefore, the optimum total gamma-ray dose of 40 kGy was selected for the amidoximation process of chromic acid pre-treated fibers. On the other hand, for HDPE and PP fibers irradiated at 40 kGy, the cografting efficiency reached only 45% and 24%, respectively. These values were much lower than that of LDPE fibers; therefore, HDPE fibers and PP fibers were not of practical use for the present purpose. This result was expected because the polymer chains of HDPE and PP stayed closer to each other than LDPE, so there was not much space between polymer chains to react with the monomers, resulting in the low cografting efficiency.

4.2.2 Amidoxime group density

The cyano group of the cografted chains was converted into the amidoxime group by chemical reaction with hydroxylamine hydrochloride solution with the amidoximation time ranging from 15 to 120 minutes. Figure 4.4 shows the trend of the result. More amidoximation time resulted in more cyano group being converted into the amidoxime group, and after all the available cyano group was converted after 75 minutes of amidoximation time, the amidoxime group density became saturated at approximately 1.85 mol/kg. Therefore, the optimized amidoximation time of 75 minutes was selected for synthesizing chromic acid pre-treated amidoxime fibers.

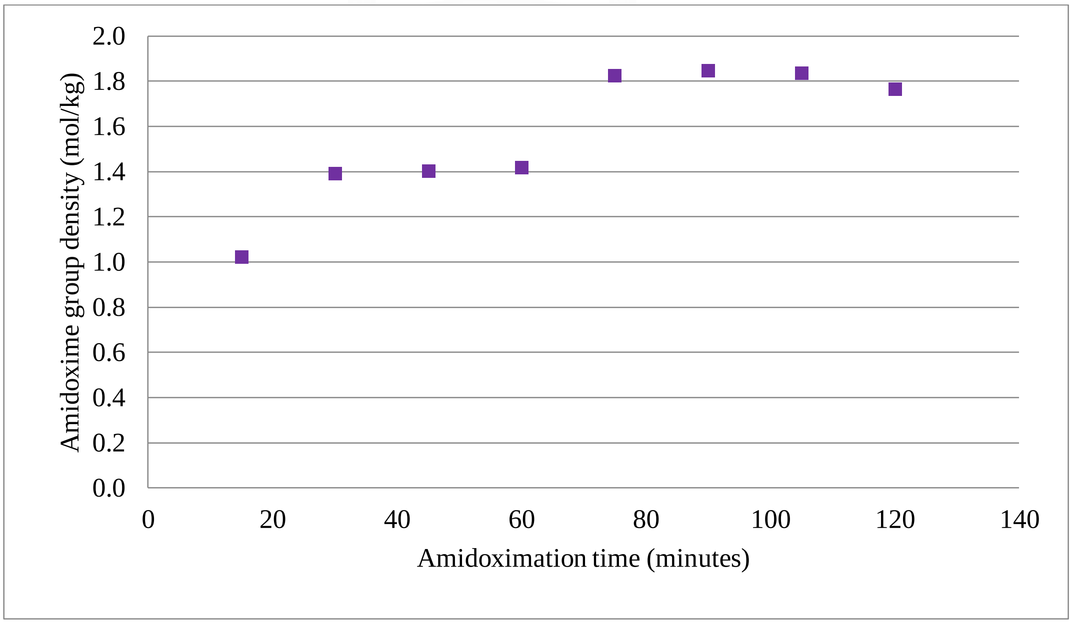


Figure 4.4 Amidoxime group density at various amidoximation times

4.2.3 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 4.5(a), the characteristic absorption bands of polyethylene at wave numbers 2850 and 1470 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 2250 and 1720 cm^{-1} due to C≡N of poly(acrylonitrile) and C=O of poly(methacrylic acid), respectively, as shown in Figure 4.5(b). After the amidoxime group conversion, the C≡N band at wave number 2250 cm^{-1} disappears, and the N-H stretch band of the amidoxime group at wave number 3180 cm^{-1} as well as the C=O band of the amidoxime group at wave number 1676 cm^{-1} become present, as shown in Figure 4.5(c).

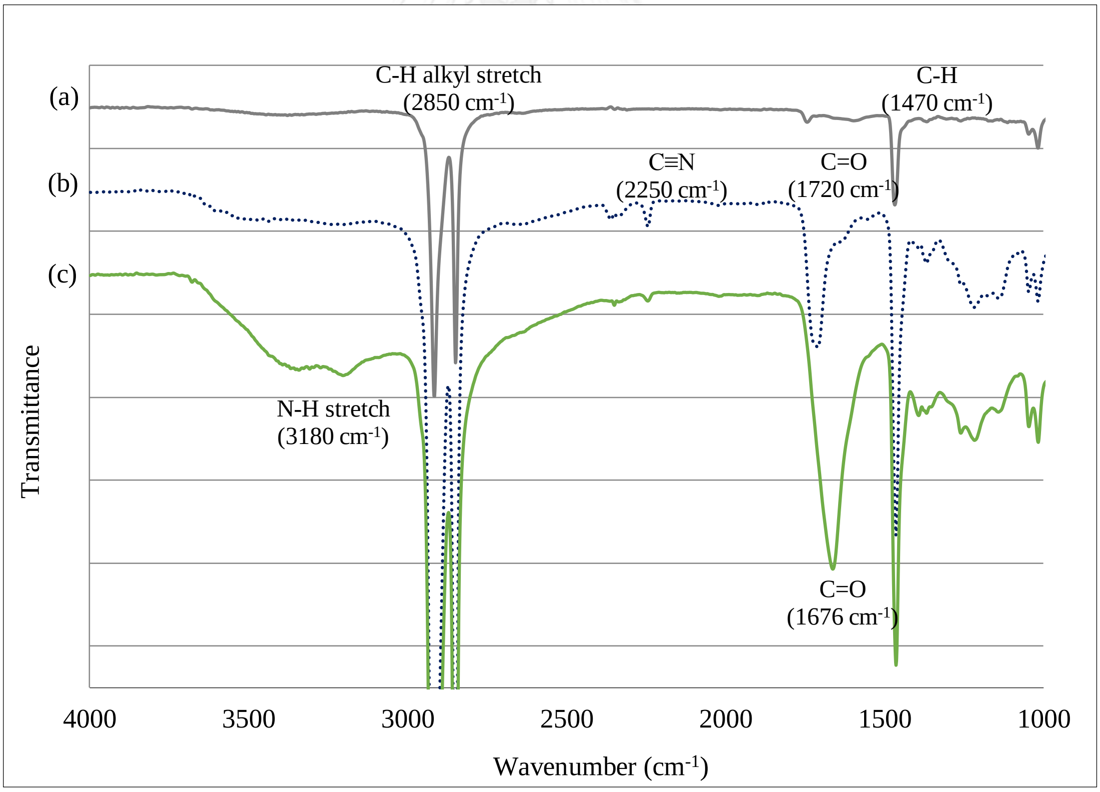


Figure 4.5 FTIR spectra of (a) LDPE fiber, (b) AN/MAA cografted fiber and (c) amidoxime fiber

4.3 Uranium concentrations in Thailand's seawater

Uranium concentrations in seawater samples collected at various depths and locations of seawater sampling stations in the Gulf of Thailand and the Andaman Sea are summarized in Table 4.1. The analysis uncertainty at approximately 3 ppb uranium concentration level was ± 1σ or ± 0.5 ppb. Thus, it appeared that uranium concentration in Thailand's seawater was generally uniform at about 3 ppb regardless of location and depth of seawater, consistent with the literature-reported value for other areas of the world (22, 23).

Table 4.1 Uranium concentrations in Thailand seawater

Region	Depth Coordinate	Surface	30 m	100 m	150 m
		Uranium concentration (ppb)			
Andaman Sea	(A) 08°56.004' N 098°05.857' E	-	3.4	-	-
	(B) 08°35.992' N 098°06.264' E	3.2	3.3	-	-
	(C) 08°17.701' N 098°11.267' E	-	3.4	-	-
	(D) 08°02.765' N 098°14.282' E	-	3.3	-	-
	(E) 08°51.096' N 097°31.207' E	-	3.2	3.1	3.1
	(F) 08°35.731' N 097°32.268' E	3.1	-	3.3	3.6
Gulf of Thailand	(G) 09°54.360' N 099°48.830' E	-	3.2	-	-
	(H) 09°33.069' N 100°21.002' E	2.9	3.3	-	-
	(I) 12°55.715' N 100°51.769' E	3.0	-	-	-

Note: "-" means no sample was collected.

4.4 Effect of chromic acid treatment on uranium adsorption efficiency

To modify the surface of the LDPE fibers with chromic acid solution, LDPE fibers produced from the extrusion machine were immersed in the chromic acid solution at 70°C for various reaction times. Figure 4.6 shows the different physical appearances between pre-treated (white) and treated (brown) LDPE fibers.

Figure 4.6 Modified LDPE fibers with chromic acid treatment

After different surface treatment durations, the cografting efficiency was determined from the degree of cografting as shown in Figure 4.7. The degree of cografting reached the maximum of about 90% at the etching time of 20 minutes, and this was as much as 30% higher than the value of about 70% reported in Ref. (2). In Figure 4.7, for each chromic acid treatment duration, 3 samples were used and the reported value was the averaged one. The standard deviations of all data points were 2.2% at most, so no error bar was included in the Figure.

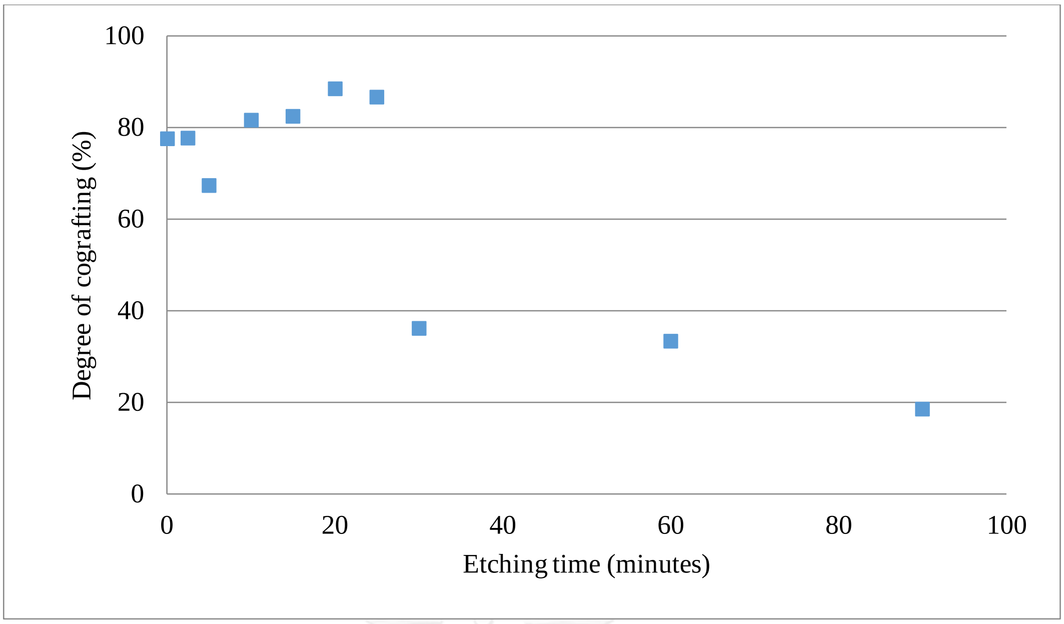


Figure 4.7 Effect of etching time on degree of cografting of chromic acid pre-treated LDPE fibers

After the amidoximation procedure of chromic-acid-treated LDPE fibers, all the fibers were submerged in a seawater sample in a 50-L plastic container at room temperature for 30 days. The seawater sample was collected from Tao Island, Surat Thani Province, Thailand with added $[UO_2(CO_3)_3]^{4-}$ to increase the uranium concentration to about 500 ppb. The uranium adsorption efficiency of chromic acid pre-treated amidoxime fibers in a laboratory scale is shown in Figure 4.8. For the etching time of 0 minute representing LDPE fiber without etching, the uranium adsorption efficiency was determined to be 0.71 g-U/kg-adsorbent. For the optimized etching time of 20 minutes, the uranium adsorption efficiency reached the maximum at 0.94 g-U/kg-adsorbent, or 32.4% higher than that of non-chromic acid pre-treated amidoxime fibers.

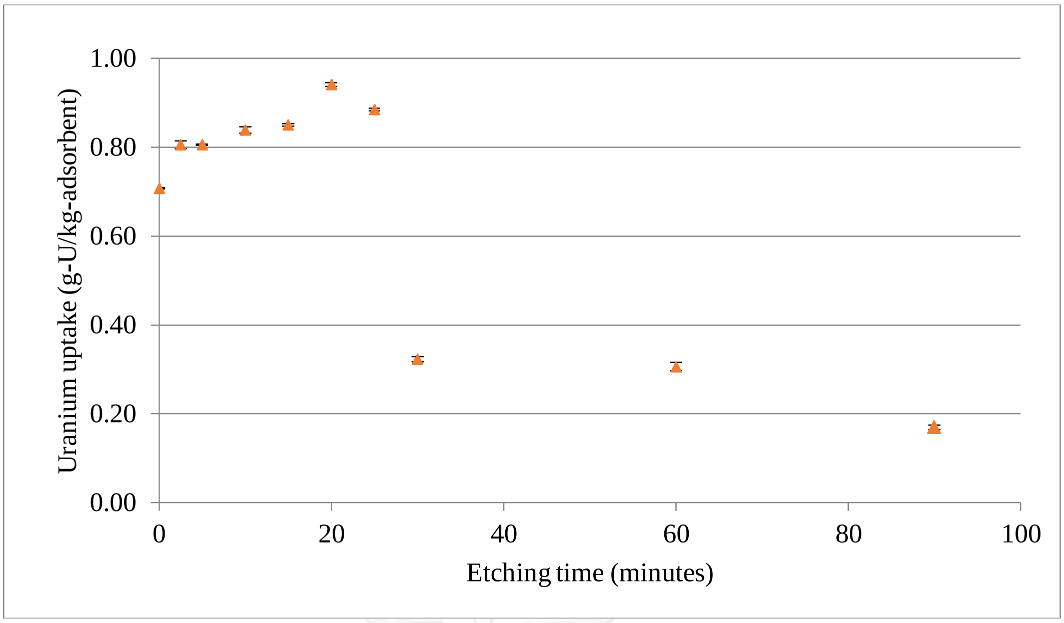


Figure 4.8 Effect of etching time on uranium uptake of chromic acid pre-treated amidoxime fibers submerged in seawater sample for 30 days

4.5 EDS analysis of chromic acid pre-treated amidoxime fibers

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique routinely used for elemental identification. EDS systems are mounted on scanning electron microscopes (SEM) and use the primary beam of the microscope to generate characteristic X-rays. The composition of the sample is determined by analyzing the energy of the characteristic X-rays.

Analyzed specimens were chromic acid pre-treated amidoxime fibers, one before submerging in seawater and the other one after submerging for 30 days. From the spectrum in Figure 4.9, before submerging in seawater, only carbon and an abundant quantity of oxygen was present, and no uranium was detected by the instrument. From the spectrum in Figures 4.10-4.11, after submerging in seawater, the amidoxime groups adsorbed many elements from seawater. Detected elements were magnesium, calcium and uranium. Sodium was also detected because it adhered to the adsorbent, but not extracted by the adsorbent. According to the inset, the weight percentage of the detected uranium was 2.6%. This confirms the presence and the ability of amidoxime functional groups on chromic acid pre-treated fibers to adsorb uranium in seawater.

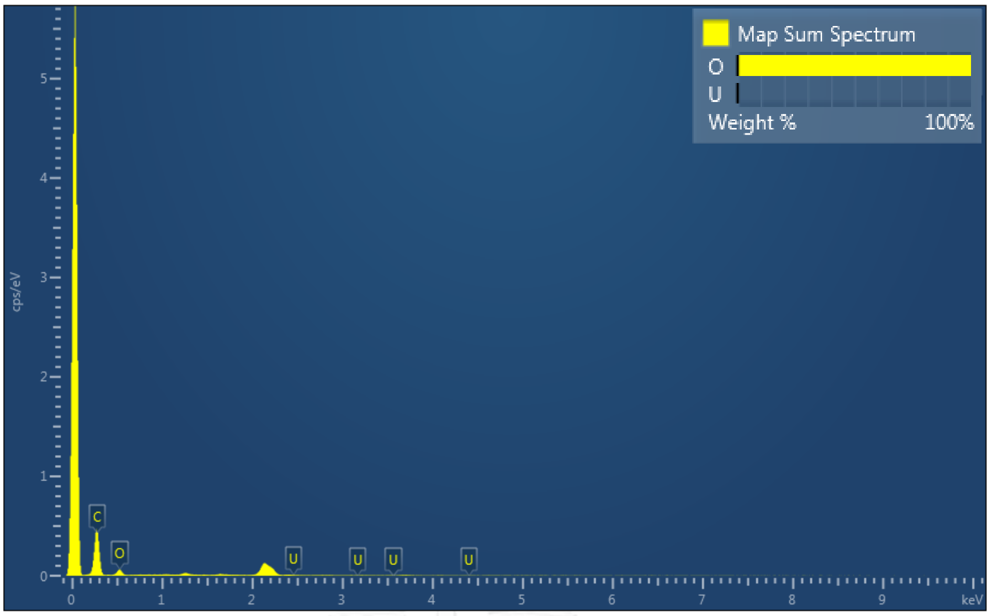
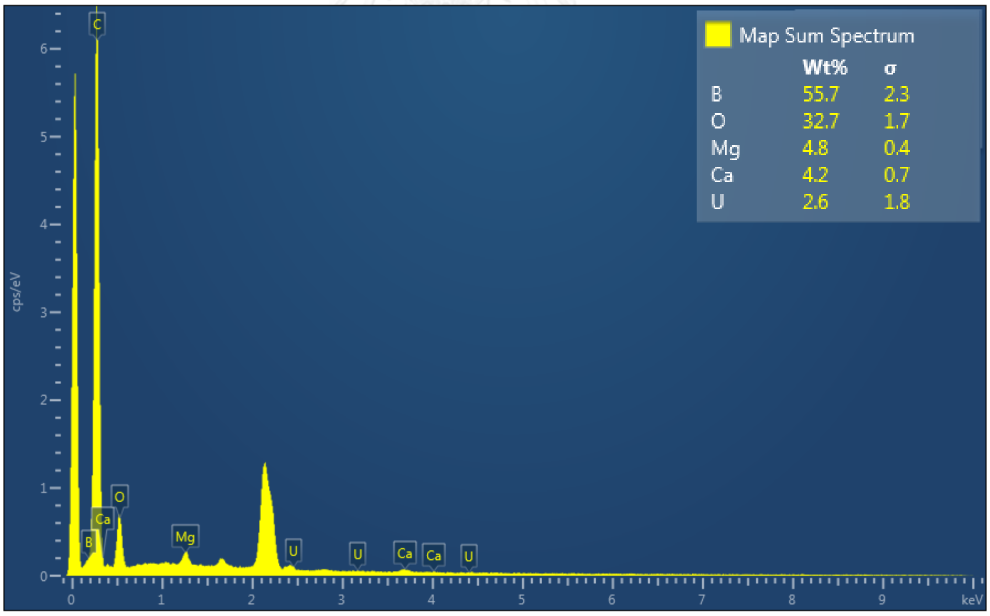


Figure 4.9 EDS spectrum of chromic acid pre-treated amidoxime fiber prior to seawater submersion



	Wt%	σ
B	55.7	2.3
O	32.7	1.7
Mg	4.8	0.4
Ca	4.2	0.7
U	2.6	1.8

Figure 4.10 EDS spectrum of chromic acid pre-treated amidoxime fiber after submerging in seawater for 21 days

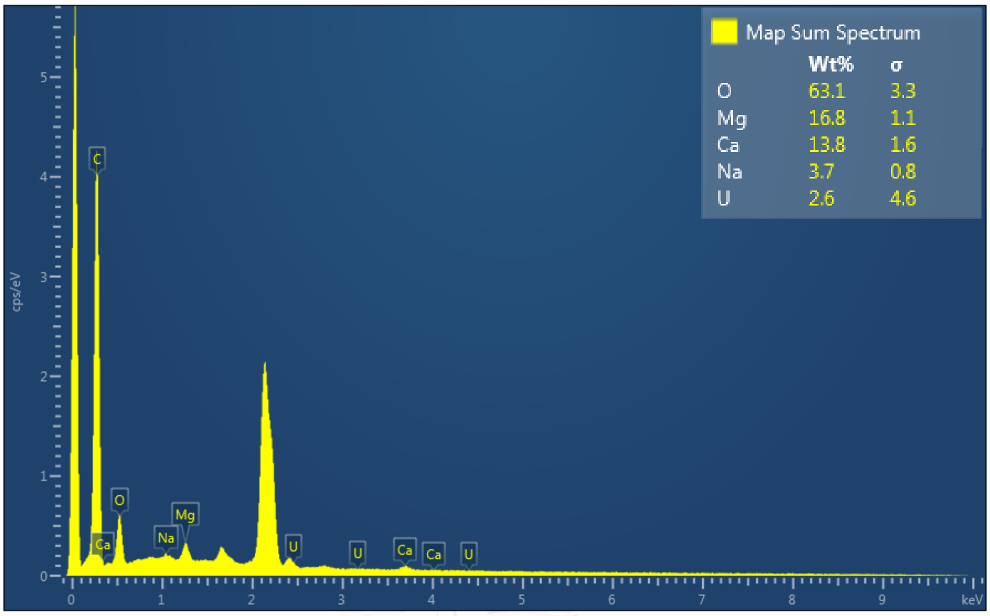


Figure 4.11 EDS spectrum of chromic acid pre-treated amidoxime fiber after submerging in seawater for 30 days

4.6 Uranium extraction from seawater

4.6.1 Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers at various submerging durations in a laboratory setup

The non-chromic acid pre-treated amidoxime fibers were submerged in a seawater sample in a 50-L plastic container in a laboratory at room temperature. The seawater sample was collected from Tao Island, Surat Thani Province, Thailand, with added $[UO_2(CO_3)_3]^{4-}$ to increase the uranium concentration to 250 ppb in order to have enough uranium for absorption of all fibers. Results of uranium adsorption efficiency vs. submerging time are presented in Figure 4.12. It was evident that the adsorption rate was high at the beginning and became reduced with increasing submerging time.

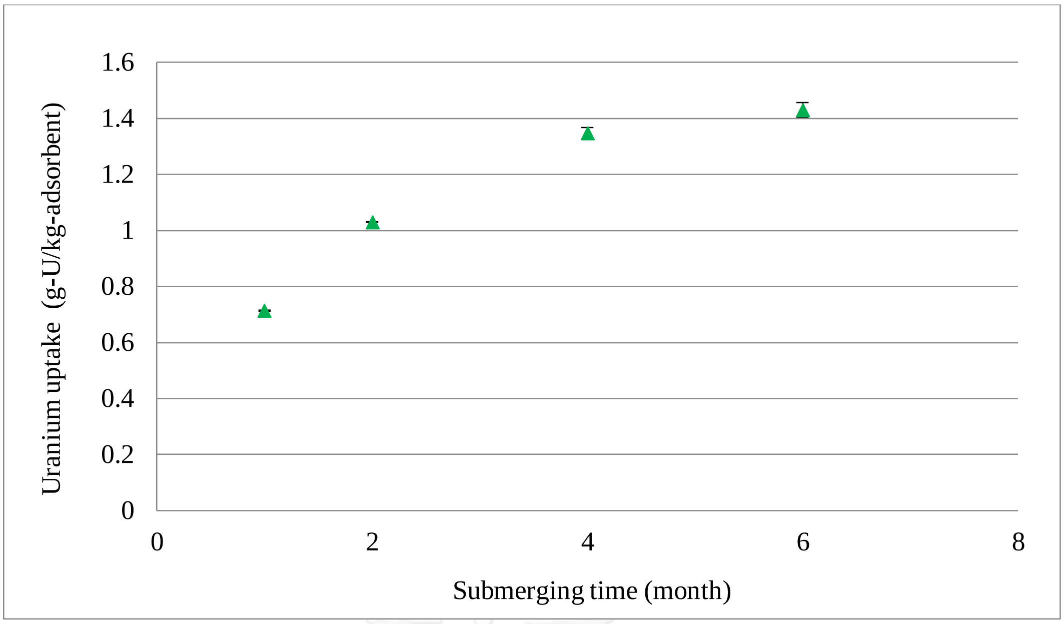


Figure 4.12 Uranium uptake of non-chromic acid pre-treated amidoxime fibers submerged in seawater sample in a laboratory setup

4.6.2 Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers at various submerging durations in Kho Loy seawater

The non-chromic acid pre-treated amidoxime fibers were submerged in shallow seawater at the depth of 10 - 12 meters at Kho Loy in Chonburi province. The submerging time was 0.5, 1, 1.5 and 2 months. Figure 4.13 shows that as the submerging time increased, the uranium adsorption efficiency increased, although very slightly. Moreover, after the first month of submersion, the fibers appeared to become almost saturated. As the seawater at Kho Loy was murky, the submerged fibers exhibited a dark appearance from adhered sedimentation, resulting in less uranium adsorbed as the sedimentation on the fibers prevented uranium from being adsorbed. This explained why the uranium uptake was extremely low.

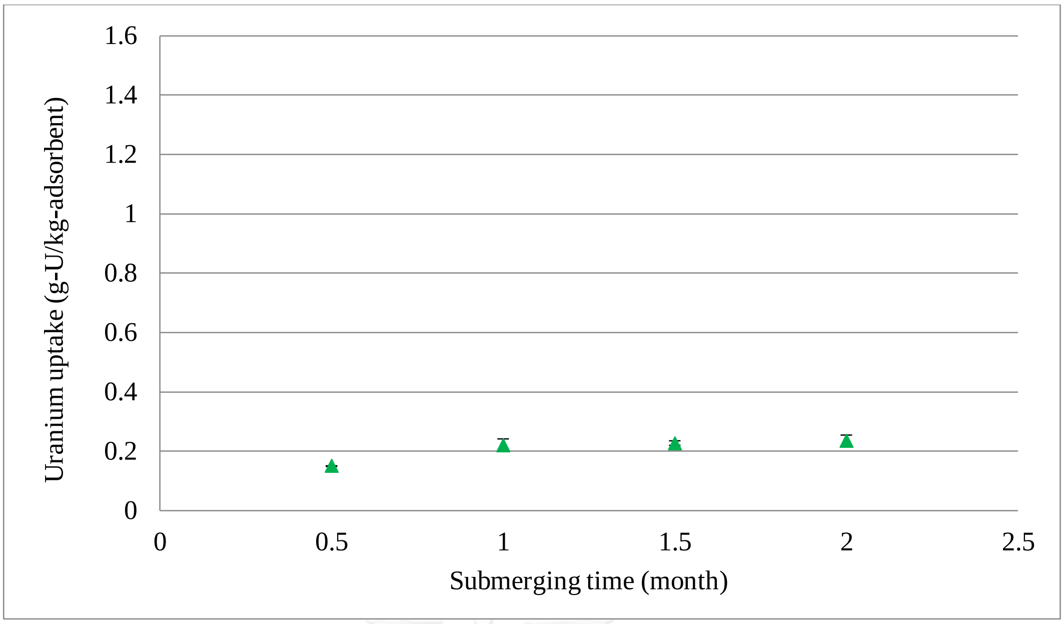


Figure 4.13 Uranium uptake of non-chromic acid pre-treated amidoxime fibers submerged in Kho Loy seawater

4.6.3 Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers at the SEA Laboratory on Redondo Beach in California, USA

The non-chromic acid pre-treated amidoxime fibers were submerged for 10 days in a seawater container at the SEA Laboratory on Redondo Beach in California, USA. The container was circulated and continually refreshed with seawater with the average temperature of 7°C. After uranium elution, results from ICP-AES analysis indicated that the adsorption efficiency was only 0.002 g-U/kg absorbent. This was substantially lower than all of the results reported in earlier sections. The submersion time of only 10 days together with the very low average seawater temperature of 7°C all contributed to this outcome. Because the temperature of seawater significantly affected the adsorption capacity, the experiment on the effect of pH and temperature on uranium extraction from seawater using non-chromic acid pre-treated amidoxime fibers was carried out and the results are reported in Section 4.8

4.6.4 Uranium adsorption efficiency of chromic acid pre-treated amidoxime fibers at various submerging durations

Uranium adsorption efficiency of chromic acid pre-treated amidoxime fibers submerged in shallow seawater in front of Phuket Marine Biological Center (PMBC) in Phuket province, Thailand, is presented in Figure 4.14 together with results from other studies.

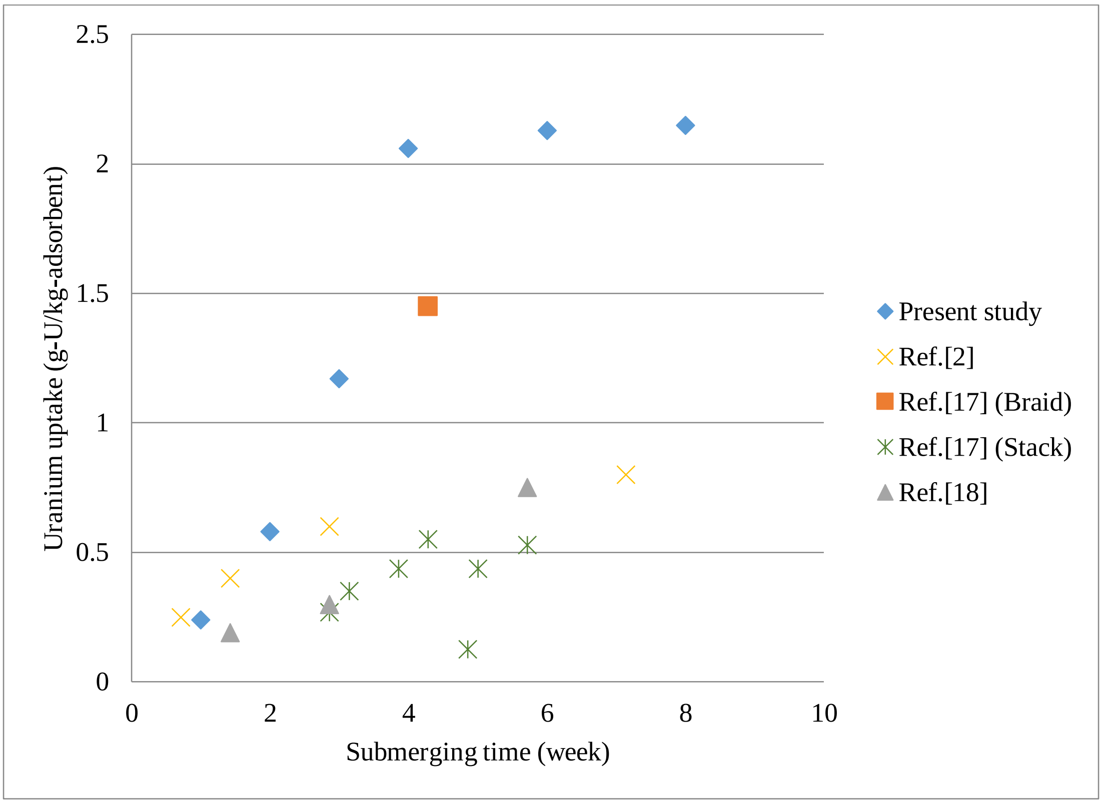


Figure 4.14 Uranium uptake of chromic acid pre-treated amidoxime fibers submerged in 30°C Phuket seawater compared to other studies

The adsorption capacities at 1, 2, 3, 4, 6 and 8 weeks were 0.24, 0.58, 1.17, 2.06, 2.13 and 2.15 g-U/kg-adsorbent, respectively. When compared with results reported by Tamada (18) on the adsorption capacity of about 1.5 g-U/kg-adsorbent of the braid-type adsorbent for the soaking time of 30 days in 30°C seawater, the present work’s adsorption efficiency of 2.06 g-U/kg-adsorbent for 30 days of submerging time in 29 - 30°C seawater was about 37% higher. Moreover, after approximately 2 weeks of submerging time, the adsorption capacity in the present study was clearly and substantially higher than those of other studies. This significantly enhanced adsorption was clearly attributable to the increased grafting efficiency from the surface treatment.

Comparison between the result in Figure 4.14 and that in Figure 4.8 revealed that submersion in open ocean for 1 month yielded the adsorption efficiency of approximately 2 times higher than submersion in seawater sample with added 500 ppb of $[UO_2(CO_3)_3]^{4-}$ in a small-scale laboratory setup. Although higher uranium concentration in seawater should be considered a prime condition for uranium uptake by the chromic acid pre-treated amidoxime fibers, the effects of natural wave motion and continuous ocean current which introduce new seawater into the adsorbent all the time would outweigh the effect of uranium concentration, making open-ocean submersion more effective.

From the result in Figure 4.14, it was also important to note that uranium uptake took place mostly within the first month of submersion. Afterward, the adsorbent appeared to be almost saturated, as continued submersion from 1 month to 2 months increased the adsorption only about 4%.

4.7 Usage repeatability

The adsorption efficiency after each 3-day cycle for up to 8 cycles is demonstrated in Figure 4.15.

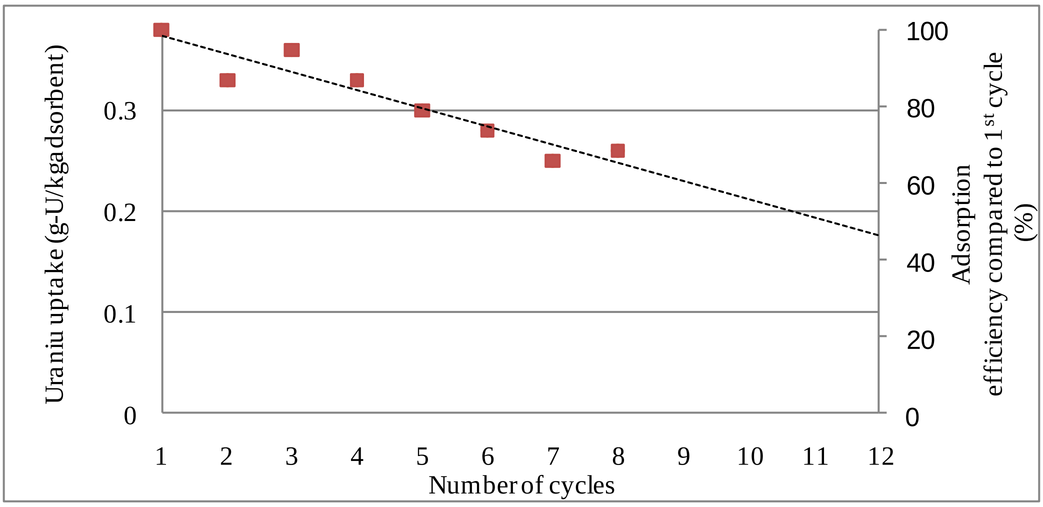


Figure 4.15 Change in adsorption efficiency after each 3-day cycle of repeated usage

From the Figure, a linear downward trend is observed. This was because every time the adsorbent underwent the elution process, some amidoxime sites were damaged. More elution cycles resulted in more amidoxime sites being destroyed. In terms of economics, it may be more favorable to continue using low-efficiency fibers than to spend resources to synthesize new ones. However, fibers with too low efficiency may make the extraction process unattractive economically. Thus, the economics of the process will determine the minimum efficiency that the fibers should have, and data in Figure 4.15 only serves to confirm the hypothesis that more elution cycles resulted in less adsorption efficiency of the non-chromic acid pre-treated amidoxime fibers. The extrapolated linear best-fit trend line shown in the Figure predicts that the adsorption capacity will reduce to about 50% after 11 cycles of usage.

However, in Saito's work (2), the 5-day period of contact with natural seawater followed by an elution period of 1 hour using 1 M HCl (temperature not indicated) and the subsequent KOH treatment, the adsorption capacity remained relatively unchanged even after 10 cycles. The underlying mechanism for the degradation of the non-chromic acid pre-treated amidoxime fibers of the present study needs to be investigated, but it is beyond the scope of the present study. However, it is possible that elution with 1 M HCl at 50°C accelerated the degradation (assuming that Saito performed HCl elution at room temperature).

4.8 Effect of pH and temperature on uranium extraction from seawater using non-chromic acid pre-treated amidoxime fibers

The influence of pH and temperature on uranium extraction from seawater using the amidoxime adsorbent was investigated. Uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers submerged in seawater samples in a laboratory at 25, 30 and 35°C and at pH of 7, 8 and 9 with a collection time of 0.5, 1, 1.5 and 2 months was evaluated.

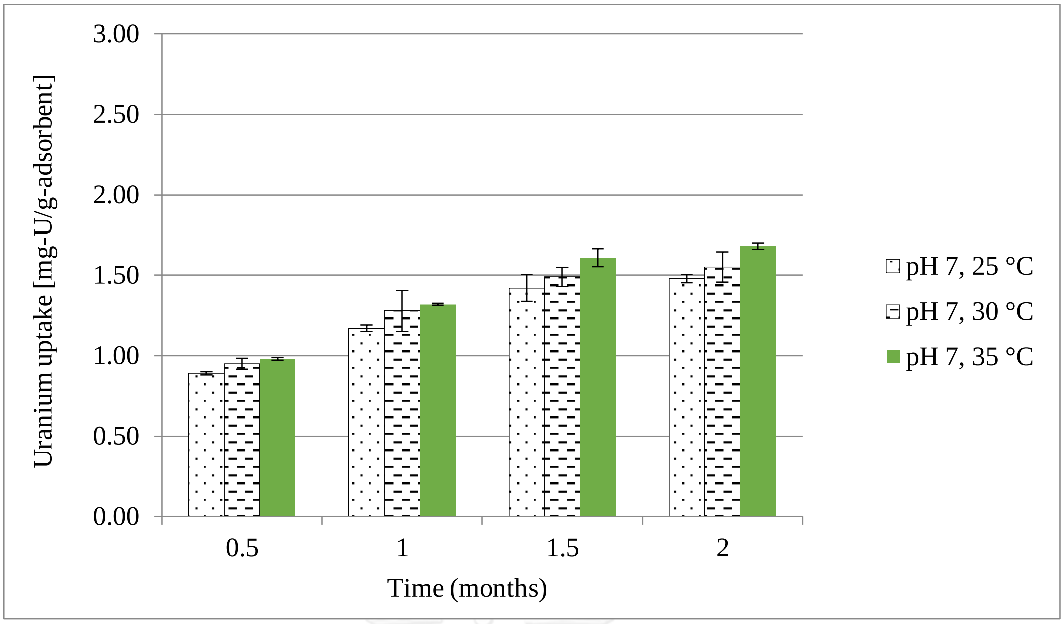


Figure 4.16 Uranium adsorption efficiency in seawater samples at pH of 7

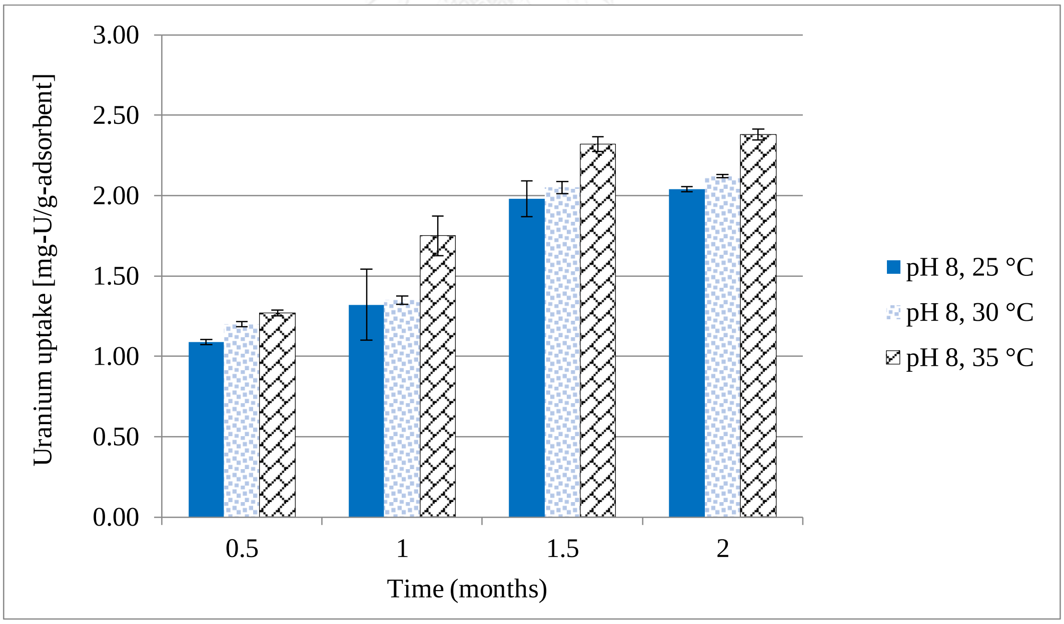


Figure 4.17 Uranium adsorption efficiency in seawater samples at pH of 8

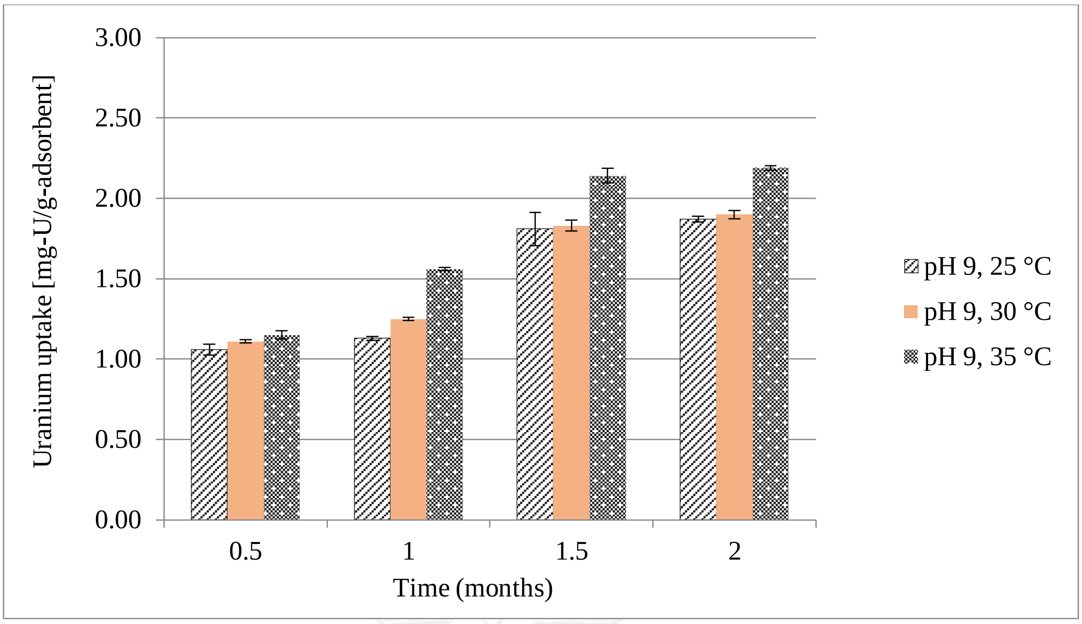


Figure 4.18 Uranium adsorption efficiency in seawater samples at pH of 9

According to results in Figures 4.16-4.18, with the pH value held constant at 8 and 9, the non-chromic acid pre-treated amidoxime fibers exhibited correspondingly higher adsorption kinetics with increasing seawater temperature. Especially at 35°C, the adsorption was fastest, while at 25 and 30°C the adsorption was significantly slower. This means that the adsorption kinetics was temperature-dependent favoring high temperature conditions.

Because the uranium adsorption process occurs in four steps in series [(1) diffusion of uranyl ions from the bulk liquid (seawater) into the boundary layer adjacent to the amidoxime fiber, (2) diffusion of ions from the boundary layer to the surface of the fiber, (3) diffusion of the ions into the interior of the fiber, and (4) the reaction of the ions with the amidoxime groups, as shown in Figure 4.19] (24-26) ,it can clearly be seen that diffusion plays an important role on the rate of uranium uptake from seawater. Since it is the well-known fact that temperature is one of many parameters governing the diffusion process, this explains why the adsorption rate in this study is temperature-dependent favoring high temperature conditions.

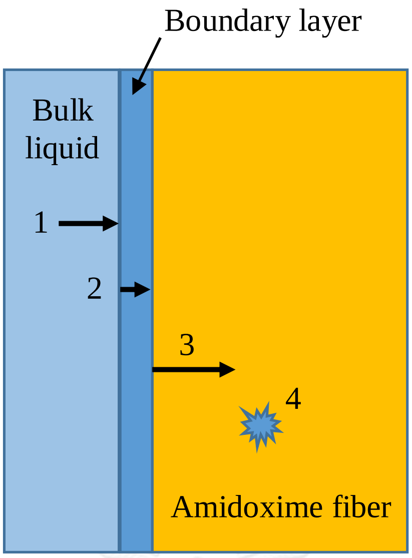


Figure 4.19 Mechanisms involved in the adsorption process: 1 – diffusion from bulk liquid; 2 – transfer from boundary layer to fiber surface; 3 – diffusion into interior of fiber; 4 – reaction with amidoxime group (25)

However, at the pH of 7, this trend with temperature was weak, although the adsorption at 35°C was still the fastest. On the other hand, with constant temperature, it can be observed that at the pH of 7, the fibers adsorbed uranium with the slowest kinetics, and this very slow kinetics help explain why the adsorption trend with temperature was weak at this particular pH value.

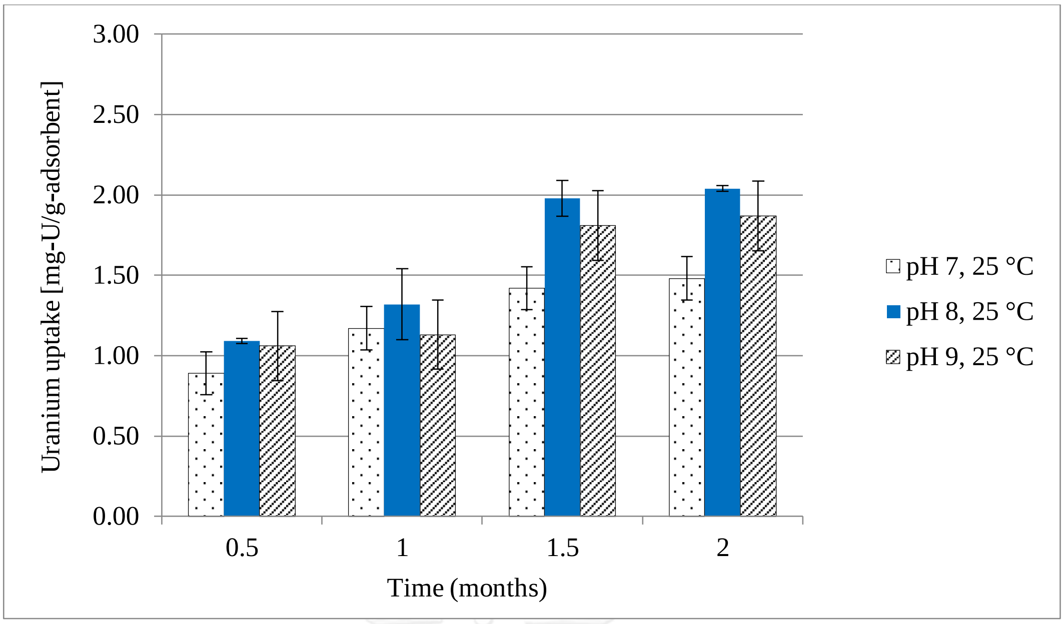


Figure 4.20 Uranium adsorption efficiency in seawater samples at 25˚C

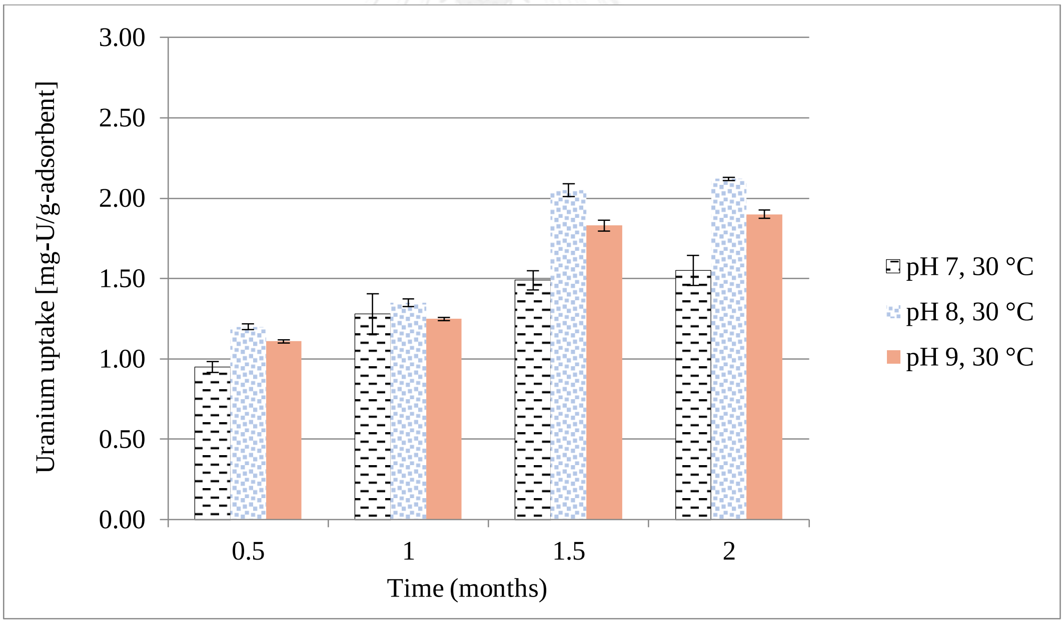


Figure 4.21 Uranium adsorption efficiency in seawater samples at 30˚C

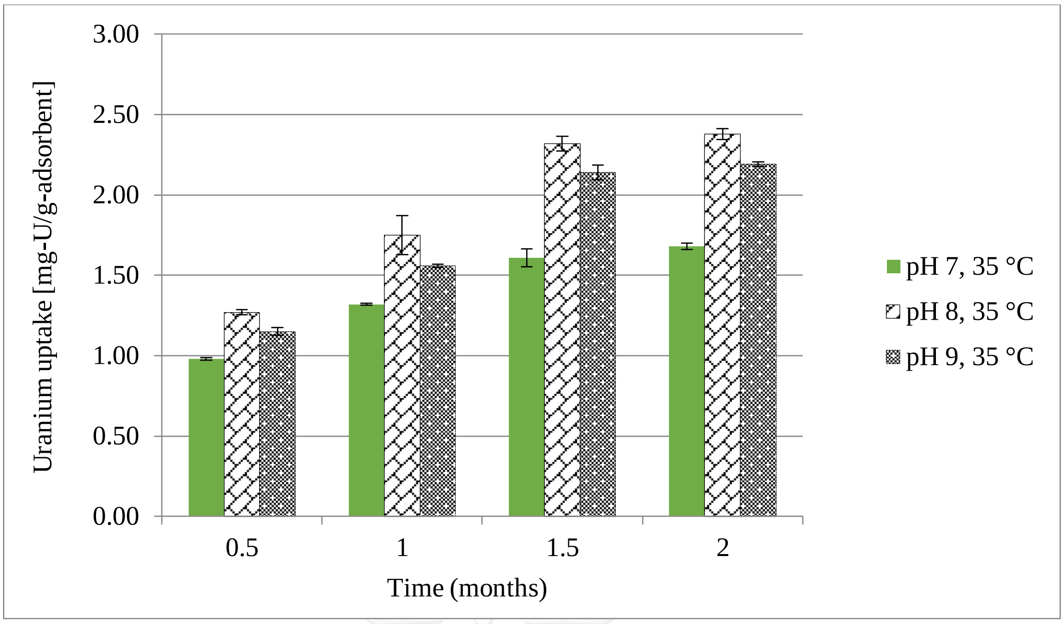


Figure 4.22 Uranium adsorption efficiency in seawater samples at 35°C

Results in Figures 4.20-4.22 revealed that at the pH of 8 corresponding to that of natural seawater, the fibers adsorbed uranium with the fastest kinetics. At the pH of 9, the fibers adsorbed uranium faster than at the pH of 7, but slower than at the pH of 8. This means that the adsorption kinetics favors the basic pH conditions with the maximum adsorption kinetics at the pH value of about 8. Therefore, this result confirmed that uranium extraction from seawater using the non-chromic acid pre-treated amidoxime fibers was appropriate in view of the pH value of seawater, and that the higher the seawater temperature, the higher the adsorption kinetics. Application of amidoxime fibers to adsorb uranium from Thailand's seawater was very favorable because of the year-round high seawater temperature facilitating high adsorption kinetics.

CHAPTER 5
CONCLUSIONS

5.1 Conclusions

Uranium exists in seawater with the average concentration of approximately 3 ppb, mainly in the tricarbonato uranylate anion form, $[UO_2(CO_3)_3]^{4-}$. For the past several decades, studies on uranium extraction from seawater utilized many different adsorbents such as porous membranes, polymers, inorganic compounds and chemical functional groups grafted onto substrates. For the case of functional groups, they were grafted onto appropriate polymers in order to adsorb uranium from seawater via the substitution of carbonate ion in $[UO_2(CO_3)_3]^{4-}$. Findings in Refs. (1, 20, 21) revealed that extraction of uranium from seawater using polymeric materials with the amidoxime functional group attaching to the surface resulted in a very high uranium adsorption capacity. Thus, the present study focused on uranium extraction from seawater using a polymeric material with the amidoxime functional group grafted onto the surface.

Synthesis of a polymeric material with the amidoxime functional group grafted onto the surface can be accomplished by radiation-induced graft-copolymerization. The present research work utilized gamma radiation from ^{60}Co source. With the appropriate dose, C-H bonds on the polymer substrate will be broken and in the presence of monomer (the mixture of AN and MAA), the cyano group will be grafted onto the polymer. Afterwards, the $NH_2OH{\bullet}HCl$ solution was used to chemically react with the cyano group under an appropriate condition to convert it into the amidoxime group. At the end, the polymeric material with the amidoxime functional group on the surface will be obtained.

A suitable substrate polymer for amidoximation must meet several criteria. The substrate material must not dissolve in water, seawater and chemicals used in the synthesis process. It must also be highly stable against physical, chemical, and biological degradation, especially in the harsh marine environment with continuous and strong currents and waves. In addition, it must not degrade under the radiation dose used in the synthesis process

Several types of polymers were tested: LDPE fibers, HDPE fibers and PP fibers. After cografting of AN/MAA onto the fibers using the simultaneous irradiation cografting technique at the dose of 40 kGy, it was found that the degrees of cografting of AN/MAA onto LDPE, HDPE and PP fibers were approximately 78%, 45% and 24%, respectively. These results were expected because HDPE is a linear polymer with almost no branches, while LDPE is a branched polymer with a large amount of short branches, and is an amorphous polymer. Therefore, monomers can react with polymer chains of LDPE more effectively than those of HDPE and PP. Therefore, the present study utilized LDPE fibers as the substrate polymer. However, as LDPE fibers are not available both domestically and internationally, they had to be fabricated in Thailand using the single screw extruder.

Benefits of grafting monomers onto LDPE surface using the radiation-initiated graft copolymerization technique are as follows: AN grafted onto LDPE will make the LDPE exhibit the ion-exchange property, while MAA will make the LDPE more hydrophilic. Thus, AN and MAA monomers were suitable monomers for grafting of amidoxime functional groups. From Kawai's work (3) on optimization of weight ratio of AN/MAA in monomer mixtures, it was found that the 60 : 40 by volume ratio of AN and MAA monomers resulted in the highest uranium adsorption from seawater.

Because the objective of this research work is to increase the efficiency of uranium adsorption from seawater using LDPE fibers with the amidoxime functional group, the effective surface area of LDPE fibers was increased by chemical surface modification using the chromic acid solution at high temperature. This resulted in LDPE fibers surface becoming rough and full of cracks. Because of the larger amount of surface area and because chemicals can flow into cracks, the cografting efficiency on chromic acid pre-treated LDPE fibers was highly enhanced. SEM analysis of chromic-acid-etched LDPE fibers at the etching time of 2.5, 5, 10, 15, 20, 25, 30, and 60 minutes indicated that the surface roughness of LDPE fibers increased with increasing etching time.

For the degree of cografting of AN/MAA onto LDPE fibers at different doses, it was found that as the total dose increased, the degree of cografting increased accordingly. For the dose of 40 kGy, the degree of cografting reached the maximum at appropriately 78%. Thus, the total gamma ray dose of 40 kGy was appropriate for the amidoximation process of chromic acid pre-treated fibers.

After the radiation-grafting copolymerization process, the cyano group was converted into the amidoxime group by the chemical process using hydroxylamine hydrochloride solution. It was found that after 75 minutes of amidoximation time, the amidoxime group density reached the maximum and became saturated at approximately 1.85 mol/kg. Thus, the amidoximation time of 75 minutes was suitable for the synthesis of chromic acid pre-treated amidoxime fibers.

FTIR spectra of the LDPE fibers revealed the absorption bands of polyethylene at 2850 and 1470 cm^{-1} and the absorption bands of cografted AN/MAA at 2250 and 1720 cm^{-1}. After the amidoxime group conversion, the absorption bands of the amidoxime group at 3180 and 1676 cm^{-1} appeared. Thus, from FTIR analysis, it was confirmed that the synthesized polymer contained the amidoxime functional group on the surface.

After surface modification of LDPE fibers using the chromic acid treatment and the subsequent amidoximation process under the appropriate condition, chromic acid pre-treated amidoxime fibers were obtained. For the etching time of 20 minutes, the degree of cografting reached the maximum value of approximately 90%, which was approximately 30% higher than that of non-chromic acid pre-treated amidoxime fibers.

The ICP-MS technique was used to determine uranium concentrations in Thailand's seawater samples. The samples were collected at various depths and locations in the Gulf of Thailand and the Andaman Sea. It was found that at every location and depth, the uranium concentration was uniform at about 3 ppb ± 0.5 ppb.

When the chromic acid pre-treated amidoxime fibers were submerged in seawater sample with added 500 ppb of $[UO_2(CO_3)_3]^{4-}$ at room temperature for 30 days, it was found that for the etching time of 0 minute (unetched), the uranium adsorption efficiency was 0.71 g-U/kg-adsorbent. For the optimized etching time of 20 minutes, the uranium adsorption efficiency reached 0.94 g-U/kg-adsorbent, which was the highest among those obtained from chromic acid pre-treated amidoxime fibers etched for other durations. This maximum adsorption efficiency was 32.4% higher than that of non-chromic acid pre-treated amidoxime fibers.

Furthermore, in order to confirm that the chromic acid pre-treated amidoxime fibers were able to adsorb uranium, the EDS technique was employed. Chromic acid pre-treated amidoxime fibers before and after seawater submersion were analyzed. It was found that before seawater submersion, only carbon and oxygen, but not uranium, were detected, and that carbon, oxygen, magnesium, calcium, and uranium were detected for the fibers submerged in seawater sample for 30 days. Moreover, results from EDS analysis revealed the weight percentage of uranium of approximately 2.6%. Therefore, these results confirmed that chromic acid pre-treated amidoxime fibers were able to adsorb uranium from seawater.

To determine uranium adsorption efficiency of chromic acid pre-treated amidoxime fibers, they were submerged in seawater in front of Phuket Marine Biological Center in Phuket province. The seawater temperature was about 29 – 30ºC. It was found that the adsorption rate was high at the beginning and became reduced with increasing submerging time. For 30 days of submerging time, the adsorption efficiency reached 2.06 g-U/kg-adsorbent and became quite saturated from this time forward. In Tamada’s work (18), where the braid adsorbent was submerged in a 30°C seawater for 30 days, the adsorption efficiency was about 1.5 g-U/kg-adsorbent, which was about 37% lower than that of the present work. This comparison indicated that the enhancement of the grafting efficiency using the chromic acid treatment resulted in the enhancement of uranium adsorption efficiency from seawater.

Comparison between submersion of chromic acid pre-treated amidoxime fibers in an open ocean and in a seawater sample in a laboratory setup with added

$[UO_2(CO_3)_3]^{4-}$ for 30 days revealed that the adsorption efficiency of the open-ocean case was about 2 times higher than that of the laboratory-scale case. This was due to the effects of natural wave motion and continuous ocean current which introduce new seawater into the adsorbent all the time. Thus, soaking the adsorbent in an open ocean will yield a higher uranium adsorption.

Experiment on submersion of non-chromic acid pre-treated amidoxime fibers in seawater at Koh Loy, Chonburi province, for 15 - 60 days resulted in a very low uranium adsorption efficiency. This was because the seawater at Koh Loy was very murky, so the adsorbent was severely contaminated with mud and suspended particles. The surface of the adsorbent became darkened and this blocked uranium in seawater. Thus, another important condition to achieve high uranium adsorption efficiency is to submerge the adsorbent in clear seawater.

The usage repeatability of the non-chromic acid pre-treated amidoxime fibers was evaluated. Each submersion cycle was 3 days and a total of 8 cycles were studied. It was observed that as the number of cycles increased, the uranium adsorption efficiency became reduced slowly. At the 8th cycle, the adsorption efficiency was approximately 65% of that of the 1st cycle. Extrapolation using a linear trend line indicated that the adsorption capacity would reduce to about 50% after the 11th round. The reason for the decrease in the adsorption efficiency was because HCl was used during the elution process. The amidoxime functional group in contact with hot HCl for 1 hour resulted in the gradual destruction of the functional group. Nonetheless, the ability of the adsorbent to be reused was desired, as it helped reduce the cost and time to synthesize a new one.

The uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers soaked in a 7°C seawater at the SEA Laboratory on Redondo Beach in California, USA, for 10 days was evaluated to be only 0.002 g-U/kg absorbent. This extremely low value was attributable to the short submersion time and the low seawater temperature. Because the temperature had a pronounced effect, an additional study on the effect pH and temperature on uranium extraction from seawater was carried out.

The study on the uranium adsorption efficiency of non-chromic acid pre-treated amidoxime fibers by submerging in seawater samples at 25, 30 and 35°C and at pH of 7, 8 and 9 for 0.5, 1, 1.5 and 2 months was carried out. Results revealed that when the pH value was held constant, the non-chromic acid pre-treated amidoxime fibers exhibited correspondingly higher adsorption kinetics with increasing seawater temperature. This means that the adsorption kinetics was temperature-dependent favoring high temperature conditions. This was because the adsorption process involves diffusion, and temperature is one of many parameters controlling the diffusion process. When the temperature was held constant, at the pH of 8 corresponding to that of natural seawater, the fibers adsorbed uranium with the fastest kinetics. This means that the adsorption kinetics favors the basic pH conditions with the maximum adsorption kinetics at the pH value of about 8. Because Thailand's seawater temperature is approximately 30 - 35°C and because the pH is about 8, this provides a prime condition to employ chromic acid pre-treated amidoxime fibers to adsorb uranium from Thailand's seawater.

5.2 Suggestions for future work

This research work synthesized chromic acid pre-treated amidoxime fibers for the purpose of uranium extraction from seawater. However, other elements can be extracted as well such as magnesium, calcium, copper, vanadium, gold, nickel, and manganese. These elements are valuable and are important resources for other industries.

Chromic acid pre-treated amidoxime fibers can be synthesized using electron beam, instead of gamma ray, during the graft copolymerization process. This topic should be investigated.

Chromic acid pre-treated amidoxime fibers could be used to extract uranium from other liquid media such as river water and brine concentrate (wastewater from a seawater reverse osmosis plant).

The present research work employed chromic acid to treat LDPE fibers to increase the surface areas. Other surface treatment techniques such as plasma treatment and other acids should be investigated.

The present research work determined uranium concentrations using ICP-AES, ICP-MS and EDS techniques. Other techniques should be used such as neutron activated analysis (NAA) and colorimetry.

Other effects besides pH and temperature on uranium extraction from seawater using amidoxime fibers should be investigated, such as uranium concentration in seawater, the flow rate and the salinity of seawater.

REFERENCES

1. Klaus S. Extraction of Metals from Seawater. Inorganic Chemistry1984.
2. Saito K, Hori, T., Furusaki, S., Sugo, T., and Okamoto, J. Porous Amidoxime-Group-Containing Membrane for the Recovery of Uranium from Seawater. I&EC Research. 1987;26:149-53.
3. Kawai Tea. Preparation of hydrophilic amidoxime fibers by cografting acrylonitrile and methacrylic acid from an optimized monomer composition. Radiation Physics and Chemistry. 2000;59:405-11.
4. Saito Kea. Characteristics of Uranium Adsorption by Amidoxime Membrane Synthesized by Radiation-Induced Graft Polymerization. Journal of Membrane Science. 1987;34:307-15.
5. Zhang A, Uchiyama, G., and Asakura, T. pH Effect on the Uranium Adsorption from Seawater by a Macroporous Fibrous Polymeric Material Containing Amidoxime Chelating Functional Group. Reactive & Functional Polymers. 2005;63:143-53.
6. Jang J, and Yang, H. The Effect of Surface Treatment on the Performance Improvement of Carbon Fiber/Polybenzoxazine Composites. Journal of Material Science. 2000;35:2297-303.
7. Noharaa Lea. Evaluation of Carbon Fiber Surface Treated by Chemical and Cold Plasma Processes. Materials Research. 2005;8:281-6.
8. Shen Wea. Surface Chemical Functional Groups Modification of Porous Carbon. Recent Patents on Chemical Engineering. 2008;1:27-40.
9. Wan YZea. Characterization of Three-Dimensional Braided Polyethylene Fiber–PMMA Composites and Influence of Fiber Surface Treatment. Journal of Applied Polymer Science. 2006;99:949–56.
10. Wang H, Chen, S., and Zhang, J. Surface treatment of LLDPE and LDPE blends by nitric acid, sulfuric acid, and chromic acid etching. Colloid Polymer Science. 2009;287:541–8.
11. Tamada M, editor Collection of uranium from seawater. Technical Meeting at IAEA; 2009; Vienna, Austria.
12. Ebewele O. Polymer Science and Technology. Washington DC: CRC Press; 2000.
13. Odian G. Principles of Polymerization. 4th edition ed. New Jersey: John Wiley & Sons, Inc.; 2004.
14. Asua JM. Polymer Reaction Engineering. UK: Blackwell Publishing; 2007.
15. Woods J, and Pikaev, K. Applied Radiation Chemistry: Radiation Processing. New York: John Wiley & Sons, Inc.; 1994.
16. Knoll G. Radiation Detection and Measurement. 3 rd ed. New York: John Wiley & Sons, Inc.; 1999.
17. Singh A, and Silverman, J. Radiation Processing of Polymers. Munich: Hanser; 1992.

18. Tamada M. Current status of technology for collection of uranium from seawater. 42nd Session of the International Seminar on Nuclear War and Planetary Emergencie; Erice, Italy2009.

19. Zhang A, Asakura, T., and Uchiyama, G. The adsorption mechanism of uranium(VI) from seawater on a macroporous fibrous polymeric adsorbent containing amidoxime chelating functional group. Reactive & Functional Polymers. 2003;57:67–76.

20. Kawai Tea. Comparison of amidoxime adsorbents prepared by cografting MAA and 2-hydroxyethyl methacrylate with AN onto polyethylene. Industrial & Engineering Chemistry Research. 2000;39:2910–5.

21. Seko N, Tamada, M., and Yoshii, F. Current status of adsorbent for metal ions with radiation grafting and crosslinking techniques. Nuclear Instruments and Methods in Physics Research Section B. 2005;236:21–9.

22. Gideon M, and Robert, F. The U-series toolbox for paleoceanography Reviews in Mineralogy and Geochemistry "Uranium Series Geochemistry". p. 1–44.

23. Ku T, Knauss, K., and Mathieu, G. Uranium in open ocean: concentration and isotopic composition. Deep-Sea Research. 1997;24:1005–17.

24. Choy KKH, Ko, D. C. K., Cheung, C. W., Porter, J. F., and McKay, G. Film and intraparticle mass transfer during the adsorption of metal ions onto bone char. Journal Colloid Interface Science. 2004;271:284−95.

25. Jungseung Kea. Characterization of Uranium Uptake Kinetics from Seawater in Batch and Flow-Through Experiments. Industrial & Engineering Chemistry Research. 2013;52:9433−40.

26. Vadivelan V, and Vasanth Kumar, K. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. Journal Colloid Interface Science. 2005;286:90−100.

APPENDICES

APPENDIX A
CALCULATION OF THE DEGREE OF COGRAFTING

The degree of cografting of AN/MAA onto chromic acid pre-treated LDPE fibers was calculated from the weight gain using the following formula:

$$\text{Degree of cografting (\%)} = \frac{(W_1 - W_0)}{W_0} \times 100$$

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

Example: The weight of the starting fibers is 1.0272 g. The fibers were immersed in a container containing a mixture of AN/MAA monomers, and were irradiated with γ-ray at the total dose of 40 kGy according to the simultaneous irradiation cografting method. After irradiation, the fibers were removed from the container and were thoroughly washed with DMF several times. The cografted fibers were dried in a forced-convection oven to obtain a constant weight of 1.9517 g. Calculation of the degree of cografting of AN/MAA onto chromic acid pre-treated LDPE fibers is as follows.

Solution

$$\text{Degree of cografting (\%)} = \frac{(W_1 - W_0)}{W_0} \times 100$$

$$= \frac{(1.9517 - 1.0272)}{1.0272} \times 100$$

$$= 90\%$$

Answer The degree of cografting of AN/MAA onto chromic acid pre-treated LDPE fibers is 90% at the total dose of 40 kGy.

****

APPENDIX B
CALCULATION OF THE AMIDOXIME GROUP DENSITY

The amidoxime group density was calculated from the weight gain using the following formula:

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

where W_1 is the weight of the cografted fibers. W_2 is the weight of the amidoxime fibers and the number 69.5 represents the molecular weight of $NH_2OH{\bullet}HCl$.

Example: The weight of the cografted fibers is 1.9517 g. The cyano groups of the cografted fibers were converted into the amidoxime groups by immersing the cografted fibers in the $NH_2OH{\bullet}HCl$ solution at 80°C for 75 minutes. After the reaction, the fibers were repeatedly rinsed with DI water and dried in a forced-convection oven to obtain a constant weight of 2.3923 g. Calculation of the amidoxime group density of chromic acid pre-treated LDPE fibers is as follows.

Solution

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

$$= \frac{(2.3923 - 1.9517)}{69.5\ (2.3923)} \times 1000$$

$$= 2.65\ \text{mol/kg}$$

Answer The amidoxime group density of chromic acid pre-treated LDPE fibers is 2.65 mol/kg.

****

REFERENCES

VITA

NAME: Ms. Vareeporn Ratnitsai

SEX: Female

NATIONALITY: Thai

DATE OF BIRTH: 22 November 1977

PLACE OF BIRTH: Chonburi, Thailand

INSTITUTIONS ATTENDED: Burapha University,

1996-2000: Bachelor of Science (Physics)

Chulalongkorn University,

2003-2006: Master of Science (Nuclear Technology)

Chulalongkorn University,

2009-2014: Doctoral of Engineering (Nuclear Engineering)

HOME ADDRESS: 200/32 Jermjormpol Rd, Sriracha, Chonburi, Thailand, 20110, Tel. 087-8017055

Email: v_vareeporn@yahoo.com