Synthesis of high efficiency amidoxime polymer adsorbents for uranium extraction from seawater by radiation-induced polymerization

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การสังเคราะห์ตัวดูดจับเอมีดอกซิมพอลิเมอร์ประสิทธิภาพสูงเพื่อใช้สกัดยูเรเนียมจากน้ำทะเลโดยการพอลิเมอไรซ์ด้วยรังสี

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
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วิจิตตรา วงศ์ใจคำ : การสังเคราะห์ตัวดูดจับเอมีดอกซิมพอลิเมอร์ประสิทธิภาพสูงเพื่อใช้สกัดยูเรเนียมจากน้ำทะเลโดยการพอลิเมอไรซ์ด้วยรังสี. (Synthesis of high efficiency amidoxime polymer adsorbents for uranium extraction from seawater by radiation-induced polymerization) อ.ที่ปรึกษาหลัก : รศ. ดร.ดุลยพงศ์ วงศ์แสวง

การศึกษานี้ได้ทำการสังเคราะห์เอมีดอกซิมพอลิเมอร์เจลเพื่อใช้ในดูดจับยูเรเนียมในน้ำทะเลโดยผ่านกระบวนการพอลิเมอไรซ์ด้วยรังสีแกมมาหรือรังสียูวี การสังเคราะห์พอลิเมอร์เจลเริ่มต้นจากการนำมอนอเมอร์ผสมระหว่างอะคริโลไนไตร์ล และเมทาคริลิคแอซิด ร่วมกับสารเชื่อมโยงเมทิลีนบิสอะคริลาไมด์ และไฮโดรเจนเปอร์ออกไซด์ในกรณีของการฉายด้วยรังสียูวี จากนั้นนำมอนอเมอร์ผสมไปฉายด้วยรังสีแกมมาที่โดสต่างๆ หรือรังสียูวีที่เวลาต่างๆ จากนั้นจึงนำพอลิเมอร์เจลที่ได้มาบดให้ละเอียดและแช่ในสารละลายไฮดรอกซิลามีนไฮโดรคลอไรด์เป็นเวลา 90 นาที เพื่อให้เกิดการเปลี่ยนหมู่ฟังก์ชันเคมีจากหมู่ไซยาโนเป็นหมู่เอมีดอกซิม การทดสอบการดูดจับยูเรเนียมในห้องปฏิบัติการพบว่า ในกรณีของเอมีดอกซิมพอลิเมอร์เจลที่พอลิเมอไรซ์ด้วยรังสีแกมมา พบว่าพอลิเมอร์เจลที่เตรียมจากสัดส่วนของมอนอเมอร์อะคริโลไนไตร์ลต่อเมทาคริลิคแอซิด ที่ 80:20, ปริมาณสารเชื่อมโยง 0.8 กรัมต่อปริมาตรมอนอเมอร์ 100 มิลลิลิตร และโดสของรังสีแกมมา 40 kGy สามารถดูดจับยูเรเนียมได้มากที่สุด ในส่วนของเอมีดอกซิมพอลิเมอร์เจลที่พอลิเมอไรซ์ด้วยรังสียูวี พบว่าพอลิเมอร์เจลที่เตรียมจากสัดส่วนของมอนอเมอร์อะคริโลไนไตร์ลต่อเมทาคริลิคแอซิด ที่ 80:20, ปริมาณสารเชื่อมโยง 1 กรัมต่อปริมาตรมอนอเมอร์ 100 มิลลิลิตร และปริมาตรไฮโดรเจนเปอร์ออกไซด์ 60 มิลลิลิตรต่อปริมาตรมอนอเมอร์ 100 มิลลิลิตร เวลาในการฉายรังสีที่ 8 ชั่วโมง สามารถดูดจับยูเรเนียมได้สูงสุด การทดสอบการใช้ซ้ำ พบว่าเอมีดอกซิมพอลิเมอร์เจลที่เตรียมจากรังสีแกมมาประสิทธิภาพการดูดจับไม่ลดลง ส่วนเอมีดอกซิมพอลิเมอร์เจลที่เตรียมจากรังสียูวีประสิทธิภาพการดูดจับลดลง 50% หลังจากการการใช้ซ้ำทั้งหมด 8 ครั้ง ส่วนผลการทดสอบการดูดจับยูเรเนียมในน้ำทะเลตามสภาวะธรรมชาติ บริเวณศูนย์วิจัยและพัฒนาทรัพยากรทางทะเลและชายฝั่งทะเลอันดามัน จังหวัดภูเก็ต เป็นเวลา 8 สัปดาห์ พบว่า เอมีดอกซิมพอลิเมอร์เจลที่เตรียมจากรังสีแกมมาดูดจับยูเรเนียมได้ 0.05 mg/g ส่วนเอมีดอกซิมพอลิเมอร์เจลที่เตรียมจากรังสียูวีดูดจับยูเรเนียมได้ 0.035 mg/g

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Wijittra Wongjaikham : Synthesis of high efficiency amidoxime polymer adsorbents for uranium extraction from seawater by radiation-induced polymerization. Advisor: Assoc. Prof. Doonyapong Wongsawaeng, Ph.D.

This study synthesized amidoxime polymer gel for uranium extraction from seawater through a polymerization process with gamma ray or UV-C radiation. The synthesis started with a mixture of acrylonitrile (AN) and methacrylic acid (MAA) monomers together with methylene bisacrylamide as a crosslinker and hydrogen peroxide in the case of UV radiation. The mixture was irradiated with gamma ray at various doses or UV-C for various durations. The resulting polymer gel was ground into fine particles and immersed in a hydroxylamine hydrochloride solution for 90 minutes in order to convert the chemical functional group from the cyano group into the amidoxime group. Results of laboratory-scale uranium extraction showed that for the case of amidoxime polymer gel prepared by gamma radiation, the ratio of monomer AN:MAA of 80:20, the amount of the crosslinker of 0.8 g/100 mL monomer, and 40 kGy gamma ray dose exhibited the highest uranium adsorption capacity. For the amidoxime polymer gel polymerized by UV-C radiation, the ratio of monomer AN:MAA of 80:20, the amount of the crosslinker of 1 g/100 mL monomer, hydrogen peroxide of 60 mL/100 mL monomer, and irradiation time of 8 hours exhibited the highest uranium adsorption capacity. The usage repeatability test indicated that after 8 cycles of repeated use, the polymer gel prepared from gamma ray did not show a decrease in the adsorption efficiency while the polymer gel prepared from UV-C showed a decrease in the adsorption efficiency of 50%. The field test results in natural seawater in front of Phuket Marine Biological Center (PMBC), Phuket province, Thailand for 8 weeks revealed that the polymer gel prepared from gamma ray exhibited the uranium adsorption of 0.05 mg/g while the polymer gel prepared from UV-C exhibited the uranium adsorption of 0.035 mg/g.

Field of Study:	Nuclear Engineering	Student's Signature ....
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CHAPTER I

INTRODUCTION

1.1 Background and statement of the problem

Energy is important to the economy and the way people live. It is a part of several factors that keeps the world moving forward. Human beings have used energy from the past to the present. In the beginning, there was the invention of water turbines for bales used in agriculture. Later, a rotary water turbine was used to generate electric power. Later, wood was utilized as a source of energy. Humans began to use energy at a rapid rate in the industrial revolution in the 19th century and began to use coal as a fuel instead of wood. Wind turbines and water were also utilized. By the end of the 19th century, coal was being used to produce electricity. At present, the world energy consumption is increasing rapidly, especially in Asia, as shown in Figure 1.1.

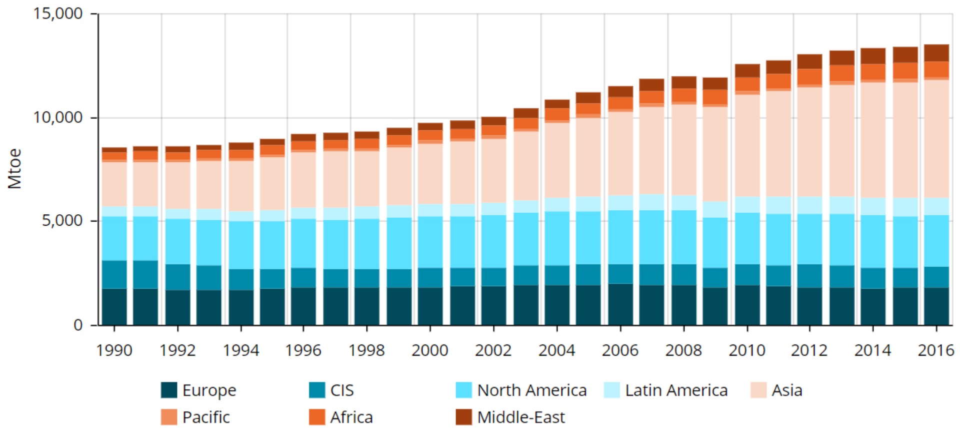

Figure 1.1 World Energy consumption [1]

Energy is divided into two major categories: consumable energy or spent energy and renewable energy. The sources of consumable energy, such as coal, natural gas, crude oil, and so on, are among the major sources of carbon dioxide emissions that cause global warming. The sources of renewable energy are such as solar, water, wind, nuclear, biomass, etc. These sources of energy are clean and environmentally friendly alternatives. Some of these renewable energies are also

Renewal Energy, which can be recycled. At present, the trend of renewable energy is increasing because it is environmentally friendly to produce electricity.

Another renewable energy is nuclear energy. This is a relatively environmentally friendly energy because it releases no carbon dioxide into the atmosphere. In 2017, there are 448 nuclear power reactors operating in 30 countries and there are 60 plants being constructed in 15 countries. The total net installed capacity is 391,744 MW_e [2]. The data of nuclear reactors in operation worldwide is shown in Figure 1.2.

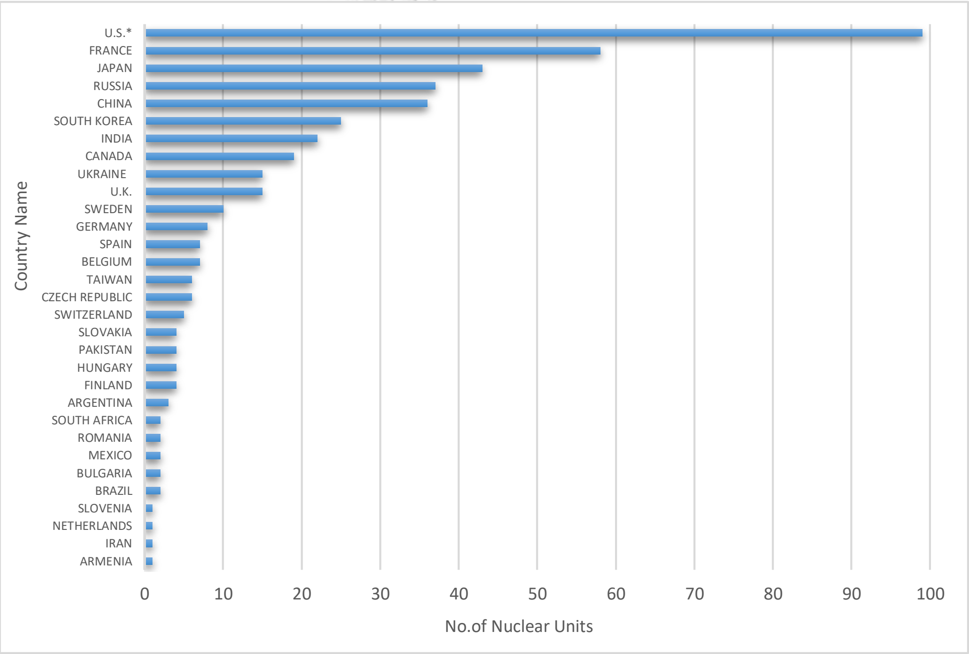

Figure 1.2 Number of nuclear reactors in operation worldwide

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Based on the data from 2016 shown in Figure 1.3, more than 13 nations utilizes nuclear power to generate at least 25% of their total electricity [3] and the largest proportion of nuclear power in the world is France, which is 72.3% . Even in Asia, such as South Korea, the proportion is 30%. This shows that nuclear power is still important to the electricity generation of these countries.

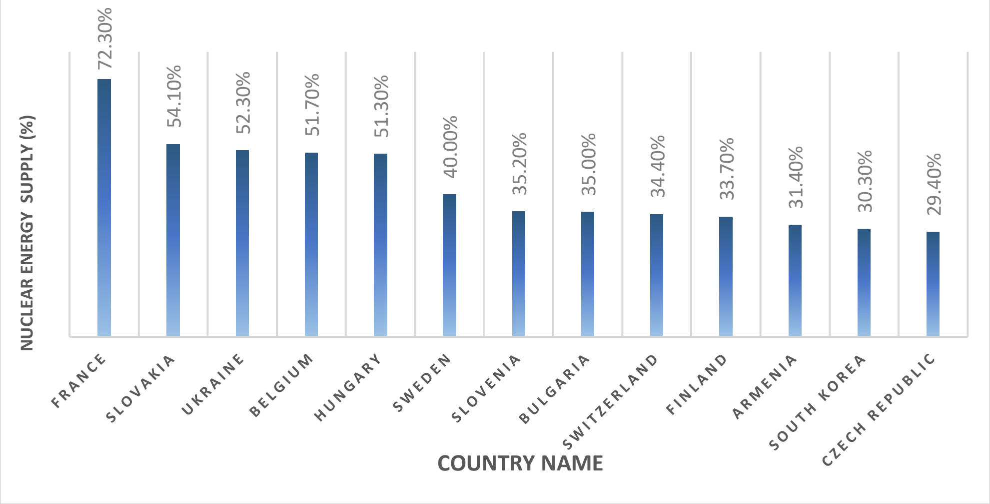

Figure 1.3 Countries relying on nuclear power for at least 25%

Usually, Uranium does not trade on an open market but buyers and sellers have to negotiate contracts privately. The uranium spot prices are published by independent market consultants which has shown in figure 1.4 for five years. It can be seen that the uranium spot price tends to decrease and the price of 24th June 2019 of 24.70 US$/lb.

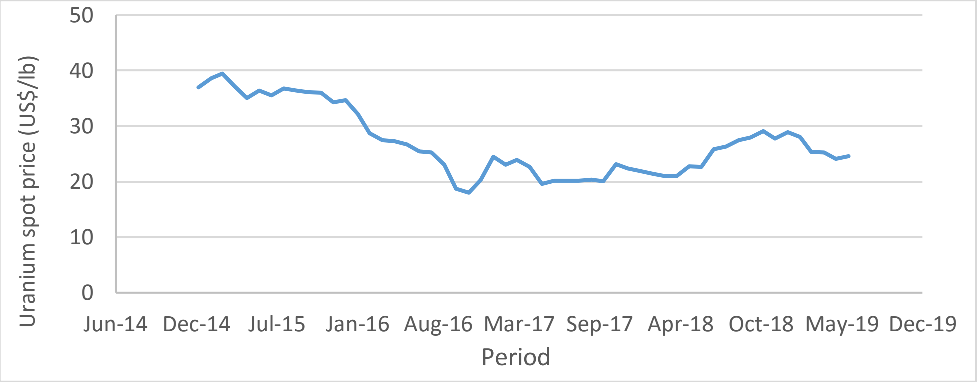

Figure 1.4 Uranium spot price [4]

Uranium is a heavy metal with the main use being a starting material for nuclear fuels. It occurs in earth's crust at the concentration of 2 - 4 ppm, totaling 5.5 million tons, and in the ocean at the concentration of 3 - 3.3 ppb. At the present consumption rate, the conventional uranium reserve will be limited. Thus, it is of interest to look for other sources such as the oceans. The entire amount of U in the oceans is estimated to be roughly 4.5 billion tons [5]. This vast quantity can be considered a sustainable source for uranium.

Seawater contains many elements with high concentrations such as Na, Cl, K, Ca, Mg, and so on. Uranium is present at a very low concentration and it's major form is uranyl tricabonate ion $[UO_2(CO_3)_3]^{4-}$ [6]. Therefore, the method to recover uranium from seawater must exhibit have high selectivity and high efficiency toward uranyl ions. Several methods have been studied for recovery of uranium from seawater, with ion exchange resins being the first to be developed. Even though the adsorption kinetic of resins is fast, uranium selectivity is very low. Solvent extraction has been utilized for specific metals; however, solvent could disappear because of entrainment or solubility [7]. The adsorption method is a famous one because of a number of choices available for adsorbents such as activated carbon, TiO_2, Galena, and polymers. Among these solid adsorbents, the amidoxime chelating functional group is most effective in terms of efficiency, cost, and operation [8, 9]. From the research of Saito et al. [10], AO-H (amidoxime-grafted) fibers were prepared by grafting acrylonitrile onto polyethylene hollow fibers and then converting the cyano functional group into the amidoxime functional group. The AO-H fibers exhibited the adsorption of 0.66 mg/g adsorbent after 25 days of testing in a continuous-flow batch. Similarly, Badawy et al. [11] performed radiation grafting of acrylonitrile/methacrylic acid onto cotton cloth followed by amidoximation for recovery of U from radioactive waste. The results showed that U adsorption reached 662 µg/g. Japanese researchers [12] performed column adsorption test of amidoximated fibrous adsorbents at ambient temperature. Seawater was filtered and was supplied at 3 L/min of flow rate. Results revealed that uranium uptake reached 300 mg U/kg adsorbent after 7 day. Amidoxime adsorbents can also be utilized to remove copper, a heavy metal, from aqueous solutions with the highest loading of amidoximated sepiolite nanohybrid material (AO-RGS) of 278 mg/g adsorbent in 30 minutes of soaking [13].

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However, previous studies focused on grafting the functional group onto substrates. The adsorbent mass includes the fiber mass and without the fiber mass, the evaluated uranium loading capacity in mg-U adsorbed/g adsorbent would be increased. Choi et al. [14] prepared amidoxime resins by radiation polymerization of acrylonitrile (AN) and acrylic acid (AA) monomer with subsequent amidoximation of cyano group of poly(AN). The amidoxime adsorbent was tested in the uranyl nitrate solution of 100 ppm at room temperature for 2 days. Results revealed that the uranium adsorption capacity for resins with the AO and AA groups was superior to those with only the AO group.

Study of Hara et al. [15] showed a hydrogel adsorbent synthesized from acrylamide and AN. The crosslinker was N,N’-Methylene bisacrylamide and the polymerization initiator was ammonium peroxodisalfate. The adsorbent was soaked in a test solution containing 4 ppb U and other elements for a period of 3 days. Results indicated that the prepared adsorbent was able to adsorb U in an very low concentration.

The purpose of this research is to synthesize the high-efficiency amidoxime polymer gel to extraction uranium from seawater. With the utilization of the crosslinking agent during radiation polymerization of monomers, a substrate will not be required. Gamma radiation and UV-C radiation will be employed as an energy source for polymerization. The adsorption capacity, the ability to be reused, as well as uranium recovery cost will be evaluated.

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1.2 Objective

To synthesize the high efficiency amidoxime polymer adsorbents for uranium extraction from seawater by using the radiation-induced polymerization technique.

1.3 Scope of study

1. Determine the optimized condition to synthesize the amidoxime polymer gel by studying the following parameters
    - Gamma irradiation dose from 0 – 40 kGy
    - UV-C irradiation time from 0 – 10 hours
    - Proportion of acrylonitrile monomer, methacrylic acid monomer, crosslink agent, and H_2O_2 (for the case of UV-C irradiation)

2. Test the optimized amidoxime polymer gel with seawater sample collected from Map Ta Phut, Rayong Province, Thailand.
3. Evaluate the repeated use capability of the optimized amidoxime polymer adsorbents.
4. Evaluate the uranium recovery cost of the optimized amidoxime polymer adsorbents.

1.4 Benefits

1. The synthesized polymer adsorbents should adsorb uranium in seawater with a higher adsorption capacity than those of the previous researches.
2. The study will provide knowledge for the development of better adsorbents in the future.
3. For environmental remediation, the optimized amidoxime polymer adsorbents may be used to adsorb uranium ions discharged into seawater following a nuclear accident.

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CHAPTER II
LITERATURE REVIEW

2.1 Uranium

2.1.1 Uranium in seawater

Most elements in seawater come from chemical weathering of minerals in the Earth's crust, while certain elements come from the atmosphere. Many elements dissolving in seawater are shown in Table 2.1; however, the 6 major ions are Cl^-, Na^+, SO_2^{4-}, Mg^{2+}, Ca^{2+}, and K^+. These ions constitute about 99% of all sea salts by weight.

Table 2.1 Ionic composition of natural seawater [7]

	Cation (ppm)		**Anion (ppm)**	
Major components	Na^+	10,500	Cl^-	19,000
	Mg^{2+}	1350	SO_4^{2-}	2650
	Ca^{2+}	400	HCO^{3-}	140
	K^+	380	Br^-	65
	Sr^{2+}	133	F^-	1.3
			H_3BO_3	260
	Li^+	0.17	I^-	0.06
	Rb^+	0.12	MnO_4^{2-}	0.01
	Cs^+	0.0005		
Minor components	Ba^{2+}	0.03	$VO_2(OH)_3^{2-}$ (as V)	0.002
	ZN^{2+}	0.01	PO_4^{3-}	0.07
	Fe^{3+}	0.01		
	Cu^{2+}	0.003		
	Mn^{2+}	0.002		
	In^{3+}	0.02		
	Ge^{4+}	0.00007		
	U^{6+}	as	$UO_2(CO_3)_3^{4-}$	0.00334

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The steady-state chemical reactions between seawater and uranium-containing rocks govern U in seawater in a way that when U is removed from seawater, the same amount is replaced by leaching from the rocks. Although the U concentration in the ocean is merely 3 mg/m^3, with 1.37 billion cubic kilometers of total ocean volume, this translates to be roughly 4.5 billion tons of U ions in the ocean.

Table 2.2 Concentrations of uranium compounds in natural seawater at 25 °C and at pH = 8.1 [6]

Compound	**Concentration (mol/l)**	**Weight fraction (wt% of U)**
UO22+	1.53x10-17	1x10-7
UO2(OH)2	1.53x10-12	1x10-2
[UO2(CO3)2]2-	5.46x10-11	0.39
[UO2(OH)3]-	2.43x10-10	1.75
[UO2(CO3)3]4-	1.37x10-8	98.82

As shown in Table 2.2, the dominant species of uranium compounds dissolved in natural seawater is uranyl tricarbonate complex which is present at 98.82% and its molecular structure is shown in Figure 2.1.

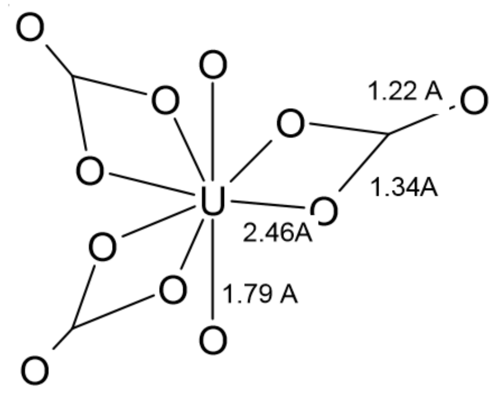

Figure 2.1 Structure of uranyl tricarbonate complex [7]

2.1.2 Method of uranium extraction

For over five decades, uranium extraction from seawater has been investigated and there have been several methods to accomplish including ion exchange, solvent extraction, foam separation, and adsorption.

2.1.2.1 Ion exchange

The ion exchange process is a reversible exchange between a solid phase and a solution phase [16], which is the processes of purification, separation, and decontamination of aqueous solutions with solid polymeric materials named " ion exchangers." Ordinary ion exchangers are ion-exchange resins, e.g., zeolites, montmorillonite, and clay. These resins cannot be used to extract uranium from seawater because of poor selectivity, but results of Harwell Research Laboratory in England show that complex resins such as resorcinol arsenic acid formaldehyde copolymer exhibited high U loading of about 1,010 μg/ g-dry for 112 days [17]. However, the problem with rapid deterioration with aging of these materials prevents them from being used in practical applications.

2.1.2.2 Solvent extraction

Solvent extraction (liquid-liquid extraction) is used to separate compounds between two immiscible liquids based on their relative solubility. Solvent extraction technique has been used widely in metals extraction because of its simplicity, speed, and wide scope [18]. Many researches reviewed that solvent with chemical functional group such as phosphonic acid, resorcinol arsenic acid, or 8-hydroxyquinoline complex in chloroform or diethyl ether [19-21] could be used to extract uranium from seawater. Especially, 8-hydroxyquinoline can be used not only in uranium research but also in extraction of copper, lead oxinates, and molypdenum [20]. However, the key problem of utilizing solvent extraction on a large scale with metals in seawater is the required large quantity of chemical reagents, volatile solvent requirement, and solvent mass loss due to entrainment and solubility [7].

2.1.2.3 Foam separation

Foam separation is a technique of surface-active components in a solution to preferentially concentrate at the solution/gas interface that can be used in collecting metal ions. For example, lauryl amine and alkylbenzyl ammonium chloride can be used to separate uranium from seawater but the recovery yield is very low. Another method is to use collector-surfactant-air system at pH 6.7. From this technique, uranium is effectively absorbed on the positively charged ferric hydroxide collector, yielding the recovery of uranium from seawater of about 82% [22]. However, the practical application of this method is unlikely at this stage due to the difficulty in recovery of the surface-active agents.

2.1.2.4 Adsorption

Many adsorbents have been investigated for extraction of U recovery from the ocean. Since the concentration of uranium in seawater is extremely low, selection of the properties of the adsorbent is very important. Examples of adsorbents studied are as follows:

- Titanium dioxide

Hydrous titanium dioxide has been studied most often to be adsorbents for uranium in seawater. There are several types of preparation processes of hydrous titanium oxide including i) neutralization method: solution is neutralized by alkali, ii) urea method: adding urea to solution and iii) thermal decomposition method: solution is heated and hydrolyzed [7, 23]. The best adsorption capacity was obtained with the urea method, which reached 1660 μg U/g Ti. Nonetheless, the major compound in seawater, $CaCO_3$, can deposit onto hydrous titanium oxide causing depressed uranium uptake.

- Galena

Galena or PbS is reported to be a good adsorbent. Koyanaka [24] researched on collection of uranium from seawater by galena and the result showed that at a very high concentration of uranium in artificial seawater (100 ppm), the cumulative amount of uranium collected on the galena was about 3.8 mg/g of galena with the recovery of 96%. Moreover, galena is not affected by corrosion from seawater; the adsorption ability remains high for uranium in natural seawater. Unfortunately, later research found that it was hard to keep the surface of galena fresh without any oxide layers which degrade the adsorption capacity.

- Activated Carbon

Activated carbon is a very effective U adsorbing agent from seawater, but the adsorption rate depends on the source of carbon material. The pyrolysis and the activation methods [25] have been used to prepare activated carbon. The advantages of the porous carbon materials are the very large internal surface area, large pore volume, and tunable pore size [26]. Moreover, porous carbon will not dissolve in concentrated eluents during the elution process [27].

- Polymers

1) Hydroxamic acid chelating polymers

Hydroxamic acids have been found to be effective chelating ligands with the ions (e.g., V^{5+}, Fe^{3+}, Mo^{6+}, UO_2^{2+})[28]. Research of Hirotsu et. al [29] found that dihydroxamic acid polymer has the U loading capacity of 40 μg-U/g after 8 days of soaking in seawater. Moreover, the polymer exhibited the selective adsorptivity for Fe, Ni, Cu, and Zn.

2) Methacryloylamidoglutamic acid polymers

Poly(2-hydroxyethyl methacrylate–methacryloylamidoglutamic acid) [p(HEMA–MAGA)] beads were developed to study uranium extraction. The result has shown that the adsorption of uranium was about 20,000 mg/g polymer for U concentration of 100 ppm and that the equilibrium was

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reached at 100 minutes with 98% recovery, but this research did not perform studies in real seawater condition [30].

3) Amidoxime polymers

There are many researches on polymers with the amidoxime chelating functional group to extract U from seawater. The popular polymer grafted with the amidoxime group was low-density polyethylene (LDPE) fibers prepared by radiation-induced graft copolymerization of acrylonitrile and methacrylic acid onto LDPE fibers. The cyano group was then converted into the required amidoxime group by 3 (w/v)% hydroxylamine hydrochloride solution ($NH_2OH{\cdot}HCl$) (water:methanol = 1:1) at 80 °C for 15 – 120 min. The fibers were subsequently washed with a methanol/water solution and soaked in 1 M hydrochloric acid solution. The fibers were washed with DI water for several times and was allowed to dry in a forced convection oven at 50 °C for 24 hours [6]. The preparation steps of the amidoxime fibers are shown in Figure 2.2.

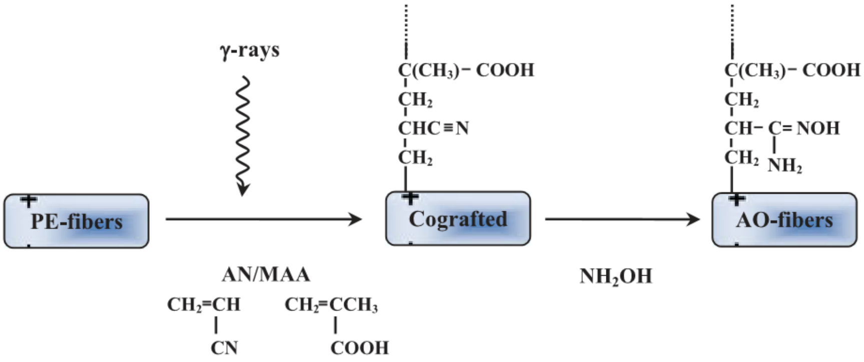


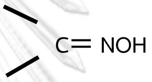
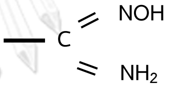
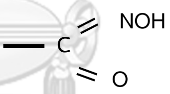
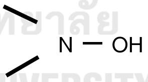
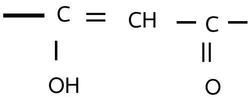
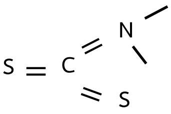
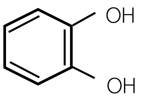
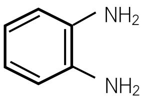
Figure 2.2 Amidoxime fiber preparation [6]

The last step was to perform a KOH treatment of the fibers in 2.5 (w/v) % KOH solution for 1 hour at 80 °C. The batch adsorption experiments for 4 weeks in shallow seawater resulted in U loading of 2.06 g-U/ kg-adsorbent. The advantages of LDPE fibers include no insolubility in seawater, almost no solubility in eluents, as well as high stability against degradation.

2.1.3 Chemical functional group of adsorbents

Functional groups of the adsorbents must form a stable chelate complex with uranyl ion in natural seawater by substitution between carbonate and functional group. Uranium-binding functional groups are chosen in accordance with their ability to displace the carbonate ions in $[UO_2(CO_3)_3]^{4-}$ at the pH of natural seawater. The functional groups are summarized in Table 2.3 [6].

Table 2.3 Functional groups which can displace the carbonate ions in uranyl ion

Functional group	**Structure**
Oximes	
Amidoximes	
Hydroxamic Acids	
Hydroxylamines	
1,3 diketones	
Dithiocarbaminates	
o-Dihydroxyaromatics	
o-Diaminoaromatics	

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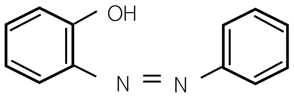
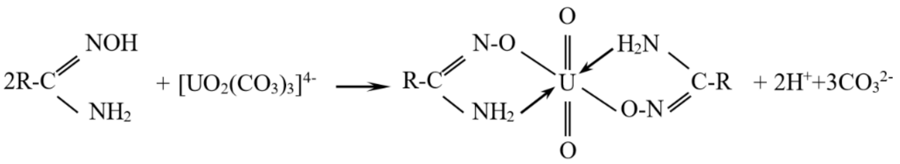
Functional group	Structure
o-Hydroxyazoaromatics	

The amidoxime functional group ($-C(NH_2)=N\text{-}OH$) is among best chemical functional groups to exhibit strong bonding with U ions, together with the high selectivity in aqueous solution [7, 9, 12, 31, 32]. The uranium adsorption mechanism by the amidoxime functional group is shown in Eq. (1).



(1)

2.1.4 Elution

Uranium in seawater collected through adsorbents is extracted by the elution process. There are two types of elution: elution by alkali and elution by acid. Many researches use alkali solution to elute the metal from sorbents such as sodium carbonate, sodium carbonate-hydrogen peroxide, sodium bicarbonate, and ammonium carbonate [17, 33]. However, alkali elution has been shown to achieve the uranium elution efficiency of about 70 - 90%.

Uranium extraction from conventional mines is typically achieved with sulfuric acid to leach uranium from the ore; therefore, the elution with an acid was adopted for uranium extraction from seawater too. Several acidic eluting agents used in the elution process are listed in Table 2.4.

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Table 2.4 Acidic eluting agents [12]

Eluting agent	**% Elution**	**C.N.**	**S.C.**
Tartaric acid	100	6	9.73
Oxalic acid	100	6	9.10
Malic acid	100	6	5.50
Maleic acid	90	6	5.15
Phthalic acid	80	6	4.38
Sulfuric acid	100	6	3.14
Acetic acid	80	6	2.70
Formic acid	70	6	2.61
Nitric acid	100	6	0.72
Hydrochloric acid	100	6	0.05

C.N. = coordination number and S.C. = stability constant.

Commonly, hydrochloric acid solution of 1.0 molar is used as an eluent to recover uranium from adsorbents based on the amidoxime functional group. Elution with acid is not specific with any metals, thus, several other metals including uranium are eluted. A major serious issue about the acid elution process is the destruction of adsorbent surface during the elution [17]. Another problem is for the repeated use because the adsorbents require an alkaline treatment step (KOH 2.5% at 80 ^{o}C) before immersing in seawater again.

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2.2 Polymer

Polymers are very large molecules comprising of thousands to millions of atoms bonded together in a repeating pattern. Their structures can be understood by using a chain as a representative, as the chain has many connected links and the atoms within the polymer are bonded to each other to form polymer chain links.

The repeat units are the molecular links in the chain formed from one or more monomer molecules. The raw materials used to produce the polymer strongly influence the structure of the repeat unit. For instance, polyethylene, which is used to make plastic bags as well as containers, consists of a very simple repeating unit of 2 carbon atoms bonded together to establish a single link [38].

2.2.1 Characteristics of polymer

Every polymer has very distinct characteristics, but most polymers have general characteristics as follows:

1) **Polymers are resistant to chemicals.** Chemical compatibility, chemical resistance, and corrosion resistance are among the greatest advantages of plastics in comparison to metals. Therefore, polymers such as plastics and rubbers are preferred in situations with physical contact with chemicals, gases, detergents, or oils.
2) **Polymers can be thermal and electrical insulators.** Polymers usually have very low thermal conductivities and suitable fillers can be added to increase the conductivity to the desired levels. The applications include household appliances, electrical cords, and electrical outlets. Thermal resistance is useful in the kitchen, as handles of pots and pans are made from polymers.
3) **Polymers are very light in weight.** Generally, plastics are organic compounds composing of carbon and hydrogen atoms. Although molecular structures are large, they exhibit low density.
4) **Polymers can be processed in several ways.** Injection molding and extrusion can produce precise parts, huge automotive body panels, thin fibers, heavy pipes, or films. Solvents can be mixed with plastics to become adhesives or paints. Elastomers and some plastics stretch are highly flexible.

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2.2.2 Origin of polymer

Polymers can be separated into two types: i) Natural polymers that occur in nature and can be extracted. They are often water-based such as starch, wool, silk, cellulose, DNA, and protein. ii) Synthetic polymers that are derived from petroleum oil and made by scientists and engineers. Examples of synthetic polymers include synthetic rubber, phenol formaldehyde resin, neoprene, nylon, PVC, polystyrene, polyethylene, and more.

2.2.3 Molecular Structure of polymer

Polymer properties depend on the weight and shape of molecule as well as the structure of the polymer chains. Molecular structure consists of linear, branched, cross-link, and network.

2.2.3.1 Linear polymer

Monomers are joined end-to-end like links along a chain. These long chains are flexible and have a virtual image of spaghetti lines. The linear polymer may be expanded by Van der Waals forces acting on hydrogen bonding as a link between the chains. These polymers are polyethylene, polystyrene, PVC, and nylon.

2.2.3.2 Branched polymer

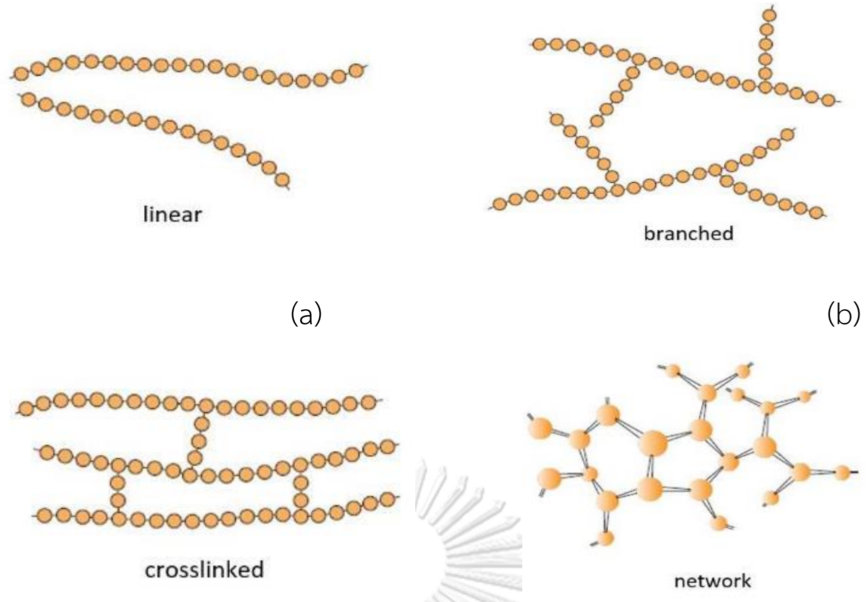
Branching takes place when a substituent, a hydrogen atom for example, on a monomer subunit is replaced by another covalently-bonded chain of that polymer. This polymer has a low density because branches will reduce the compression performance. Examples of branched polymers include low density polyethylene (LDPE).

2.2.3.3 Crosslinked polymer

Crosslinking represents a covalent or an ionic bond linking between two polymer chains. Polymer chains can be synthetic polymers (such as rubber tire) or natural polymers (such as proteins).

2.2.3.4 Network polymer

A polymer composing of trifunctional mer units that form three-dimensional molecules through permanent covalent bonds confers unique properties to network polymers. This can enhance mechanical and thermal properties. For example, the modulus and elasticity can be increased. The creep rates can be lower. The resistance to solvent can become higher and the high temperature stability can be enhanced.



(a) (b)

(c) (d)

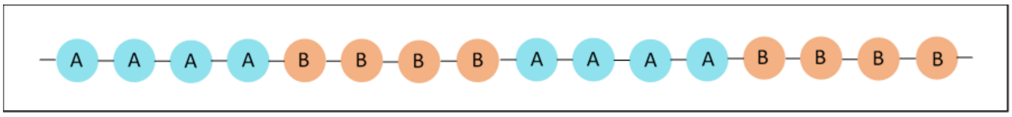
Figure 2.3 Polymer molecular structure: (a) linear, (b) branched, (c) crosslinked, and (d) network [34]

2.2.4 Homopolymer and Copolymer

A homopolymer is formed by a single type of monomer, so it consists of only one type of repeating unit. Homopolymers are generally synthesized from addition polymerization. Polypropylene, polyethylene, polystyrene, polytetrafluoroethylene, and poly (methyl methacrylate) are examples of homopolymers. A part of copolymer is formed by two and/or more monomers. Usually, most copolymers are formed through condensation polymerization. Examples of copolymers are polyvinyl acetate, polyethylene oxide, and polyethylene terephthalate [35].

Copolymers can be classified into 4 types: block copolymers, alternating copolymers, statistical copolymers, and graft copolymers.

- Block copolymers: A long sequence or block of one monomer is joined to a block of the second monomer



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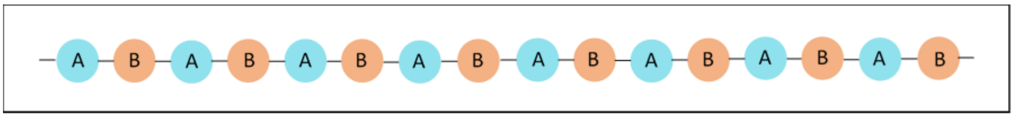
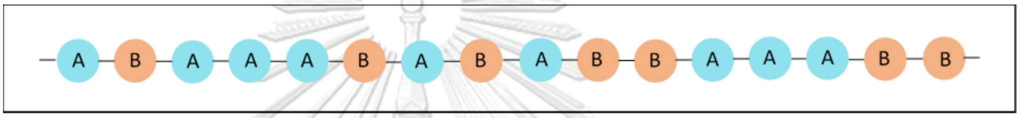
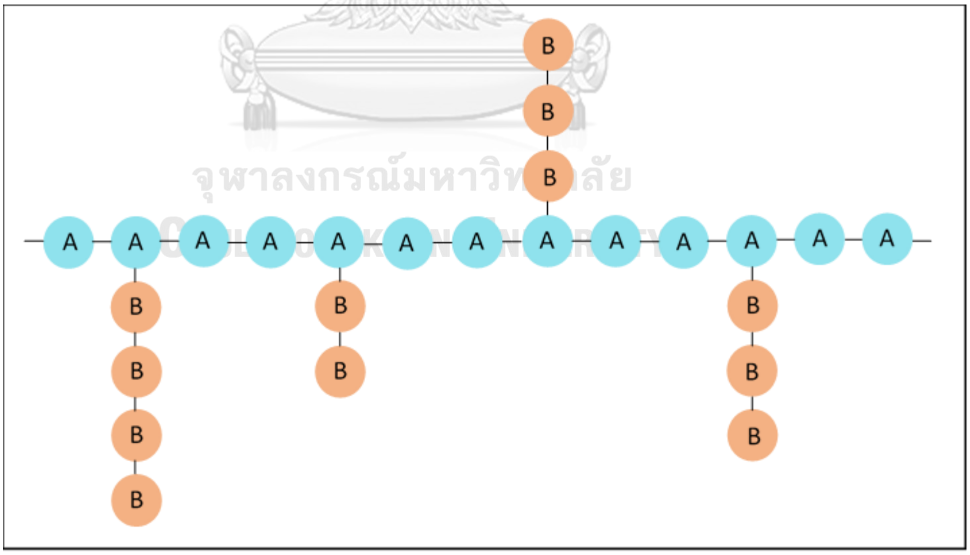
- Alternating copolymers: Consists of only two types of repeat units, with alternating arrangement along the polymer chain



- Statistical copolymers or random copolymers: The sequence of repeating units obeys known statistical laws. Random copolymers are an example of statistical copolymers that have a random distribution of repeat units



- Graft copolymers: A special type of branched copolymer when the side chains are structurally different from the main chain.



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2.2.5 Polymerization reaction

Polymerization is a process when monomers chemically combine to result in a very large chain and/or network molecule. Monomers can be the same or different compounds. It typically takes a minimum of 100 monomer molecules to combine to result in a product with unique physical properties. As most monomers are hydrocarbon compounds, the bond between hydrogen and carbon is a covalent bond, which have both single bond and double bond.

Polymerization is divided into two classes, which are condensation polymerization and addition polymerization.

Condensation polymerization or stepwise polymerization. Two small molecules react with each other at reactive site, forming larger structural units and releasing smaller molecules as a by-product, which most likely is water.

Addition polymerization or chain polymerization. This process is caused by unsaturated monomers reacting with each other and becoming a long chain. During the reaction, the unit that is sensitive to the reaction or double bond in the monomer will break to be a single bond and react with the existing monomer until the formation of polymer. This process has no by-product or something out of the reaction.

In this dissertation, addition polymerization will be considered and the reaction with catalyst is a three-step process as follows: Initiation, propagation, and termination.

Initiation: The reaction is started by using a catalyst or an initiator to break the monomer bond. The monomer is broken into 2 identical parts with an unpaired electron, which is a free radical, on each molecule. The unpaired electron then initiates a sequence of the reaction by establishing a bond to one of the C atoms in the double bond of the monomer. The reaction is shown in Equation 2.

$$\text{Initiator} + CH_2 = CH_2 \xrightarrow{In^*} In - CH_2 - CH_2^* \qquad (2)$$

Propagation: The activated monomer attacks and attaches to the double bond of another monomer. This addition continues, resulting in the long polymer chain as illustrated by Equation 3.

$$In - CH_2 - CH_2^* + CH_2 = CH_2 \longrightarrow In - CH_2 - CH_2 - CH_2 - CH_2^* \qquad (3)$$

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Termination: The last stage of polymerization occurs when two free radicals meet and their unpaired electrons pair to form a covalent bond linking the chains together as shown in Equation 4.

$$\begin{gathered}\mathrm{In-CH_2\{CH_2-CH_2\}CH_2^{*}} \;+\; \mathrm{{}^{*}CH_2\{CH_2-CH_2\}CH_2-In} \\ \downarrow \\ \mathrm{In-CH_2\{CH_2-CH_2\}CH_2-CH_2\{CH_2-CH_2\}CH_2-In}\end{gathered} \tag{4}$$

2.3 The G-value of polymer

The G-value is the measurement of radiation chemical yield which polymer molecules are formed per 100 eV of absorbed energy. There are two numbers, G(x) and G(s), which are indicated those polymers become crosslinking or degradation. The G(x) is the number of networks formed per 100 eV of absorbed energy, while G(s) is the number of chain scissions formed per 100 eV of absorbed energy.

The general method to measure G(x) and G(s) is via solubility test. The gel fraction is the weight ratio of the dried network polymer to that of the polymer before washing by solvent, while the dissolved part in solvent is defined as a soluble fraction. When ratio of G(s) to G(x) more than 1.0, polymer tends to be degradation, and when ratio of G(s) to G(x) less than 1.0, polymer is likely to be crosslinking.

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2.4 Radiation Characteristics

2.4.1 Linear energy transfer

Radiation interaction with a medium results in energy loss through interaction with the atoms. Linear energy transfer (LET) refers to the average amount of energy lost per unit path length travelled. LET depends on the nature of radiation and type of material traversed. The standard unit is keV/µm and is defined in Equation 6 as follows:

$$LET = dE/\ dx \tag{5}$$

where dE represents the average energy locally deposited to the medium by a charged particle of specified energy when travelling a distance dx.

Particles with mass and charge (alpha and beta particles, for example) exhibit high LET values. Low-energy neutrons also exhibit a high LET. Electromagnetic radiation such as x-rays and gamma rays also exhibit low LET because they have no mass or charge. These low-LET radiation can penetrate tissues easier than high-LET radiation and deposits energy very infrequently. However, high-LET radiation can result in more tissue damage per unit of exposure than radiation with low LET.

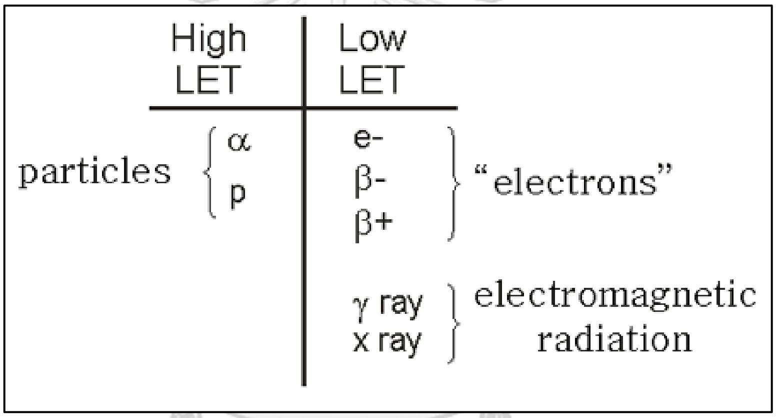

Figure 2.4 LET of different types of radiation

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2.4.2 Interaction of gamma ray

Gamma rays have the highest energy and the smallest wavelengths in the electromagnetic spectrum. Gamma rays are emitted from radioactive nuclei and from explosion of nuclear weapon. Gamma rays interact with matter and deposit energy through photoelectric effect, Compton scattering, and pair production.

2.4.2.1 Photoelectric effect

The photoelectric effect occurs by the incident low-energy gamma ray interacting with an entire atom. The gamma ray vanishes and an electron of the atom is ejected. The atom also recoils but carries little kinetic energy (K.E.) equal to the incoming photon energy ($h\nu$) less the binding energy (E_b) of the electron in its particular orbit. The interaction is most pronounced with a bound electron of high-Z materials and for low-energy photons (< 0.5 MeV) [39].

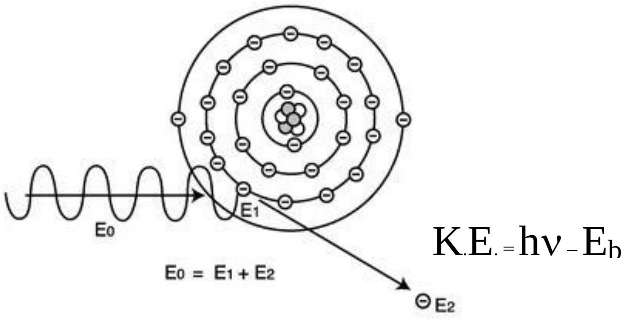

Figure 2.5 Schematic of the photoelectric effect [36]

If gamma ray achieves in ejecting a bound electron, the hole is filled by one of the outer electrons and a characteristic x-ray, usually from filling the k shell, will be released.

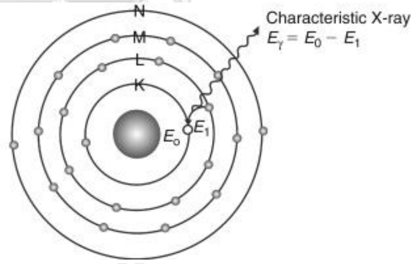

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Figure 2.6 Schematic of characteristic x-ray [37]

2.4.2.2 Compton scattering

Compton scattering refers to the inelastic scattering of a photon with an electron. In this process, conservation of energy and momentum is obeyed. As shown in Figure 2.7, the incident photon with energy (E) and wavelength (λ_1) is scattered through the angle (θ) and the struck electron recoils. Because the recoiling electron carries with it some kinetic energy, the scattered photon energy (E') is lower than E and the wavelength of the scattered photon (λ_2) is longer than λ_1.

Following the conservation of energy and momentum, the following relation can be obtained:

$$E^{'} = \frac{E}{1 + (E/m_0\, c^2)(1 - cos\theta)} \tag{6}$$

where $m_o c^2$ = 0.511 MeV is rest-mass energy of the electron.

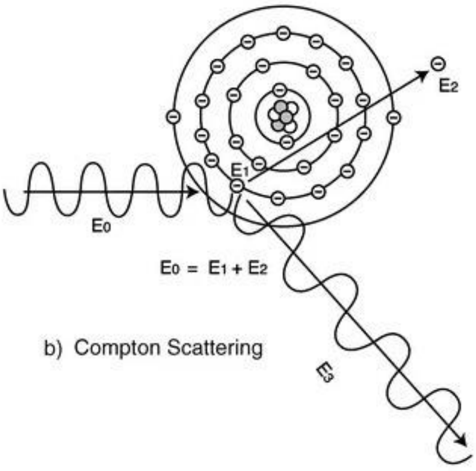

Figure 2.7 Schematic of Compton scattering [36]

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2.4.2.3 Pair production

In this process, the photon interacts with a strong electromagnetic field around a nucleus, disappears and then becomes a positron and a negatron pair. Because a positron and a negatron each has a rest mass energy of $2m_0c^2$ = 1.022 MeV, pair production cannot occur if the photon carries energy less than 1.022 MeV. The positron will interact with a nearby electron forming short-lived positronium which then vanishes resulting in two annihilation photons of 0.511 MeV each. These new 0.511 MeV photons may or may not interact with the medium.

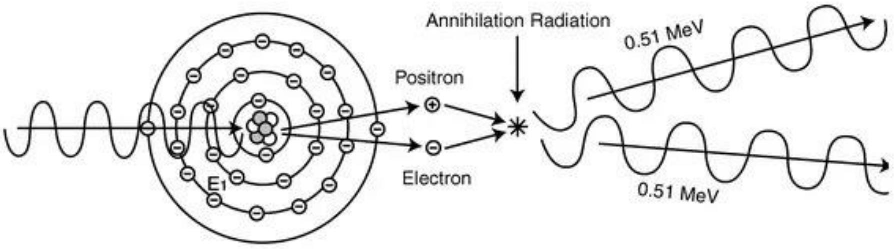

Figure 2.8 Schematic of Pair production [36]

2.4.3 Ultraviolet

Ultraviolet (UV) is an electromagnetic radiation with a wavelength of 10 - 400 nm as shown in Figure 2.9, which is shorter than that of visible light but longer than X-rays. About 10% of the total light output from the sun is ultraviolet radiation. Most of the ultraviolet radiation in sunlight is absorbed by oxygen in the Earth’ s atmosphere. Moreover, it can also be generated by electric arcs and specialized lights, for example, mercury-vapor lamps, tanning lamps, and black lights. UV radiation with long wavelength can affect chemical reactions and can cause many substances to fluoresce. Thus, the chemical and biological effects are beyond just the heating effects, and several UV applications rely on the interactions with organic molecules. High-energy UV photons can cause ionization and break chemical bonds. This behavior is beneficial for chemical processing, but it can also negatively impact materials and living tissues. UV can also disinfect surfaces, but it can also be harmful to skins and eyes, which are most affected by higher-energy UVB and UVC radiation [38]. UV radiation can be categorized into 3 sub-bands:

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- UVA, or near UV (315 - 400 nm)
- UVB, or middle UV (280 - 315 nm)
- UVC, or far UV (180 - 280 nm)

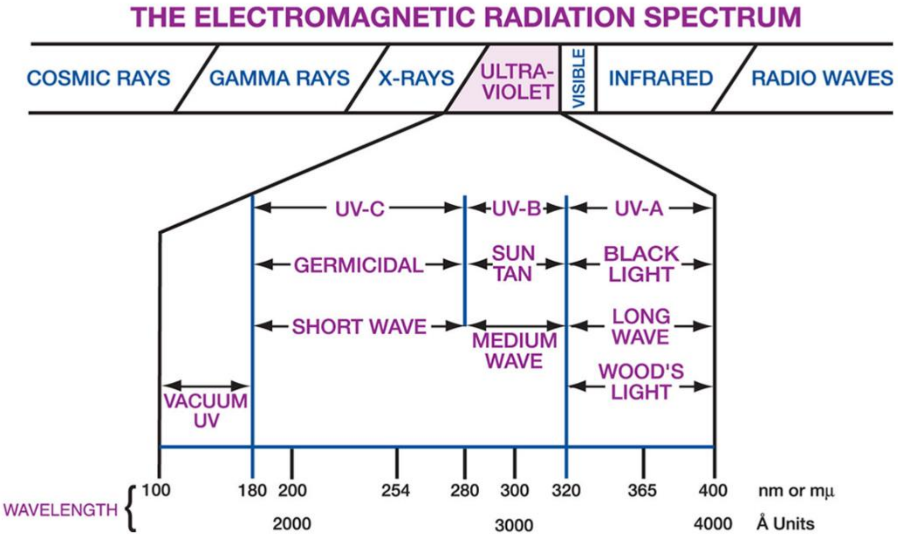

Figure 2.9 Electromagnetic spectrum [39]

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2.5 ICP-OES technique

Inductively Coupled Plasma-Optical Emission Spectrometry or ICP-OES is a technique which can analyze the elements composed in samples by plasma (ICP) and a spectrometer. The source of plasma ions with high temperatures in the range of 7,000 to 10,000 K makes the atoms of various elements change the state from the ground state to the excited state or ionized state. When the atoms of the element decay to a lower state through thermal or radiative energy transitions, the energy emitted will be electromagnetic radiation during various spectra. Each stimulated element releases a spectrum that has a specific wavelength of each element that is measured with a spectrometer. The light intensity of the specific wavelength is measured and calculated into a concentration.

2.6 Researches related to uranium adsorption

Examples of researches related to uranium adsorption from aqueous solution based on grafting the amidoxime functional group onto substrates are shown in Table 2.5.

Table 2.5 Examples of researches on uranium adsorption from aqueous solution

Author	**Objective**	**Experiment**	**Result**
Seko et al. [11]	To optimize the composition of cografting for uranium recovery from seawater.	Fibrous adsorbents were prepared by co-grafting of AN and MAA. Adsorbents containing amidoxime group were experimented in column test at temperature 298 K and flow rate of filtered seawater of 3 l/min.	Total uranium adsorption in five cyclic tests were 292 mg U/kg dry adsorbent. The AN/MAA ratio of 70/30 exhibited the highest performance.
Zhang, Asakura and Uchiyama [8]	To adsorb and recover uranium (VI) from seawater by microporous fibrous material containing amidoxime group.	The adsorption experiment of microporous fibrous material was performed in the pH range of 1.0-8.5 and in the various concentrations of U(VI) from $2x10^{-4}$ to $1x10^{-3}$ M with contact time up to 60 min.	The adsorption ability of microporous fibrous material for U(VI) increased from pH 2.0-6.0 and decreased from pH 6.0-9.0. The highest adsorption was at pH of about 6.0.

Table 2.5 Examples of researches on uranium adsorption from aqueous solution (cont.)

Author	**Objective**	**Experiment**	**Result**
Choi et al. [13]	To recover uranium ions from seawater by resins with amidoxime (AO) and amidoxime/carboxylic acid (CA)	The resin adsorbents (1.0 g) was experimented in a uranyl nitrate solution of 100 ppm for a fixed time.	After 48 hr at room temperature, the uranium uptake for resins with AO and AO/CA group were 914 mg/g and 924 mg/g, respectively.The equilibrium adsorption was achieved at 24 hr.
Vernon and Shah [35]	To perform the uranium-sorbing of poly(amidoxime)/poly(hydroxamic acid) microbead resin and fibre by continuous seawater extraction process.	Batch sorption of uranium was performed in a 10 mM uranium solution in 0.5 M NaCl at pH =7.8. The best candidate was collected to test in seawater.	Resins showed higher U adsorption capacities than fibre (0.9 and 0.6 mmol/g dry, respectively). For seawater test, resin (as a sandwich structure) was immersed over a period of up to 4 mounts and achieved a uranium loading of 72 μg/g resin.
Saito et al. [9]	To propose a novel fixed bed adsorbent charged with hollow fibers and perform the adsorption with a low flow resistance.	The hollow fibers grafted with amidoxime group were experimented in a continuous flow. 2 L of the seawater flowed through the column at temperature 298 K for 25 days.	Uranium adsorption of 0.66 mg/g of AO-H fiber was achieved.

Table 2.5 Examples of researches on uranium adsorption from aqueous solution (cont.)

Author	**Objective**	**Experiment**	**Result**
Yu et al. [4]	To investigate the uranium recovery from the palygorskite/amidoxime polyacrylonitrite composite as a function of pH, contact time and initial feed concentration.	All experiments were conducted by mixing 100 mL of aqueous U(VI) solutions with 0.05 g of composite, shaking at 100 rpm, 30 °C, pH range of 2-8 and the initial uranium concentration of 10-60 ppm.	The maximum adsorption capacity was found to be 78.13 mg/g at pH ~5. The adsorption was quick for the first 30 minutes and the initial uranium concentration of 60 ppm showed the highest adsorption capacity.
Das et al. [7]	To enhance the efficiency of uranium adsorption from natural seawater by the cyclic imide dioxime loaded poly(acrylamidoxime) adsorbent.	The adsorbents were experimented for uranium adsorption efficiency with 5 gallons of simulated seawater spiked with 8 ppm uranium in a batch reactor. The pH of the solution was 7.8 and all experiments were performed at room temperature.	The adsorbent showed uranium uptake at 4.48 g-U/kg-ads. after 56 days.

Table 2.5 Examples of researches on uranium adsorption from aqueous solution (cont.)

Author	**Objective**	**Experiment**	**Result**
Badawy et al. [10]	To recover the uranium from radioactive waste obtained from nuclear fuel fabrication laboratories by cloth fiber with amidoxime/carboxyl groups.	The cloth filter with an area of 25 cm^2 was immersed in the alkaline ammonium fluoride solution (residual soluble uranium concentration of 26.6 ppm), pH 9-9.5 and was stirred.	The results indicated that the equilibrium time of about 1 hr was required for 95% adsorption. The adsorption capacity of 662 μg/g filter was obtained.
Ratnitsai, Wongsawaeng and Chankow [5]	To enhance uranium extraction from seawater by chromic acid-treated amidoxime adsorbents.	The chromic acid-treated amidoxime fibers of about 20 g were submersed in shallow seawater at Phuket Marine Biological Center (PMBC) in Phuket, Thailand with the depth of 3-6 m. The average temperature of seawater was 29-30 ^{o}C and the submerging time was 1, 2, 3, 4, 6 and 8 weeks.	The amidoxime adsorbents exhibited the adsorption capacity of 2.15 g-U/kg-ad for 8 weeks.

CHAPTER III

METHODOLOGY

3.1 Materials and equipment

3.1.1 Acrylonitrile (AN)

3.1.2 Methacrylic acid (MAA)

3.1.3 Dimethyl sulfoxide (DMSO)

3.1.4 N,N'–Methylenebisacrylamide (MBA)

3.1.5 Hydrogen peroxide (H_2O_2)

3.1.6 N,N –dimethylformamide (DMF)

3.1.7 Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$)

3.1.8 Methanol (CH_3OH)

3.1.9 Potassium hydroxide (KOH)

3.1.10 Hydrochloric acid (HCl)

3.1.11 Nitric acid (HNO_3)

3.1.12 Deionized water (DI water)

3.1.13 Seawater sample

3.1.14 Tricarbonate uranylate solution

3.1.15 Plastic container

3.1.16 Gamma radiator at TINT, Thailand

3.1.17 UV-C lamp (Total output 60 W, intensity = 547.2 mW/cm^2)

3.1.18 Scanning electron microscope (SEM)

3.1.19 Fourier Transform Infrared Spectrometer (FTIR)

3.1.20 Inductively Couples Plasma Atomic Emission Spectrometer (ICP-AES)

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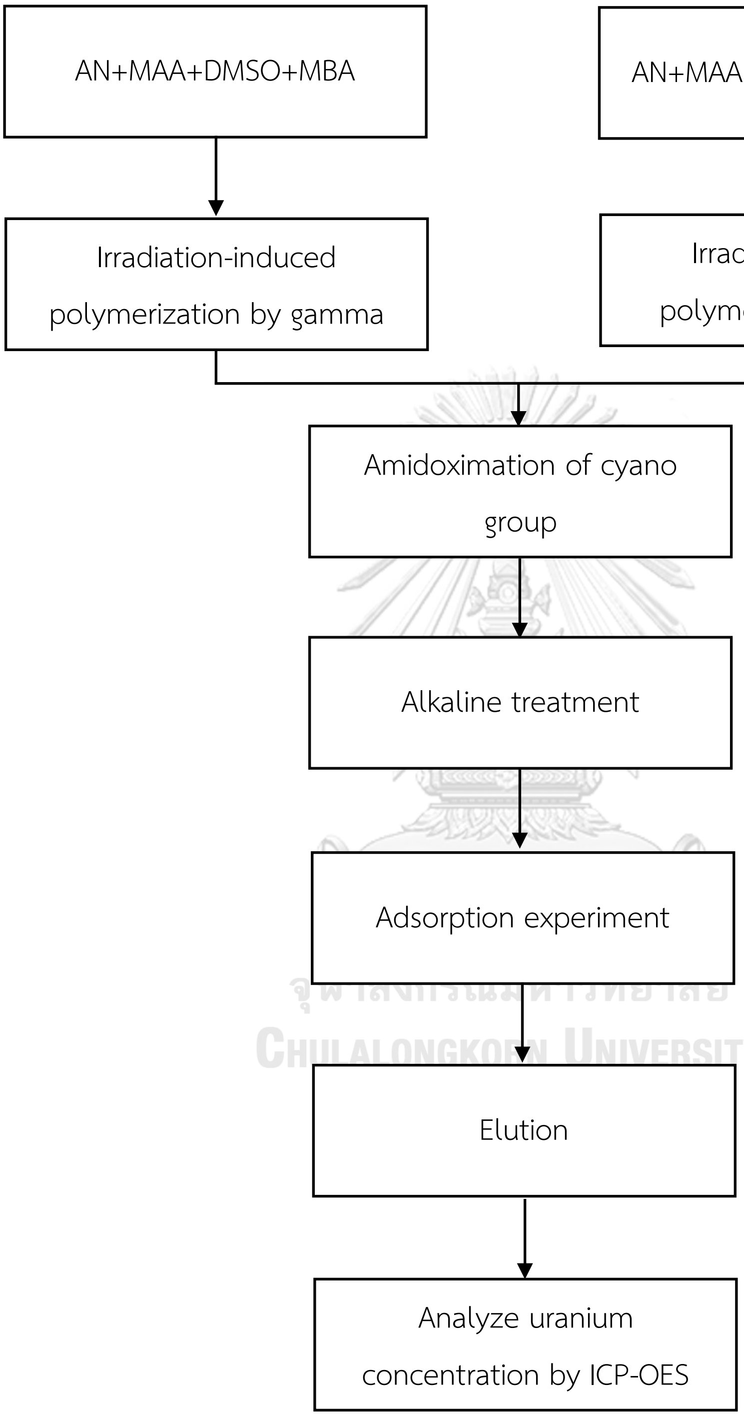
3.2 Methodology flow chart



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3.3 Synthesis

3.3.1 Irradiation-induced polymerization by gamma ray

AN and MAA monomers were mixed in a beaker with the mixing ratio of 40:60, 60:40, and 80:20 by volume. These mixtures were diluted using 50 (w/w)% DMSO as a solvent. For each mixing ratio above, the crosslinking agent was added at the following concentrations: 0.2, 0.4, 0.6, and 0.8 g/100 ml monomer. Then, they were irradiated with gamma radiation from Co-60 at different absorbed doses of 20, 30, and 40 kGy as summarized in Table 3.1. The monomer mixture was put into container as shown in figure 3.1 for radiation. After the irradiation, the formed polymer gel was turned into small particles by mechanical means. The particles were submerged in DMF overnight to remove unreacted monomers and the formed homopolymer. The prepared adsorbent was placed in a forced-convection oven for 24 hours at 50 ^{o}C.

Table 3.1 Condition for synthesis of polymer by gamma radiation

Parameter	Value
AN : MAA ratio	40:60
	60:40
	80:20
Concentration of crosslinking agent (g/100 ml monomer)	0.2
	0.4
	0.6
	0.8
Absorbed dose (kGy)	20
	30
	40

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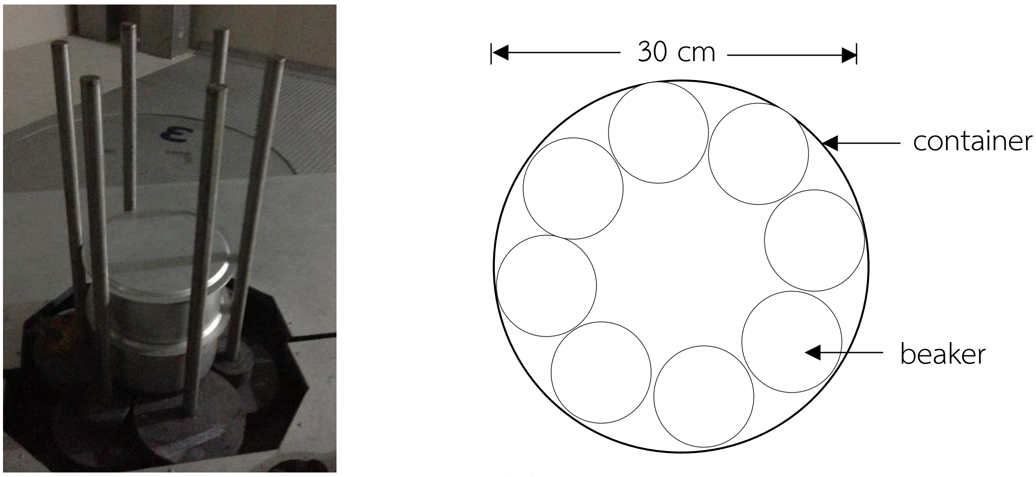

(a) (b)

Figure 3.1 Container and radiator (a) and geometry of beaker in the container (b)

3.3.2 Irradiation-induced polymerization by ultraviolet (UV-C)

The mixture solutions of AN and MAA monomers with a mixing ratio of 90:10, 80:20, 70:30, and 60:40 by volume with 50 (w/w)% DMSO as a solvent were prepared. With each volume ratio, the following concentrations of the crosslinking agent was added: 0.25, 0.5, 1, and 2 g/100 ml monomer. For each condition, hydrogen peroxide was added at 50, 60, 70, and 80 ml/100 ml monomer as summarized in Table 3.2. These solutions were irradiated with UV-C lamps for 4, 6, 8, and 10 hours with the temperature during irradiation of 45 or 80 °C as shown in figure 3.2. After completion of UV-C irradiation, the processes were identical to the experiment with gamma radiation.

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Figure 3.2 UV-C chamber

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Table 3.2 Condition for synthesis of polymer by ultraviolet radiation

Parameter	Value
AN : MAA ratio	60:40
	70:30
	80:20
	90:10
Concentration of crosslinking agent (g/100 ml monomer)	0.25
	0.50
	1.0
	2.0
Concentration of H_2O_2 (mL/100 ml monomer)	50
	60
	70
	80
Duration of irradiation (h)	4
	6
	8

Parameter	Value
	10
Irradiation temperature (°C)	45
	80

3.3.3 Amidoximation of cyano group

Polymer particles synthesized by gamma ray or ultraviolet were immersed in a hydroxylamine hydrochloride solution (prepared by dissolving 54 g of $NH_2OH \cdot HCl$ in DI water-methanol solution (1:1 by volume) and adjusted to pH = 7 by KOH solution) at 73 °C with stirring. After 90 minutes, the polymer particles were rinsed for several times with DI water-methanol solution and placed in a forced-convection oven for 24 hours at 50 °C. The characteristic peaks of the cyano group ($C\equiv N$) and the amidoxime group were examined by Fourier-transform infrared spectroscopy (FTIR).

3.3.4 Alkaline treatment

After the amidoximation process, the amidoxime polymer adsorbent was submerged in 1 M HCl solution for a duration of 15 minutes and was alkaline treated with 2.5% (w/v) KOH solution at 80 °C for 60 minutes. The polymer particles were repeatedly rinsed with DI water until the rinsed water pH became 9 and were placed in a forced-convection oven at 50 °C for 48 hours. Finally, about 0.15 - 0.2 g of the adsorbent particles were placed inside a filter cloth and a fabric mesh for submersion in seawater. Figure 3.1 depicts the most probable reactions occurring during the synthesis of the adsorbent using UV-C radiation. [40]

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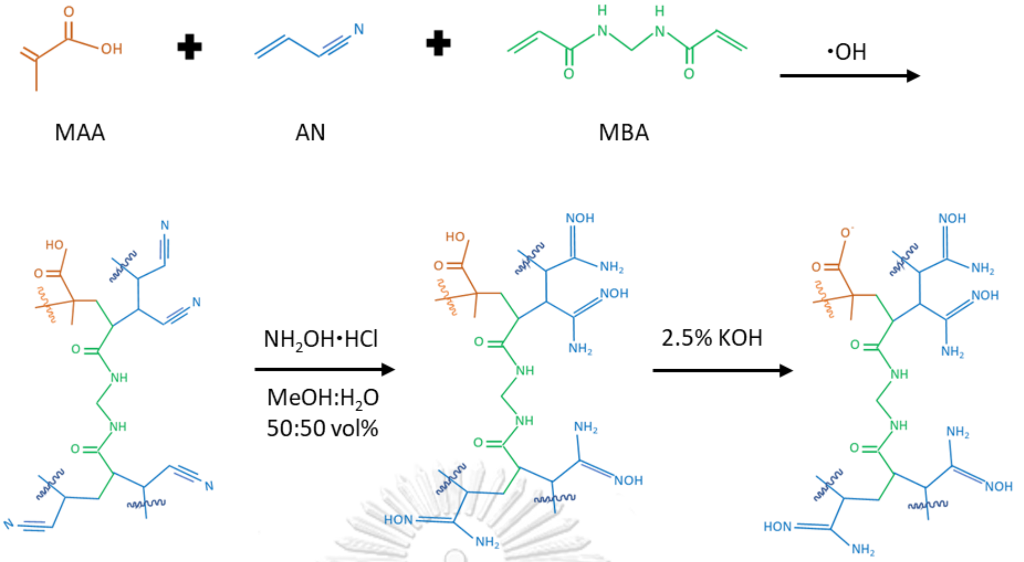

Figure 3.3 Most probable reactions during synthesis of the amidoxime polymer gel.

3.4 Adsorption Experiment

Sets of the amidoxime particle adsorbent were immersed in seawater sample in a 100-l plastic container with a small fish tank submersible water pump placed at the bottom to provide circulation. The sample of seawater was obtained at the sea of Mab Ta Phut port, Rayong Province, Thailand. Synthesized $[UO_2(CO_3)_3]^{4+}$ was injected to the seawater sample to raise the U concentration to about 10 ppm. The duration of adsorption experiment was 1 week. The 100-l container was located in the laboratory at room temperature.

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3.5 Uranium elution

After being removed from the 100-l container, the adsorbent was submerged in DI water for a period of 2 days. This procedure was performed to remove uranium ions present in the seawater sample on the particle surfaces. The adsorbent was immersed in 1 M HCl solution for 1, 2, or 4 hours at 50 $^{\circ}$C. The adsorbent was taken out of the solution, which was slowly boiled until a solid residue of yellowish color appeared at the bottom. The solid residue was dissolved by 1% nitric acid solution and the U concentration in the solution was analyzed by ICP-OES.

3.6 Water absorbency

About 0.2 - 0.3 g of the gel adsorbent was submerged in DI water or seawater sample to evaluate the kinetic of water absorption. After every 5 or 10 minutes, the amidoxime particles were taken out of the DI water or the seawater sample to measure the weight increase. Tissue papers were used to absorb excess water on the particle surfaces. The swelling ratio can be calculated according to Eq. (7):

$$\text{Swelling ratio (g/g)} = \frac{m_2 - m_1}{m_1} \quad , \tag{7}$$

where m_1 and m_2 are the weight of the dry and swollen adsorbent, respectively.

3.7 Reusability performance

Figure 3.2 indicates the process of the experiment on adsorption repeatability. To evaluate the usage repeatability of the amidoxime polymer adsorbents, the adsorbents were submerged in seawater sample collected from surface water at Map Ta Phut, Rayong Province, Thailand and was added with $[UO_2(CO_3)_3]^{4+}$ to increase the uranium concentration to 500 ppb. For every cycle (72 hours), the adsorbents were taken out of the seawater and underwent the elution step. After that, the adsorbents were treated with 2.5% (w/v) KOH solution at 80 °C for 60 minutes and continuously washed with DI water until the pH of the drain water equal to 9 before submersion in seawater again.

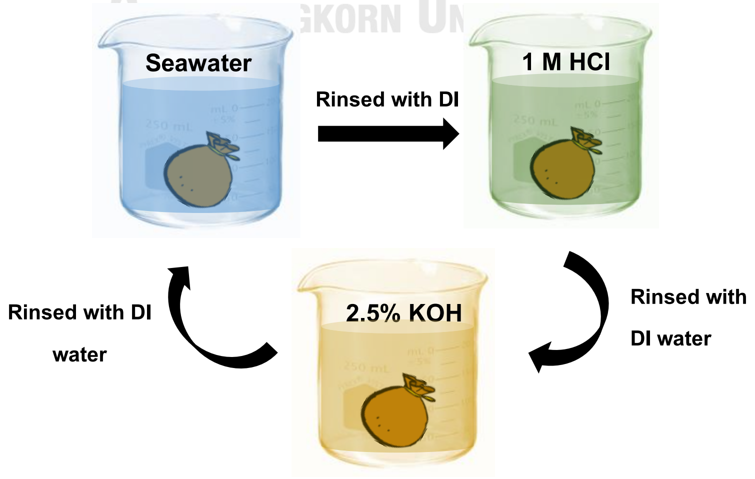

Figure 3.4 Process of experiment on adsorption repeatability

3.8 Field experiment

To test an actual performance of the adsorbent based on natural seawater conditions with a uranium concentration of only 3 - 3.3 ppb, including wind currents, ocean currents, and other suspended particles or other competitive ions which are important factors that can affect the amount of adsorbed uranium, the adsorbent was immersed in an open ocean in front of Phuket Marine Biological Center (PMBC), Thailand at the depth of 1 meter for 2, 4, 6, and 8 weeks.

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CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Results of polymer gel prepared from gamma ray radiation

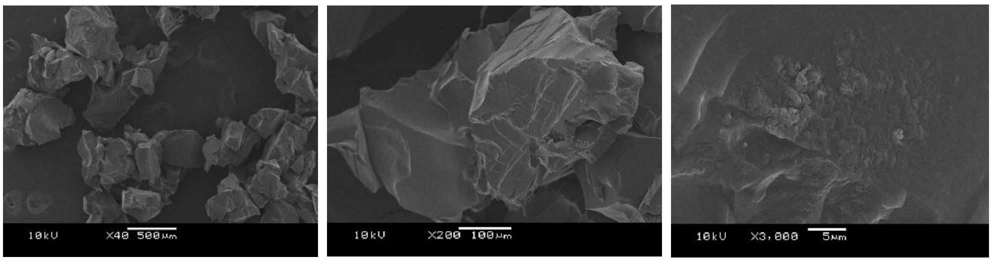
4.1.1 Optical and SEM analysis

The optical and SEM analysis of dried adsorbent prepared under different conditions are shown in Figure 4.1

(a) (b) (c)

Figure 4.1 Physical appearance of dried polymer gels. Synthesis conditions: 40 kGy, crosslinker 0.8 g/100 mL, AN:MAA = (a) 40:60, (b) 60:40, and (c) 80:20

The color change of adsorbent from white to dark yellow occurs due to an increasing AN portion. Impurities in the AN resulted in the dark yellow color. Figures 4.2(a) – 4.2(c) illustrate the SEM micrographs of the adsorbent particles under various magnifications.



(a) (b) (c)

Figure 4.2 SEM micrographs of amidoxime particle gel. Synthesis conditions: 40 kGy, crosslinker 0.8 g/100 mL, AN:MAA 80:20

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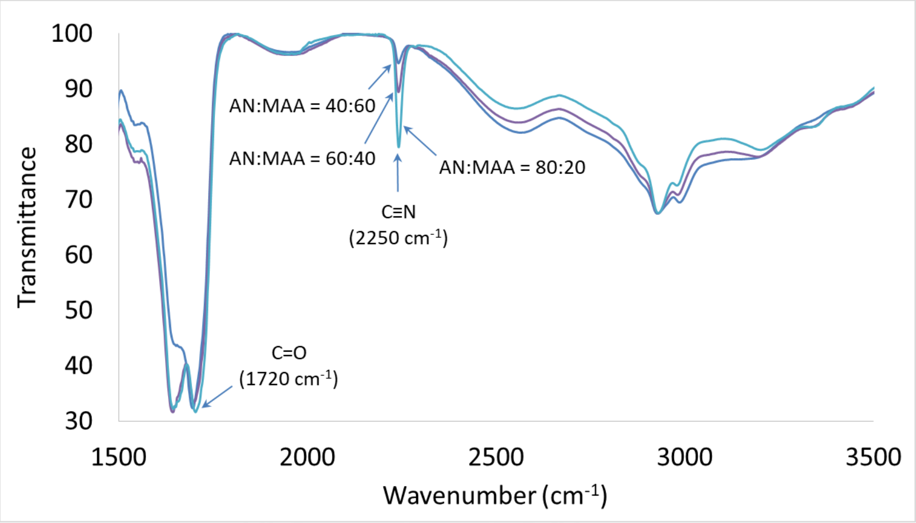
The average size of the particles is around < 500 μm. Particles also have rough surfaces, which is desirable because it help increase the surface area in contact with seawater.

4.1.2 FTIR analysis

Figures 4.3(a) - 4.3(b) illustrate characteristic peaks of chemical functional group of polymer particles prior to and after the amidoximation process with different monomer ratios (preparation conditions: gamma ray dose of 40 kGy, crosslinker 0.8 g/100 mL, AN:MAA 80:20, 60:40, and 40:60).



(a)

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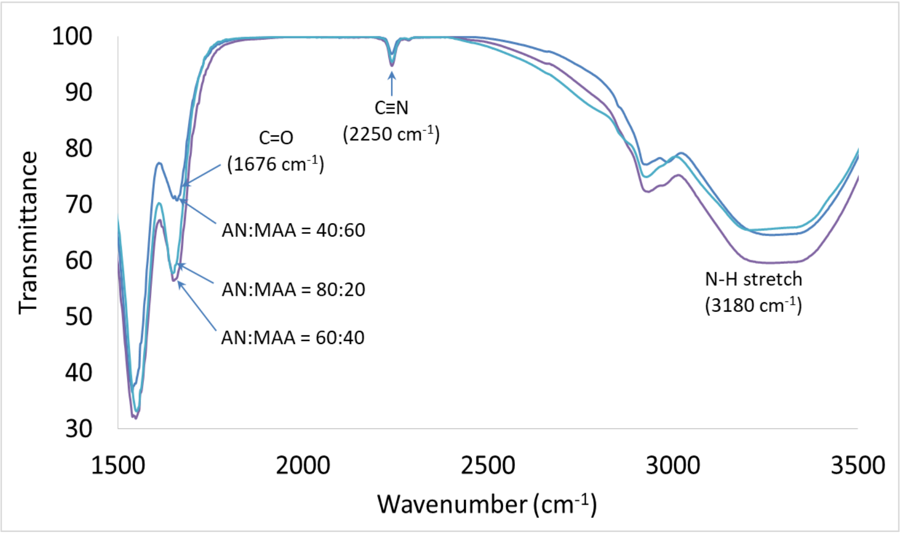

(b)

Figure 4.3 FTIR spectra of polymer gel (a) prior to and (b) after amidoximation.

For the polymer gel before amidoximation (Figure 4.3 (a)), bands at 2250 cm^{-1} from $C\equiv N$ of poly(acrylonitrile) and at 1720 cm^{-1} from $C=O$ of poly(methacrylic acid) [6] indicates the cyano group and the carbonyl group, respectively. After the conversion procedure, the $C\equiv N$ peak vanished almost entirely and the characteristic bands of the amidoxime group ($C=O$ band at 1676 cm^{-1} and N-H stretch band at 3180 cm^{-1} [6]), became visible as shown in Figure 4(b). These results showed that almost all of the cyano group was converted into the amidoxime functional group.

Moreover, the spectra in Figure 4.3(a) provides information that the higher the ratio of AN:MAA, the higher the absorption peak of the $C\equiv N$ group at 2250 cm^{-1} and vice versa for case of $C=O$ band at 1676 cm^{-1} in Figure 4.3(b). The $C=O$ band was highest for AN:MAA = 60:40 because MMA provided the carbonyl group in poly(methacrylic acid).

4.1.3 Effects of gamma ray dose, ratio of AN:MAA, and concentration of crosslinker on loading capacity of adsorbent

The gamma ray dose of 40 kGy was selected to evaluate the effects of AN:MAA ratio and crosslinker concentration on the uranium loading capacity of the polymer gel. The experimented AN:MAA ratio was 40:60, 60:40, and 80:20 with the crosslinker concentration of 0.2, 0.4, 0.6, and 0.8 g/100 mL monomer. The experiment was carried out in seawater sample spiked with 300 ppb U. The immersion duration was 1, 2, and 4 weeks. Figure 4.4 depicts the results of the adsorption.

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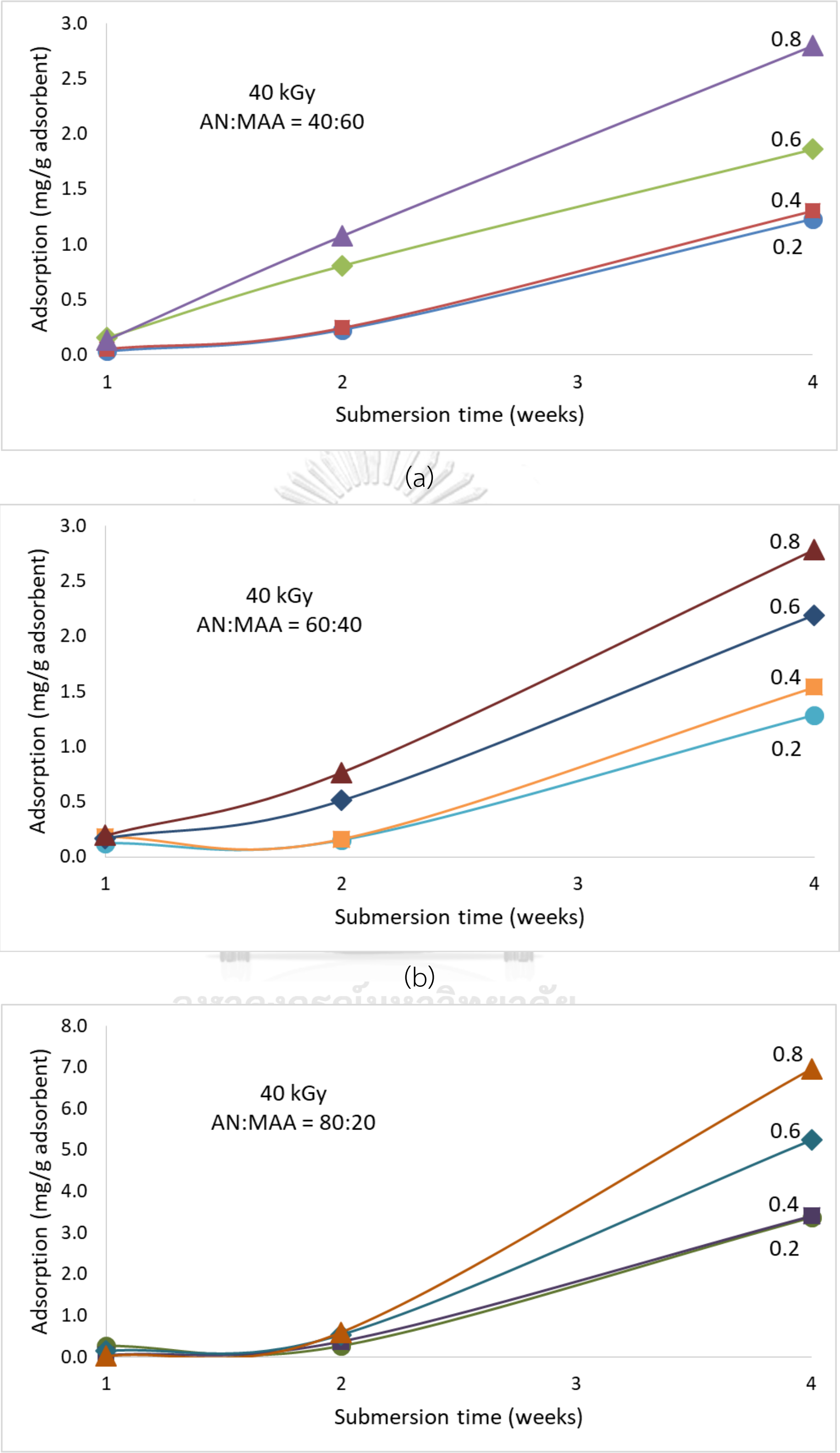

(a)

(b)

(c)

Figure 4.4 Results of U uptake in seawater sample with added 300 ppb U. AN:MAA = (a) 40:60, (b) 60:40, and (c) 80:20

For every AN:MAA ratio, after 1 week of submersion, the adsorption capacities were hardly distinguishable from one another because the adsorptions were very low. However, at 4 weeks of submersion, more U was adsorbed with higher crosslink agent concentration. Also, the higher ratio of AN:MAA resulted in more U loading capacity and the difference in the adsorption became distinctive. The AN:MAA ratio of 80:20 and the crosslinker concentration of 0.8 g/100 mL resulted in the highest U loading capacity of 6.96 mg/g for 4 weeks of soaking. These represent the best set of parameters for further studies.

To evaluate the effect of gamma dose on the adsorption capacity, the dose of 10 - 40 kGy was studied. The sets of adsorbents were prepared using AN:MAA of 80:20 and the concentration of crosslinker of 0.6 and 0.8 g/100 mL. The soaking duration was 4 weeks in seawater sample injected with 840 ppb U at room temperature.

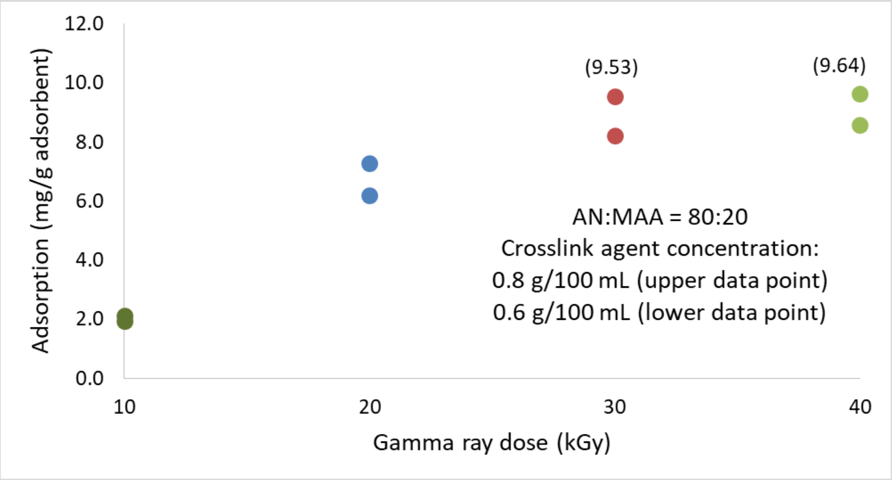

Figure 4.5 Effect of gamma ray dose on U uptake

The results shown in Figure 4.5 indicate that the crosslink agent concentration of 0.8 g/100 mL is better than 0.6 g/100 mL for all gamma ray doses. Also, higher gamma ray dose resulted in increased adsorption capacity. The crosslinker concentration of 0.8 g/100 mL with 40 kGy gamma ray dose exhibits the highest adsorption capacity of 9.64 mg/g-adsorbent for the scope of this research.

As the uranium uptake appears to increase with increasing crosslink agent concentration, the effect of crosslinker concentration on U uptake was determined. The adsorbents prepared using 40 kGy gamma ray, AN:MAA = 80:20, and the crosslinker concentration between 0.6 to 4 g/100 mL were evaluated. The results are demonstrated in Figure 4.6.

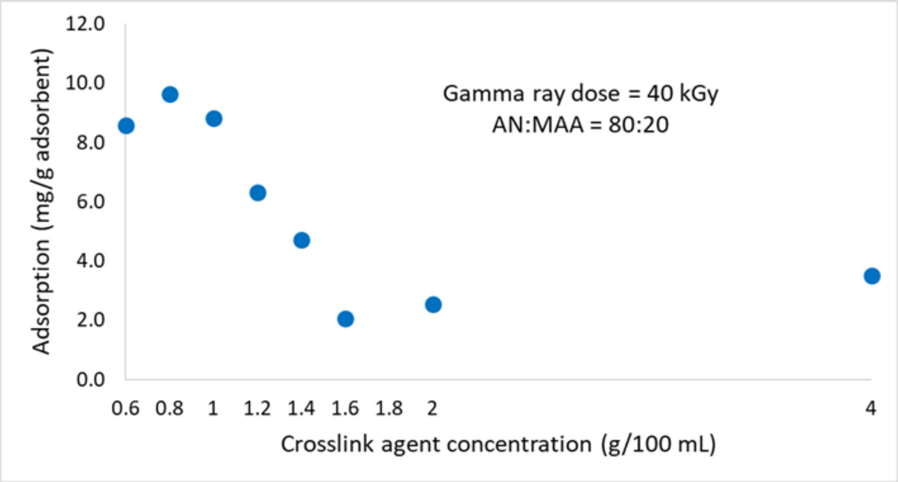

Figure 4.6 Effect of crosslink agent concentration on uranium adsorption

Following Figure 4.6, if the crosslink agent concentration is increased beyond 0.8 g/100 mL, the adsorption capacity decreases significantly. Even with the concentration of 4 g/100 mL, the adsorption capacity is still low. Therefore, the optimum concentration of crosslink agent is 0.8 g/100 mL.

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In conclusion within the scope of this study, from all the results, the amidoxime polymer gel prepared from AN:MAA of 80:20, crosslinker concentration of 0.8 g/100 mL, and the gamma ray dose of 40 kGy presents the best adsorbent for U recovery from seawater to obtain high uranium loading capacity.

All experiments were performed in the seawater sample with 300 or 840 ppb of added U. In addition, to test the uranium loading capacity in high concentration of uranium in seawater (level of ppm), the amidoxime adsorbent was soaked in seawater sample with added 30 or 2,140 ppm U at room temperature for a week. The results are shown in Table 4.1, which also includes other studies utilizing different types of adsorbents. It can be observed that the adsorption capacity of the amidoxime polymer particles in the seawater sample spiked with 2,140 ppm U is comparable to that of ref. [41]. For the 30 ppm U concentration case, the uranium loading is superior to other studies (ref. [32] and [42]) with approximately 20 – 40 ppm of added uranium.

Table 4.1 Comparison of the present results with other studies

Ref.	Uranium concentration in solution (ppm)	Reported adsorption (mg/g)
Present*	2,140	409
[41]	2,000	442.3
[5]	170	200.5
[43]	150	145
[44]	99.25	44.0
[42]	70	312.06
[32]	50	78.13
Present*	30	334
[45]	9.54	0.38
Present*	0.84	9.64
Present*	0.30	6.96

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* Condition of polymer gel preparation: AN:MAA = 80:20, crosslinker concentration = 0.8 g/100 mL, gamma ray dose = 40 kGy.

4.1.4 Kinetic of water absorption

Figure 4.7 illustrates the results of the water absorption kinetic study.

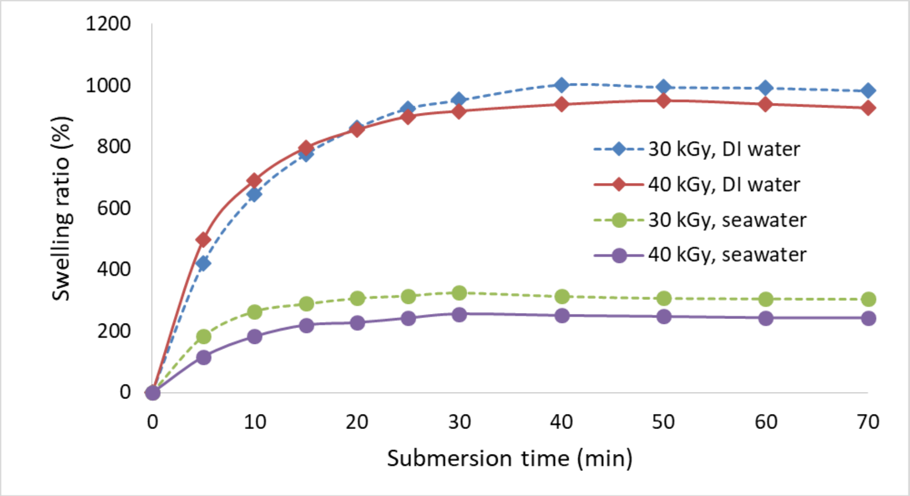

Figure 4.7 Result of water absorption kinetic study

Figure 4.7 indicates that the absorption of the polymer gel was quite rapid for DI water and seawater. With DI water, the absorption equilibrium was attained after 40 minutes, and after 30 minutes for the case of seawater. Also, to compare the effect of gamma ray dose, the highest swelling ratio for the 30 kGy case was slightly higher than the 40 kGy case.

In general, the swelling ratio of this adsorbents in seawater is less than in DI water, this data can be explained based on osmotic pressure. When the adsorbent was immersed in seawater, the osmotic pressure is very low because the external solution contains many ions. The ions presenting in the outer solution results decreasing of osmotic swelling pressure operation due to the difference of counter ions in the gel phase and solution phase. When increasing of concentration of ions in the swelling medium, the difference between the concentration of counter ions in the gel phase and solution phase decreases, consequently, resulting a decrease in swelling ratio of adsorbent [46].

Even though the maximum water retention capacity of the polymer gel was not high compared to other hydrogels or superabsorbent materials (about 50,000%) [47], the main purpose of this polymer gel is to adsorb uranium in seawater and the retention ability is just one of the factors that promote the performance of the polymer gel. This experiment also indicates the presence of the carbonyl group (COO-) which assists water diffusion into the interior of the polymer gel.

4.1.5 Elution time

4.1.5.1 Effect of elution time on uranium extraction

The effect of elution time on uranium extraction from the adsorbent is illustrated in Figure 4.8.

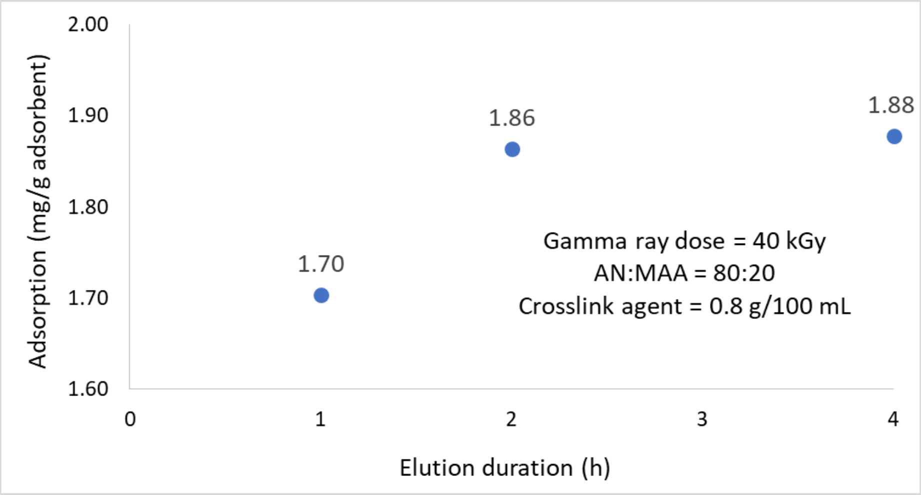

Figure 4.8 Effect of elution time on uranium extraction from adsorbent

Removal of uranium from the polymer gel requires sufficient elution time to obtain high quantity of uranium. Figure 4.8 suggested that the elution process must be longer than 1 hour to extract uranium effectively. At 2 hours of elution time, the eluted uranium was 1.86 mg/g and at 4 hours, the amount was 1.88 mg/g, a mere 1% increase. Therefore, the optimized elution time is 2 hours.

4.1.5.2 Effect of parameters affecting adsorbent mass loss during elution

As many papers have reported that hydrochloric acid solution, the eluting agent, is a major cause of adsorbent mass loss and physical damage, this study was performed to evaluate factors which may be the cause of polymer gel mass loss. The studied factors are the elution duration and dose of gamma ray. The result is presented in Figure 4.9.

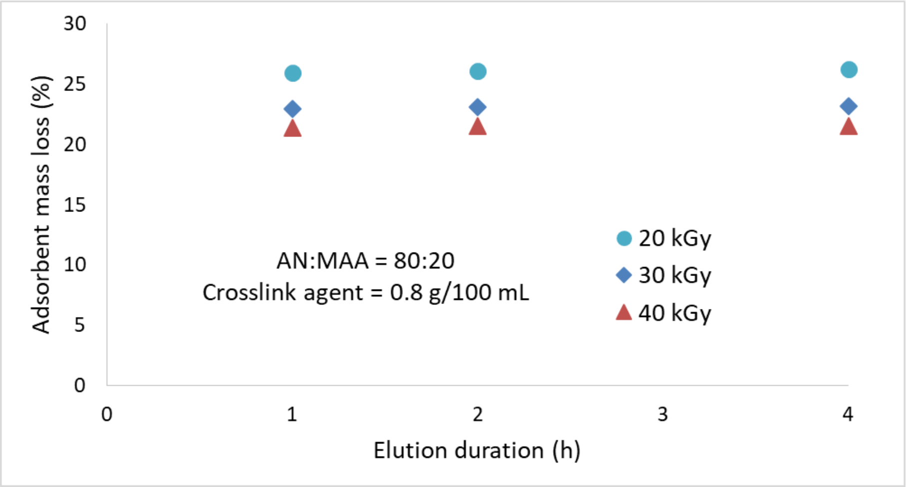

Figure 4.9 Effect of elution duration and dose of gamma ray on polymer gel mass loss during elution procedure.

The results of polymer gel mass loss from Figure 4.9 indicates that the polymer mass loss is constant when increasing the elution duration. The dose of gamma ray affects the polymer mass disappearance in such a way that the stronger the dose, the less mass loss. Because the dose of gamma ray affects the polymerization and crosslinking processes of monomers, the stronger the dose, the more these processes become completed, making the polymer gel stronger. From the trend in Figure 4.9, it appears that increasing the gamma ray dose beyond 40 kGy should result in less mass loss. However, too much gamma ray dose might destroy the chemical bonds of the polymer gel which will affect the ability of adsorption.

4.1.6 Usage repeatability

The reusability performance up to 8 cycles is shown in Figure 4.10.

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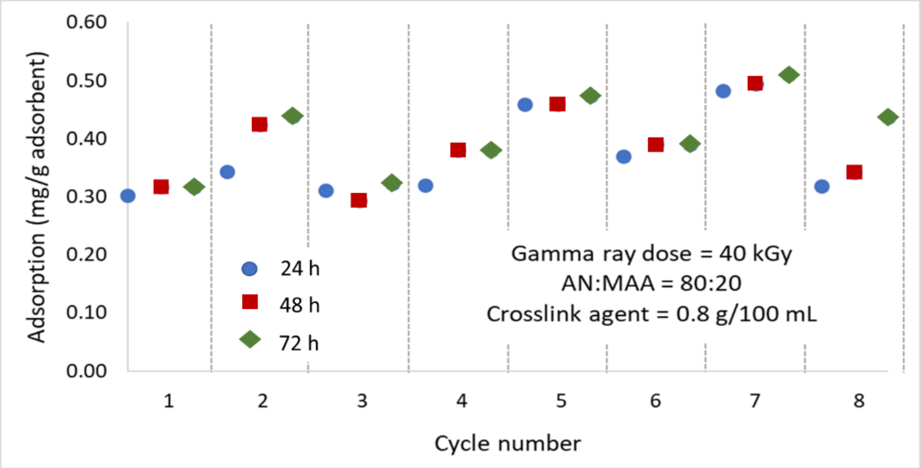
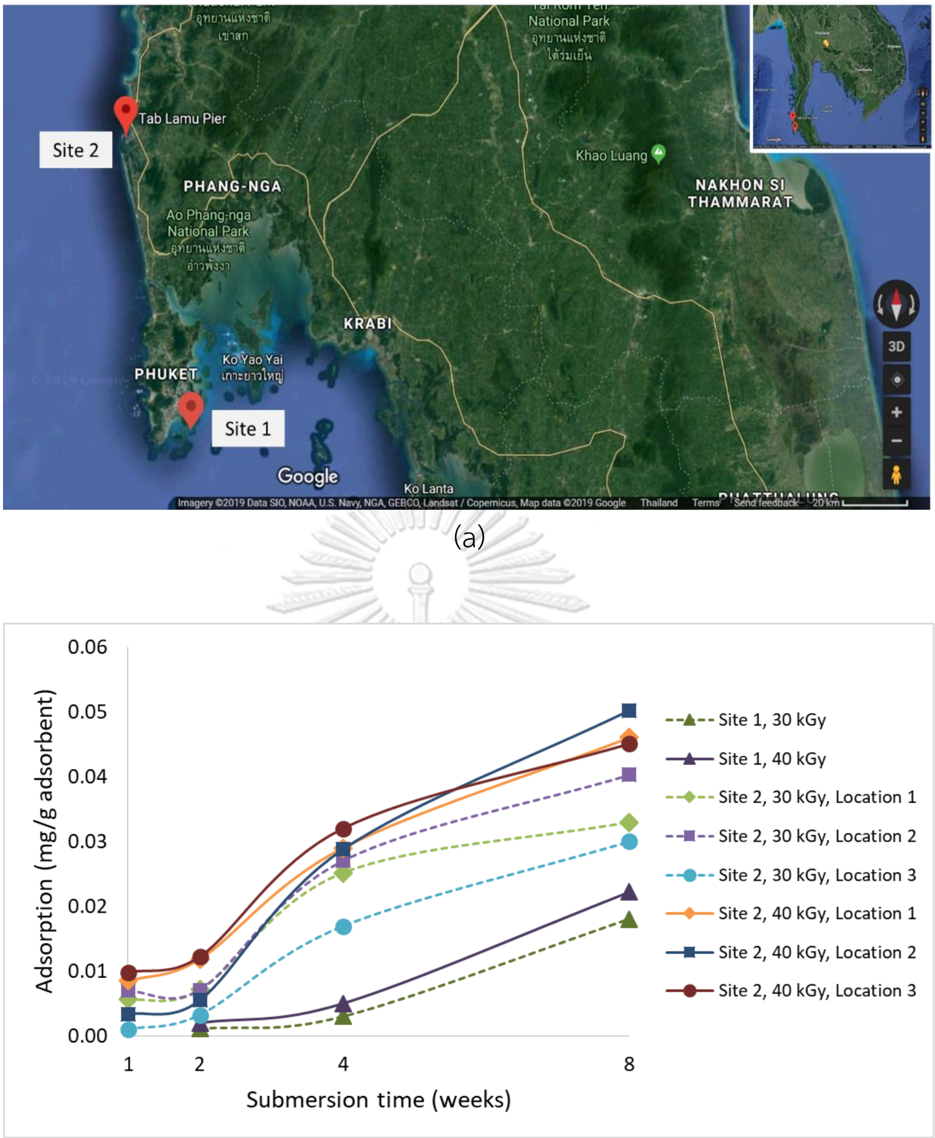


Figure 4.10 Results of usage repeatability experiment

Results indicate that the uranium adsorption capacity of the adsorbent does not decrease after 8 times of repeated use. Nevertheless, mass loss of the adsorbent still occurs during each elution due to the eluting agent. This result corresponds with Saito's work [48] which immersed an amidoxime fiber in natural seawater for a period of 5 days followed by hydrochloric acid elution solution. The performance of uranium adsorption does not decrease after 10 times of repeated use.

4.1.6 Open-ocean submersion

The adsorbents were submersed at several sites of open ocean for 1, 2, 4, and 8 weeks as shown in Figure 4.11. These experiments happened to be performed during a rainy season where the seawater contains many suspensions and mud that attached and contaminated the adsorbents. These factors would obstruct seawater from contacting the surface of the adsorbent and result in severely reduced uranium uptake.



(a)

(b)

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Figure 4.11 (a) Open-ocean submersion sites and (b) results of open-ocean submersion of the adsorbent

The results indicate a low uranium uptake in the first 1-2 weeks. At 4 and 8 weeks, the adsorption increased quite substantially, but the maximum adsorption was only about 0.05 mg/g at 8 weeks, which is still low when compared with other works. This problem indicates that it is more difficult to work with real situation than inside the laboratory because there are many factors that cannot be controlled.

Suggestions are provided to obtain high uranium uptake when soaking the adsorbent in an open ocean as follows. The adsorbent should be immersed in seawater far from the coast because the seawater of that area is clearer with much less suspended particles. The adsorbent should not be submerged in the area where seawater is relatively stagnant because less uranium ions will be carried in. The adsorbent should be immersed at sufficient depth under seawater surface to receive the least amount of sunlight to avoid algae formation, which will obstruct uranium adsorption.

4.2 Results of polymer gel prepared from UV-C curing

4.2.1 Effect of UV-C curing time

The effect of UV-C curing time was evaluated using the amidoxime polymer gel synthesized from the ratio of AN:MAA = 80:20, crosslinker concentration of 1 g/100 mL, and H_2O_2 of 60 mL/100mL. The result is displayed in Figure 4.12.

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(a) (b) (c) (d)

Figure 4.12 Effect of UV-C curing time: (a) 4, (b) 6, (c) 8, and (d) 10 hours

From Figure 4.12, after 4 hours (Figure 4.12(a)) of UV curing, the solution turned into a very soft gel, but a liquid phase was still present. After 6 hours of curing, as can be seen in Figure 4.12(b), the solution turned into a soft gel almost completely. After 8 hours (Figure 4.12(c)), although the solution became completely solidified, it was still soft. Adequate softness was needed so that the formed gel can still be crushed into small particles to be used. After 10 hours of curing as depicted in Figure 4.12(d), the formed gel turned completely rigid and it was very difficult to crush into tiny particles.

The results of gel fraction and equilibrium swelling ratio can be employed to explain the effect of exposure time, as shown in Figure 4.13 in order to select the adequate curing time for further experiments. The increased gel fraction corresponds directly with curing time from 4 to 10 hours. The reaction yield reached its maximum of approximately 87% at 10 hours. The swelling ratio also became higher with longer curing time, but at 10 hours the value decreased significantly. This can be explained that at 10 hours, the formed polymer gel became very rigid rendering water diffusion into the interior of the polymer gel very ineffective. Hence, the UV-C curing duration of 8 hours was selected due to the above reasons.

The following reasons can explain these behaviors. For a short curing time, the amount of produced OH free radicals was still low and the degrees of polymerization, crosslinking, and polymerization was insufficient. For a curing time that was too long, polymerization had been completed but crosslinking became excessive resulting in a very rigid polymer.

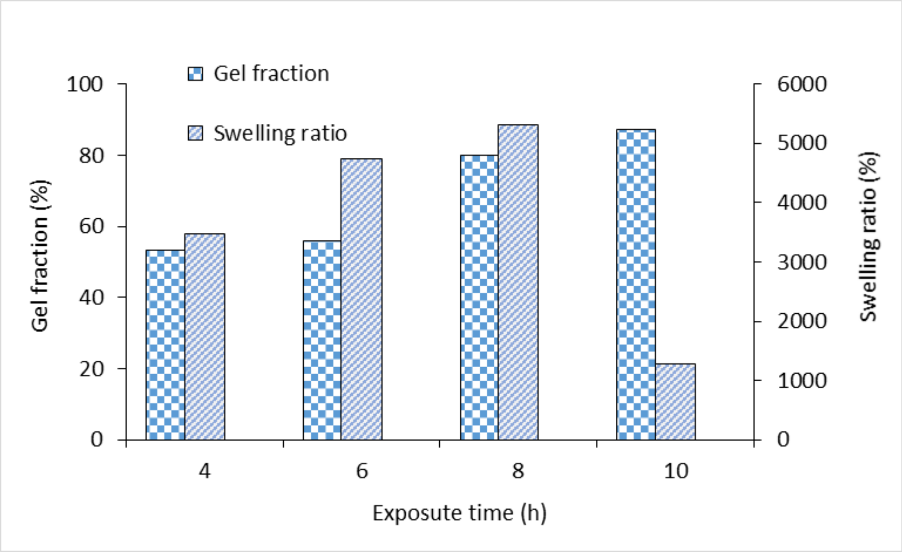

Figure 4.13 Effect of curing time on gel fraction and equilibrium swelling ratio

4.2.2 Nitrile and amidoxime groups characterization.

The chemical functional groups of the amidoxime gel synthesized from the ratio of AN:MAA = 80:20, crosslinker concentration of 1 g/100 mL, and H_2O_2 of 60 mL/100 mL were determined by FTIR and the characteristic absorption bands are displayed in Figure 4.14.

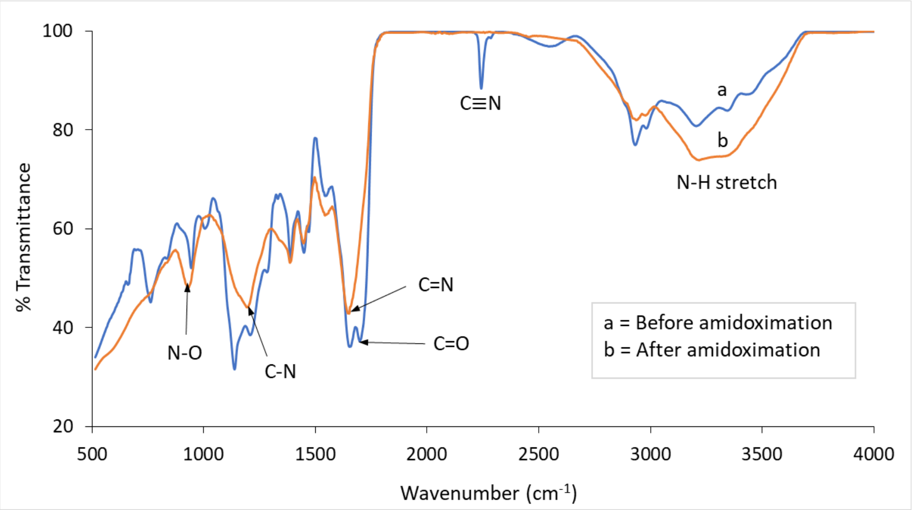

Figure 4.14 The characteristic absorption bands of polymer gel prepared from UV-C curing

The identified functional groups of AN/MAA before amidoximation are shown in Figure 4.14. The peak at 2243 cm^{-1} represents the C≡N group, which confirms the cyano group of poly(AN) in the formed gel, and the two split small peaks at 1653 and 1700 cm^{-1} represent the carbonyl group (C=O) of poly(MAA) [49]. Following the amidoximation, the C≡N peak vanishes entirely and the appearance of C=N (1652 cm^{-1}), N—O (934 cm-1), C—N (1200 cm^{-1}) [4], and N-H vibration (3200 - 3500 cm^{-1}) [[6],[11],[50]] indicates the conversion of cyano group into the amidoxime group.

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4.2.3 Effect of monomer ratio, hydrogen peroxide content, and crosslinking agent concentration on uranium adsorption.

To determine the effect of monomer ratio on U loading, the adsorbent prepared by UV-C irradiation time of 8 hours, crosslinker concentration of 1 and 2 g/100 mL, and H_2O_2 of 60 mL/100 mL was selected. Lower crosslinker concentrations (0.25 and 0.5 g) were not considered in this experiment because it will be shown later that this would result in a small U uptake. The batch experiment was performed under the condition described in Section 3.4. Figure 4.15 shows the results.

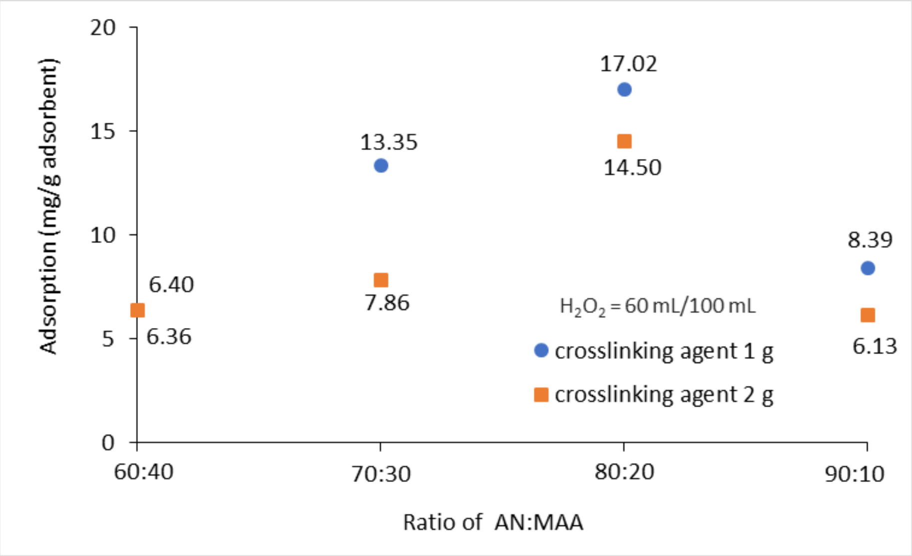

Figure 4.15 Effect of monomer ratio on U uptake

For all the ratios of AN:MAA, the crosslinker concentration of 2 g results in higher uranium uptake than for the case of 1 g (except for the ratio of 60:40). Moreover, the AN:MAA of 80:20 exhibits the maximum adsorption capacity. A higher AN proportion means a higher concentration of the amidoxime group, which is required to capture uranium ions. However, the adsorbent also needs a hydrophilic group of the MAA monomer in which seawater can diffuse into the interior of the adsorbent to adsorb uranium apart from adsorption at the polymer surface. Thus, the 80:20 AN:MAA ratio is the optimal one.

Both H_2O_2 solution (photoinitiator) and MBA (crosslinker) are important factors affecting uranium adsorption. To evaluate the effect of hydrogen peroxide and crosslinker concentrations on uranium uptake, H_2O_2 of 50, 60, 70, and 80 mL/100 mL-monomer and the crosslinking agent of 0.25, 0.5, 1, and 2 g/100 mL-monomer were studied under the 80:20 AN:MAA ratio. The results are illustrated in Figure 4.16.

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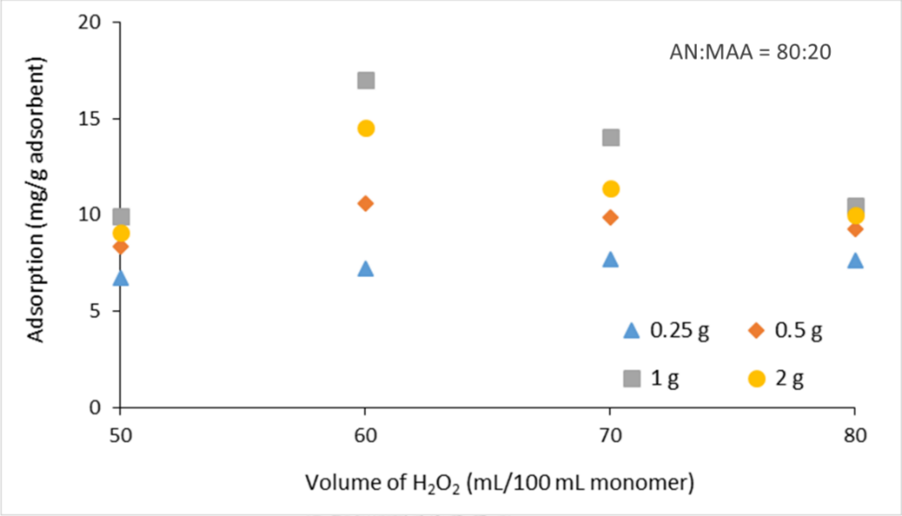

Figure 4.16 Effect of hydrogen peroxide and crosslinking agent concentrations on U uptake

As depicted in Figure 4.16, U uptake increases with increasing hydrogen peroxide content from 50 to 60 mL. Beyond 60 mL, the adsorption decreases. For the hydrogen peroxide concentration less than 60 mL, the created OH free radicals are insufficient to form network and polymerization [47, 51-53], resulting in low crosslinking density [54] and low adsorption capacity. Beyond 60 mL, increasing the hydrogen peroxide concentration lowered the macromolecule's molecular weight as the OH free radicals produced in abundance destroyed the polymer chains and increased the number of polymer chain ends, which do not lead to the absorption capacity [51, 55]. A supporting equation is the equation of Seymour and Carraher [55, 56], which states that the number-averaged degree of polymerization ($\bar{X}_n$) is inversely proportional to the square root of the initiator concentration as expressed by Eq. (3):

$$\bar{\mathrm{X}}_{\mathrm{n}} = \frac{[\mathrm{M}]}{[\mathrm{I}]^{1/2}}\mathrm{k}', \qquad (3)$$

where [I] and [M] represent the concentrations of the initiator and the monomer, respectively; $k' = k_p/(2k_d k_t \mathrm{f})^{1/2}$ is a combination constant; k_p, k_d, and k_t represent the rate constants for propagation, initiation, and termination, respectively. Hence, for a specified monomer and crosslinker concentrations and

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polymerization temperature, the higher photoinitiator content leads to the lower polymer molecular weight [55].

The crosslinker concentration is one among factors affecting uranium adsorption characteristics and mechanical properties of the adsorbent. The result of U loading capacity vs. crosslinker concentration is shown in Figure 4.16. When the concentration increased from 0.25 to 1 g, the U loading increased. Then, the adsorption dropped with a further increase in the crosslinking agent concentration. The highest U loading capacity was 17.02 mg/g-adsorbent with 1 g/100 mL crosslinker concentration.

The crosslinker content < 1 gram provides a lower crosslinking density and crosslinking point [54] of the polymer gel, making the gel physically very soft with less water absorption, yielding small U uptake. For the crosslinker concentration of 2 g, the polymer gel has more crosslinking points to form tree-dimensional network, impeding seawater diffusion into the inside of the polymer gel, resulting in less uranium uptake as well [52]. These results conform with Flory's theory [57] and previous studies [47, 52, 58].

In conclusion, the most suitable set of parameters for adsorbent synthesis using UV-C radiation is: AN:MAA = 80:20, crosslinker concentration = 1 g/100 mL monomer, and photoinitiator concentration = 60 mL/100 mL.

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4.2.4 Elution duration.

To determine sufficient elution time to remove uranium from the adsorbent, 1 M hydrochloric acid had been used to perform elution for 1, 2, and 4 hours with the adsorbent prepared under the AN:MAA ratio of 80:20, crosslinker concentration of 1 g/100 mL, and H_2O_2 of 60 mL/100 mL. Results are shown in Figure 4.17.

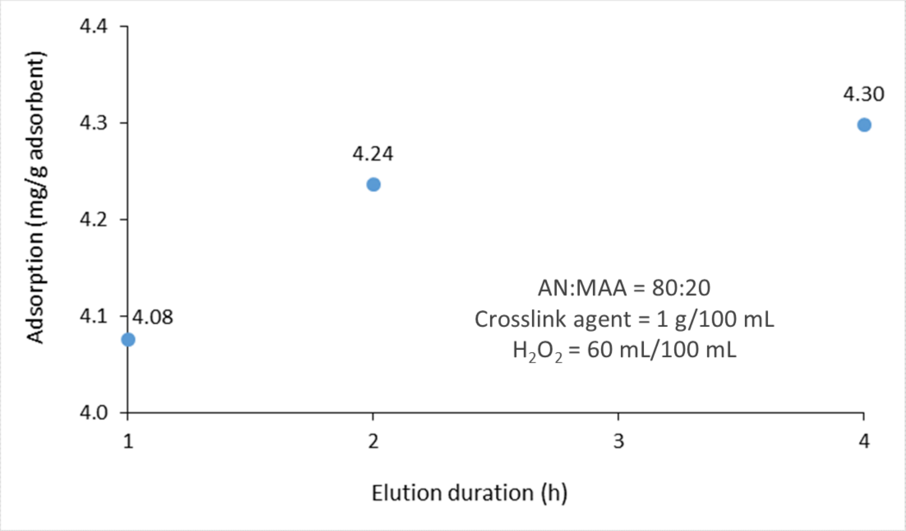

Figure 4.17 Effect of elution duration on U removal from adsorbent

The results demonstrate the required elution time of at least 2 hours at 50 °C with 1 M HCl solution. When the elution time was increased from 2 to 4 hours, additional U of only 1.4% was obtained. Thus, 2 hours of elution is adequate and all studies in this work (UV-C) followed the 2 hours elution time.

4.2.5 Swelling ratio in DI water and seawater.

To evaluate the swelling ratio of the polymer gel in DI water and seawater, the polymer prepared from AN:MAA = 80:20, crosslinker concentration of 1 g/100 mL monomer, and H_2O_2 of 50 or 60 mL/100 mL was selected.

From Figure 4.18, the adsorbent synthesized from 60 mL/100 mL H_2O_2 showed a better swelling ratio than that synthesized from 50 mL/100 mL H_2O_2 for both DI water and seawater immersion. For the 60 mL/100 mL H_2O_2 case, the equilibrium swelling ratio of 3,800% in DI water was attained after 10 minutes, and 1,400% in seawater after 20 minutes. The amidoxime polymer particles synthesized from gamma radiation (Section 4.1.4) reached 1,000% equilibrium swelling ratio in DI water, thus, the performance of polymer particles synthesized by UV-C is almost four times higher.

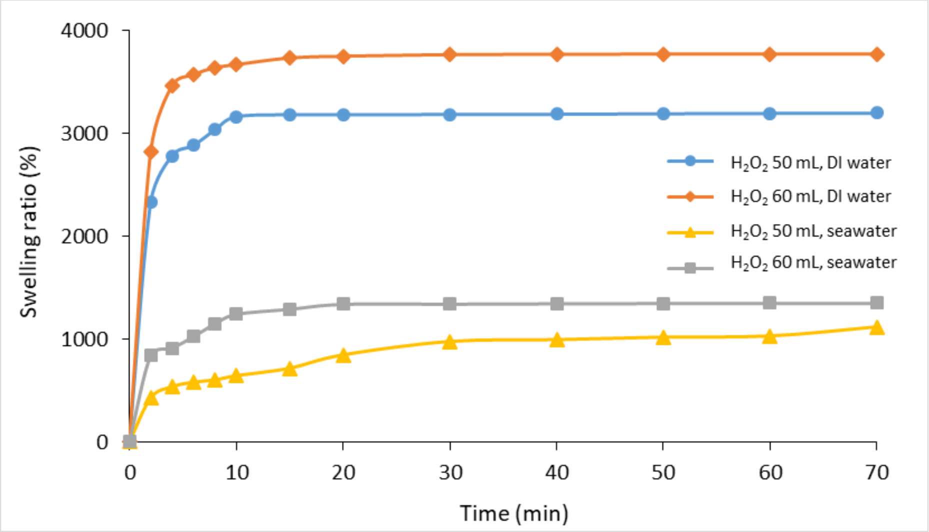

Figure 4.18 Result of absorption kinetic of polymer gel in DI water and seawater

4.2.6 Reusability evaluation.

The reusability of the polymer adsorbent is crucial for real applications. The adsorption capacity of the amidoxime adsorbent (AN:MAA of 80:20, crosslinker of 1 g/100 mL, H_2O_2 of 60 mL/100 mL) for eight adsorption-elution cycles is displayed in Figure 4.19. The amidoxime polymer gel can be reused for a minimum of eight cycles, but the adsorption at the eight cycle is reduced by 50% compared to the first cycle. This result is similar to the researches of Yu [5] and Seko [12], which found that the uranium adsorption of their adsorbents decreased when using over 5 times.

When comparing this result with the adsorbent prepared by gamma irradiation (Section 4.1.6) which showed that the adsorption did not decrease after 8 cycles, the reason could be that gamma ray possesses a much higher penetrating power than UV radiation, so it generates stronger bonding among monomers. Thus, when the adsorbent prepared from UV-C radiation was exposed to HCl solutions and alkaline solutions for several times, the polymer became degraded and the adsorption efficiency become reduced.

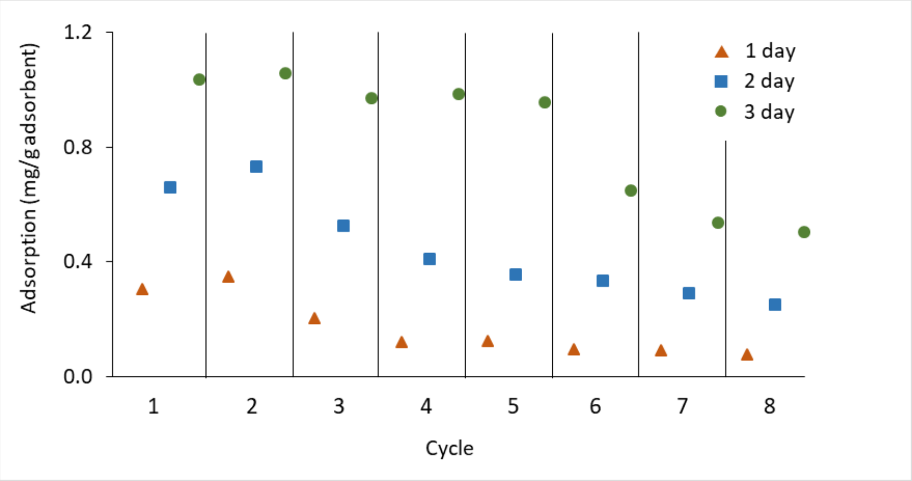

Figure 4.19 Repeatability test of amidoximated polymer particles

4.2.7 Open ocean test

The amidoxime polymer gel prepared from optimal parameters concluded in Section 4.2.3 was submersed in an open ocean for 2, 4, 6, and 8 weeks. The results are illustrated in Figure 4.20.

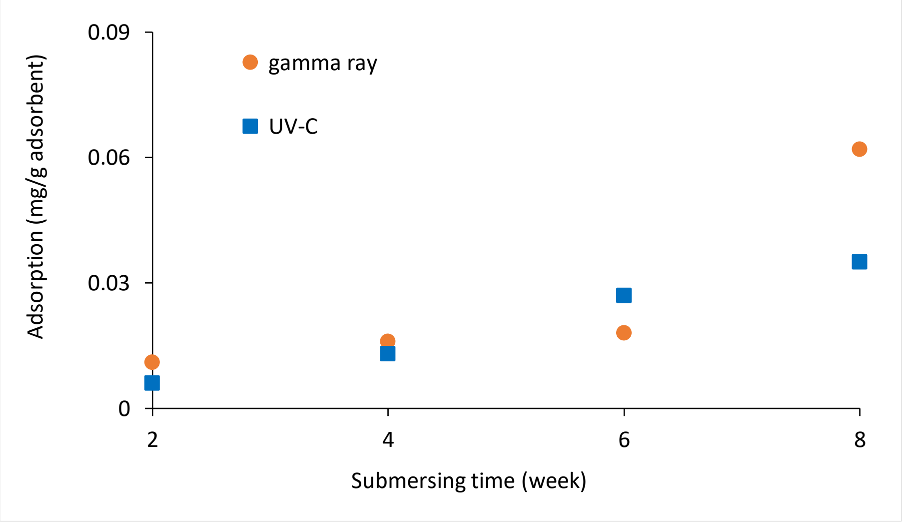

Figure 4.20 The open ocean test of amidoximed polymer particles

It can be seen that the uranium adsorption from open ocean is very low in the first two weeks, then the trend is higher in 4-8 weeks, the maximum in week 8, which results in uranium adsorption of 0.035 mg/g. This result is very low because of many faced problems during submersion. The most problem is a lot of mud and biofouling cover around the filter that containing adsorbent inside which prevent seawater flow through into the adsorbent that causing a low uranium uptake capacity. The technique to get high amount of uranium during open ocean submersion is similar to description of section 4.1.6. When comparing the uranium adsorption capacity to adsorbent prepared from gamma ray radiation, it seems that this adsorbent (UV-C) is lower than that of almost 2 times.

4.3 Uranium recovery cost estimation

Estimation of the uranium recovery cost for both adsorbents (gamma radiation and UV-C radiation) was determined from the optimal parameters to synthesize the adsorbents under the following assumptions and scopes:

- Uranium extraction of 500 kg and 1,000 kg for both adsorbents.
- Both gamma and UV-C adsorbents can adsorb uranyl ions of 1% and 5% of the maximum adsorption capacity. For the case of the adsorbent prepared from gamma radiation, the maximum adsorption capacity is 569.47 mg/g; therefore, the uranium adsorption capacity is 5.69 mg/g and 28.47 mg/g for 1% and 5%, respectively. For the case of the adsorbent prepared from UV-C, the maximum adsorption capacity is 475.28 mg/g, so, the uranium adsorption capacity is 4.75 mg/g and 23.76 mg/g for 1% and 5%, respectively.
- Installation, maintenance, reaction apparatus, electricity, and labor costs were not included.
- Uranium recovery cost was calculated as of July 3rd, 2019.
- The cost calculation was based on 8 cycles of repeated use.

Calculation of the adsorbent mass required to obtain 500 kg and 1,000 kg U is shown in Table 4.2-4.5 for the case of gamma radiation and in Table 4.6-4.9 for the case of UV-C radiation.

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Table 4.2 Calculation of adsorbent mass by gamma radiation to obtain 500 kg uranium (1% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 20.5%)	Obtained uranium (kg)
1st	5.695	21,416.55	17,026.16	121.96
2nd	5.695	17,026.16	13,535.80	96.96
3rd	5.695	13,535.80	10,760.96	77.08
4th	5.695	10,760.96	8,554.96	61.28
5th	5.695	8,554.96	6,801.19	48.72
6th	5.695	6,801.19	5,406.94	38.73
7th	5.695	5,406.94	4,298.52	30.79
8th	5.695	4,298.52	3,417.33	24.48
			Total obtained uranium	500.00

Table 4.3 Calculation of adsorbent mass by gamma radiation to obtain 500 kg uranium (5% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 20.5%)	Obtained uranium (kg)
1st	28.474	4,283.32	3,405.24	121.96
2nd	28.474	3,405.24	2,707.17	96.96
3rd	28.474	2,707.17	2,152.20	77.08
4th	28.474	2,152.20	1,710.00	61.28
5th	28.474	1,710.00	1,360.24	48.72
6th	28.474	1,360.24	1,081.39	38.73
7th	28.474	1,081.39	859.71	30.79
8th	28.474	859.71	683.47	24.48
			Total obtained uranium	500.00

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Table 4.4 Calculation of adsorbent mass by gamma radiation to obtain 1,000 kg uranium (1% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 20.5%)	Obtained uranium (kg)
1st	5.695	42,833.30	34,052.47	243.92
2nd	5.695	34,052.47	27,071.72	193.92
3rd	5.695	27,071.72	21,522.01	154.17
4th	5.695	21,522.01	17,110.00	122.56
5th	5.695	17,110.00	13,602.45	97.44
6th	5.695	13,602.45	10,813.95	77.46
7th	5.695	10,813.95	8,597.09	61.58
8th	5.695	8,597.09	6,834.69	48.96
			Total obtained uranium	1,000.00

Table 4.5 Calculation of adsorbent mass by gamma radiation to obtain 1,000 kg uranium (5% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 20.5%)	Obtained uranium (kg)
1st	28.474	8,566.65	6,810.49	243.92
2nd	28.474	6,810.49	5,414.34	193.92
3rd	28.474	5,414.34	4,304.40	154.17
4th	28.474	4,304.40	3,421.00	122.56
5th	28.474	3,421.00	2,720.49	97.44
6th	28.474	2,720.49	2,162.79	77.46
7th	28.474	2,162.79	1,719.42	61.58
8th	28.474	1,719.42	1,366.94	48.96
			Total obtained uranium	1,000.00

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Table 4.6 Calculation of adsorbent mass by UV-C radiation to obtain 500 kg uranium (1% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 25%)	Obtained uranium (kg)
1st	4.753	32,112.00	24,084.00	152.62
2nd	4.753	24,084.00	18,063.00	114.47
3rd	4.477	18,063.00	13,547.25	80.87
4th	4.477	13,547.25	10,160.44	60.65
5th	4.387	10,160.44	7,620.33	44.57
6th	2.980	7,620.33	5,715.25	22.71
7th	2.471	5,715.25	4,286.43	14.12
8th	2.329	4,286.43	3,214.83	9.98
			Total obtained uranium	500.00

Table 4.7 Calculation of adsorbent mass by UV-C radiation to obtain 500 kg uranium (5% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 25%)	Obtained uranium (kg)
1st	23.764	6,422.41	4,816.81	152.62
2nd	23.764	4,816.81	3,612.61	114.47
3rd	22.386	3,612.61	2,709.45	80.87
4th	22.386	2,709.45	2,032.09	60.65
5th	21.934	2,032.09	1,524.07	44.57
6th	14.900	1,524.07	1,143.05	22.71
7th	12.357	1,143.05	857.29	14.12
8th	11.644	857.29	642.97	9.98
			Total obtained uranium	500.00

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Table 4.8 Calculation of adsorbent mass by UV-C radiation to obtain 1,000 kg uranium (1% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 25%)	Obtained uranium (kg)
1st	4.753	64,224.40	48,168.30	305.25
2nd	4.753	48,168.30	36,126.23	228.93
3rd	4.477	36,126.23	27,094.67	161.74
4th	4.477	27,094.67	20,321.00	121.31
5th	4.387	20,321.00	15,240.75	89.14
6th	2.980	15,240.75	11,430.56	45.42
7th	2.471	11,430.56	8,572.92	28.25
8th	2.329	8,572.92	6,429.69	19.97
			Total obtained uranium	1,000.00

Table 4.9 Calculation of adsorbent mass by UV-C radiation to obtain 1,000 kg uranium (5% of maximum adsorption capacity)

Cycle	Uranium adsorption capacity (mg/g)	Initial weight of adsorbent (kg)	Weight of adsorbent after elution (kg) (mass loss 25%)	Obtained uranium (kg)
1st	23.764	12,844.87	9,633.65	305.25
2nd	23.764	9,633.65	7,225.24	228.93
3rd	22.386	7,225.24	5,418.93	161.74
4th	22.386	5,418.93	4,064.20	121.31
5th	21.934	4,064.20	3,048.15	89.14
6th	14.900	3,048.15	2,286.11	45.42
7th	12.357	2,286.11	1,714.58	28.25
8th	11.644	1,714.58	1,285.94	19.97
			Total obtained uranium	1,000.00

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The data shown in Tables 4.2 - 4.9 indicate that the mass of adsorbent prepared from UV-C is higher than that prepared from gamma irradiation due to the decreasing adsorption capacity in each cycle. Moreover, for the adsorbent prepared from UV-C, the rate of adsorbent mass loss higher than for the gamma ray case.

The production cost of adsorbents, elution cost and regeneration cost are summarized in Table 4.10.

Table 4.10 Summary of uranium recovery cost

Type of cost (US$/kg)	Gamma				UV-C			
	500 kg (1%)	500 kg (5%)	1000 kg (1%)	1000 kg (5%)	500 kg (1%)	500 kg (5%)	1000 kg (1%)	1000 kg (5%)
Production cost	2,906.35	581.28	5812.69	1162.55	249.50	42.77	427.66	83.26
Elution cost	12.00	2.40	24.01	4.80	15.80	3.16	31.61	6.32
Regeneration cost	6.98	1.40	13.96	2.79	8.67	1.73	17.34	3.47
Total	**2,925.34**	**585.08**	**5,850.66**	**1,170.15**	**273.98**	**47.66**	**476.61**	**93.05**

The detailed calculation of uranium recovery cost suggests that UV-C irradiation results in a lower cost than gamma irradiation. For gamma irradiation, the irradiation cost per 1 kg of monomer mixture is approximately 64.52 US$ based on the service price rate of Thailand Institute of Nuclear Technology (TINT), Thailand. For UV-C irradiation, the 4 UV lamps with 4 reflectors costed about 331.35 US$ with the useful life of 9,000 hours [59]. At the normal irradiation time of 8 hours, the irradiation can be performed for up to 1,125 times or over 1 year, so the irradiation cost was calculated to be 0.29 US$/time. Thus, the uranium recovery cost using gamma radiation is about 10.7 times higher.

CHAPTER V

CONCLUSIONS

5.1 Conclusions of research

The amidoxime polymer gel for U compound recovery from seawater had been prepared by radiation technique. Effects of ratio of AN/MAA monomers, crosslinker concentration, hydrogen peroxide content, gamma ray dose, and curing time of UV-C had been evaluated.

The synthesis of the adsorbents utilizes two different radiation sources: gamma radiation and UV-C radiation. For the case of gamma radiation, several AN:MAA monomer ratios with different MBA concentrations were irradiated with different gamma ray doses. For UV-C radiation, different AN:MAA monomer ratios with different MBA and hydrogen peroxide concentrations were irradiated in a chamber consisting of four UV-C lamps under various durations. The resulting polymer gels which contained the nitrile group was soaked in the hydroxylamine hydrochloride solution in order to convert the nitrile group into the amidoxime group. The amidoximated polymer gels were treated with potassium hydroxide solution and dried in an oven. The FTIR technique was used to analyze the chemical functional groups of the polymers, and the ICP-OES technique was employed to analyze U concentration in the eluent.

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The AN:MAA monomer ratio of 80:20 with 0.8 g/100 mL crosslinking agent at the gamma ray dose of 40 kGy as shown in table 5.1 exhibited the highest uranium adsorption capacity in the laboratory experiment of 6.96 mg/g in seawater sample with added 300 ppb U for 4 weeks of soaking time. The reusability test of this adsorbent indicated that the adsorption efficiency did not decrease after using for at least 8 cycles. The field experiment in an open ocean indicated that the U loading capacity increased with longer submersion duration with the highest uranium uptake of 0.05 mg/g.

For the adsorbent prepared from UV-C radiation with the AN:MAA monomer ratio of 80:20, 1 g/100 mL crosslinking agent, and hydrogen peroxide content of 60 mL/100 mL under the curing time of 8 hours, as illustrated in table 5.1, the highest uranium adsorption capacity in the laboratory experiment of 17.02 mg/g in seawater sample with added 10 ppm U for 1 week of soaking time was obtained. The reusability evaluation indicated that the adsorption efficiency of the adsorbent reduced to 50% after 8 cycles of adsorption and elution. The field test in natural seawater indicated that the U loading capacity increased with longer submersion duration and the highest uptake capacity of 0.035 mg/g was obtained after 8 weeks of immersion.

Table 5.1 Conclusions of optimal parameter for synthesis of adsorbent

Parameter	Gamma ray	UV-C
Ratio of AN:MAA	80:20	80:20
Crosslinker concentration (g/100 mL)	0.8	1
H_2O_2 (mL/100 mL)	Not required	60
Absorbed dose/Exposure time	40 kGy	8 h

Evaluation of the uranium recovery cost to obtain 500 kg and 1,000 kg uranium revealed that the adsorbent synthesized by gamma radiation has a higher recovery cost than that synthesized by UV-C radiation of approximately 10.7 times.

In conclusion, these amidoxime polymer gels can be considered as alternative adsorbents for uranium recovery from seawater. These adsorbents not only adsorb uranium in natural seawater, but also adsorb uranium in seawater highly contaminated with uranyl ions.

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5.2 Recommendations for future research

1. To enhance the uranium loading capacity, the adsorbents should to be improved to have higher effective surface area.
2. The methacrylic acid monomer could be changed to other monomers with the hydrophilic property to improve the adsorption capacity.
3. Different crosslinkers should be tried to improve the adsorption capacity.

REFERENCES

1. Enerdata. Total energy consumption Slight recovery in energy consumption in 2016. 2016 [cited 2017 August 10]; Available from: https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html.
2. PRIS. The Database on Nuclear Power Reactors. 2017 [cited 2018 February 13]; Available from: https://www.iaea.org/PRIS/home.aspx.
3. Institute, N.E. World Statistics Nuclear Energy Around the World. 2017.
4. Cameco. Uranium Price. 2019 [cited 2019 July 3]; Available from: https://www.cameco.com/invest/markets/uranium-price.
5. Yu, H.W., et al., Recovery of uranium ions from simulated seawater with palygorskite/amidoxime polyacrylonitrile composite. Applied Clay Science, 2015. 111, 67-75.
6. Ratnitsai, V., Wongsawaeng, D. and Chankow, N. Enhancement of uranium extraction from seawater using chromic-acid-treated amidoxime adsorbent prepared by simultaneous irradiation grafting technique. Journal of Nuclear Science and Technology, 2015. 52(9), 1151-1161.
7. Sodaye, H., et al., Extraction of uranium from the concentrated brine rejected by integrated nuclear desalination plants. Desalination, 2009. 235(1), 9-32.
8. Das, S., et al., Novel poly(imide dioxime) sorbents: Development and testing for enhanced extraction of uranium from natural seawater. Chemical Engineering Journal, 2016. 298(Supplement C), 125-135.
9. 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 and Functional Polymers, 2003. 57(1), 67-76.
10. Saito, K. et al., Recovery of uranium from seawater using amidoxime hollow fibers. AIChE Journal, 1988. 34(3), 411-416.
11. Badawy, S.M., et al., Cloth filter for recovery of uranium from radioactive waste. Radiation Physics and Chemistry, 2005. 73(2), 125-130.

จุฬาลงกรณ์มหาวิทยาลัย
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12. Seko, N., et al., Fine fibrous amidoxime adsorbent synthesized by grafting and uranium adsorption–elution cyclic test with seawater. Separation Science and Technology, 2004. 39(16), 3753-3767.
13. Taimur, S., Hassan, M.I. and Yasin, T. Removal of copper using novel amidoxime based chelating nanohybrid adsorbent. European Polymer Journal, 2017. 95(Supplement C), 93-104.
14. Choi, S.H., et al., Adsorption of uranium ions by resins with amidoxime and amidoxime/carboxyl group prepared by radiation-induced polymerization. Radiation Physics and Chemistry, 2003. 67(3), 387-390.
15. Hara, K., et al., Attempts to capturing ppb-level elements from sea water with hydrogels. Progress in Nuclear Energy, 2016. 92, 228-233.
16. Harland, C.E., Ion Exchange. Theory and Practice 2nd Edition. 1994, Thomas Graham House, The Science Park, Milton Road, Cambridge CB4 4WF,UK: The Royal Society of Chemistry.
17. Yun, C.K., Development of a process for continuous extraction of uranium from seawater. 1982, International Atomic Energy Agency.
18. Kislik, V., et al., Solvent Extraction: Classical and novel approaches. Institute of Applied Chemistry The Hebrew University of Jerusalem Campus Givat Ram, Jerusalem 91904, Israel. 2011.
19. Davies, R.V., et al., Extraction of uranium from sea water. Nature, 1964. 203, 1110.
20. Milner, G.W.C., et al., The determination of uranium in sea water by pulse polarography. Journal of Electroanalytical Chemistry (1959), 1961. 2(1), 25-38.
21. Misra, N.L.D., Mudher, S., Singh, K.D. Uranium determination in seawater by total reflection X-ray fluorescence spectrometry. Spectrochimica Acta. Part B, Atomic Spectroscopy, 2006. 61, 1166-1169.
22. Kim, Y.S. and Zeitlin, H. Separation of uranium from seawater by adsorbing colloid flotation. Analytical Chemistry, 1972. 44(1), 181-181.
23. Kanno, M., Present status of study on extraction of uranium from sea water. Journal of Nuclear Science and Technology, 1984. 21(1), 1-9.
24. Koyanaka, Y. Collection of uranium from sea water by Galena. Journal of

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Nuclear Science and Technology, 1970. 7(8), 426-427.

25. Folkendt, D.G.A.M. Uranium from seawater 1982, Lawrence Livermore Laboratory: United Stated of America.

26. Ismail, A.F. and Yim, M.S. Investigation of activated carbon adsorbent electrode for electrosorption-based uranium extraction from seawater. Nuclear Engineering and Technology, 2015. 47(5), 579-587.

27. Dulama, M.I., Deneanu, N. Treatment of uranium contaminated wastewater – a review. in NUCLEAR 2013 the 6th annual international conference on sustainable development through nuclear research and education. 2013. Pitesti, Romania: Institute for Nuclear Research Pitesti.

28. Hassan, K.F., et al., Preparation of poly(hydroxamic acid) for separation of Zr/Y, Sr system. Chromatography Research International, 2011. 2011, 1-7

29. Hirotsu, T. et al., Recovery of uranium from seawater. Proceedings of an International Meeting: Tokyo, Japan: Atomic Energy Society of Japan.1984.

30. Denizli, A., et al., Methacryloylamidoglutamic acid incorporated porous poly(methyl methacrylate) beads for heavy-Metal removal. Industrial & Engineering Chemistry Research, 2004. 43(19), 6095-6101.

31. Ma, J., et al., Amidoximated fluorescent polymer based sensor for detection of trace uranyl ion in aqueous solution. Talanta, 2017. 168, 10-15.

32. Sekiguchi, K., et al., Uranium uptake during permeation of seawater through amidoxime-group-immobilized micropores. Reactive Polymers, 1994. 23(2), 141-145.

33. Pan, H.B., et al., Carbonate-H2O2 leaching for sequestering uranium from seawater. Dalton Transactions, 2014. 43(28), 10713-10718.

34. Donnelly, P. Lecture # 9 Polymer structure Characteristic ,Applications and processing of polymers Learning objectives: 1- Describe a typical polymer molecule in terms. 2015 [cited 2019 January 11]; Available from: https://slideplayer.com/slide/3504778/.

35. Yashoda. Difference Between Homopolymer and Copolymer. 2016 [cited 2017 November 1]; Available from: http://pediaa.com/difference-between-homopolymer-and-copolymer.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

36. Vagabond, J. How do photons interact with matter? simper scatter, compton scatter, pair production 2014 [cited 2019 April 20]; Available from: https://johnvagabondscience.wordpress.com/tag/photoelectric-effect/.

37. Isaksson, M., Hansson, M. and Berg, G. Determination of iodine in Vivo and in Vitro by X-Ray fluorescence analysis: Methodology and Applications. 2009. 29-37

38. Lucas, J., What Is Ultraviolet Light?. . 2017 [cited 2017 November 3]; Available from: www.livescience.com/50326-what-is-ultraviolet-light.html.

39. Spectroline. UV protective eye and face wear for EPROM. 2019 [cited 2019 February 18]; Available from: http://spectroline.com/iso-certification/.

40. Wongjaikham, W., Wongsawaeng, D. and Hosemann, P. Synthesis of amidoxime polymer gel to extract uranium compound from seawater by UV radiation curing. Journal of Nuclear Science and Technology, 2019. 56(6), 541-552.

41. Wang, Y., et al., Amidoxime-grafted multiwalled carbon nanotubes by plasma techniques for efficient removal of uranium(VI). Applied Surface Science, 2014. 320, 10-20.

42. Gao, Q., et al., Radiation synthesis of a new amidoximated UHMWPE fibrous adsorbent with high adsorption selectivity for uranium over vanadium in simulated seawater. Radiation Physics and Chemistry, 2016. 122, 1-8.

43. Das, S., et al., Chemical aspects of uranium recovery from seawater by amidoximated electron-beam-grafted polypropylene membranes. Desalination, 2008. 232(1), 243-253.

44. Xu, C., et al., Adsorption of uranium by amidoximated chitosan-grafted polyacrylonitrile, using response surface methodology. Carbohydrate Polymers, 2015. 121, 79-85.

45. Kim, J., et al., Uptake of uranium from seawater by amidoxime-based polymeric adsorbent: Field experiments, modeling, and updated economic assessment. Industrial & Engineering Chemistry Research, 2014. 53(14), 6076-6083.

46. Gupta, N.V. and Shivakumar, H.G. Investigation of swelling behavior and mechanical properties of a pH-sensitive superporous hydrogel composite, 2012. 11, 481-93.

47. Wan, T., et al., Synthesis and swelling behaviors of microcrystal muscovite

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composite superabsorbent by photopolymerization. Journal of Wuhan University of Technology-Mater. Sci. Ed., 2016. 31(1), 151-156.

48. Saito, K., et al., Porous amidoxime-group-containing membrane for the recovery of uranium from seawater. Industrial & Engineering Chemistry Research, 1987. 26(10), 1977-1981.

49. Das, S., et al., Novel poly(imide dioxime) sorbents: Development and testing for enhanced extraction of uranium from natural seawater. Chemical Engineering Journal, 2016. 298, 125-135.

50. Wongjaikham, W., et al., Enhancement of uranium recovery from seawater using amidoximated polymer gel synthesized from radiation-polymerization and crosslinking of acrylonitrile and methacrylic acid monomers. Journal of Environmental Chemical Engineering, 2018. 6(2), 2768-2777.

51. Wan, T. et al., Preparation of a Kaolinite–poly(acrylic acid acrylamide) water superabsorbent by photopolymerization. Journal of Applied Polymer Science, 2006. 102, 2875–2881.

52. Li, A., Wang, A. and Chen, J. Studies on poly(acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization. Journal of Applied Polymer Science, 2004. 92(3), 1596-1603.

53. Tao, W., et al., Preparation of bentonite–poly[(acrylic acid)-acrylamide] water superabsorbent by photopolymerization. Polymer International, 2006. 55(12), 1413-1419.

54. Mohan, M., et al., Swelling properties of chemically crosslinked poly(acrylamide-co-maleic acid) hydrogels. International Journal of Polymeric Materials and Polymeric Biomaterials, 2006. 55(7), 513-536.

55. LIU, Z.S., Rempel, G.L. Preparation of superabsorbent polymers by crosslinking acrylic acid and acrylamide copolymers. Journal of Applied polymer science, 1998. 64(7), 1345-1353.

56. T., W.E.F., Polymer chemistry: An introduction. Raymond B. Seymour and Charles E. Carraher, Jr., Marcel Dekker AG, New York, 1981. British Polymer Journal, 1982. 14(1), 36-37.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

57. Flory, P.J., Principles of Polymer Chemistry. First Edition ed. 1953, Ithaca, United States: Cornell University Press.
58. Weiqing, R., et al., Superabsorbent hydrogel of acrylic acid/potassium acrylate copolymers by ultraviolet photopolymerization: Synthesis and properties. Journal of Applied Polymer Science, 2006. 101(2), 1181-1187.
59. Philips. TUV T8. 2018 [cited 2018 October 21]; Available from: http://www.assets.lighting.philips.com/is/content/PhilipsLighting/fp928048604003-pss-global.

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