Enhancement of Extraction of Uranium from Seawater – Final Report

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Executive Summary

Even at a concentration of 3 μg/L, the world's oceans contain a thousand times more uranium than currently know terrestrial sources. In order to take advantage of this stockpile, methods and materials must be developed to extract it efficiently, a difficult task considering the very low concentration of the element and the competition for extraction by other atoms in seawater such as sodium, calcium, and vanadium. The majority of current research on methods to extract uranium from seawater are vertical explorations of the grafting of amidoxime ligand which was originally discovered and promoted by Japanese studies in the late 1980s. Our study expands on this research horizontally by exploring the effectiveness of novel uranium extraction ligands grafted to the surface of polymer substrates using radiation. Through this expansion, a greater understanding of uranium binding chemistry and radiation grafting effects on polymers has been obtained.

While amidoxime-functionalized fabrics have been shown to have the greatest extraction efficiency so far, they suffer from an extensive chemical processing step which involves treatment with powerful basic solutions. Not only does this add to the chemical waste produced in the extraction process and add to the method's complexity, but it also significantly impacts the regenerability of the amidoxime fabric. The approach of this project has been to utilize alternative, commercially available monomers capable of extracting uranium and containing a carbon-carbon double bond to allow it to be grafted using radiation, specifically phosphate, oxalate, and azo monomers. The use of commercially available monomers and radiation grafting with electron beam or gamma irradiation will allow for an easily scalable fabrication process once the technology has been optimized.

The need to develop a cheap and reliable method for extracting uranium from seawater is extremely valuable to energy independence and will extend the quantity of uranium available to the nuclear power industry far into the future. The development of this technology will also promote science in relation to the extraction of other elements from seawater which could expand the known stockpiles of other highly desirable materials.

Accomplishments v. Goals/Objectives

Although the main objective of this project focused on developing novel materials for the efficient extraction of uranium from seawater, our approach to this objective can be broken up into the following parts:

1. Enhancing the loading capacity of uranium on the adsorbent fabric.
2. Acceleration of the kinetics of uptake of uranium on the adsorbent fabric.
3. Improving the regeneration capacity of the adsorbent fabric.
4. Developing a reliable and reproducible procedure for grafting the adsorbing species on the polymer under “green chemistry” conditions (aqueous medium).

The loading capacity of the adsorbent fabric relies on two factors, mainly the choice of monomer and the amount of monomer available for extracting uranium on the surface of the grafted fabric. The initial selection of uranium extraction monomers was based on the combination of functional groups with known affinities for uranium and allyl or vinyl groups which could be used to graft the monomer to the surface of a chosen fabric. The phosphate, oxalate, and azo monomers chosen for grafting showed exceptional extraction efficiencies at uranium concentrations of 1 ppm when tested on activated charcoal. Attempts to graft these monomers to the surface of fabric resulted in materials that had lower extraction efficiencies than in the benchmark tests performed with the monomer adsorbed on activated charcoal most likely due to grafting densities and morphologies that were not optimized for uranium extraction. Following suit, the loading capacities of the produced fabrics were not very high at low concentrations of uranium, but this is in part due to the mechanism for testing uranium extraction wherein the total amount of uranium present in the vials used for exposing the grafted fabrics to uranium was far removed from the amount the fabrics would be exposed to in an ocean environment. Efforts to enhance the grafting are on-going and we expect that loading capacities of the fabrics can approach and surpass those obtained with the charcoal experiments.

The kinetics of uptake of the uranium on the adsorbent fabric can be improved somewhat by the choice of monomer and more importantly the surface area of fabric exposed to seawater. The catalog of monomers used in this project were chosen for the kinetics exhibited during the preliminary charcoal experiments. The subsequent grafting of these monomers was focused on improving the grafting morphology so that the amount of uranium extracting groups exposed to seawater was maximized. Ideally, indirect grafting of monomer would produce long, straight polymer chains, but unfortunately efforts to perform indirect grafting were unsuccessful. Concurrently, direct grafting experiments performed created modules of monomer on the surface of the fabric fibers. Irradiation conditions were aimed at reducing the size and increasing the density of these modules on the surface of the fibers. Doing so would decrease the amount of uranium adsorbing functional groups that were trapped inside the grafted modules of homopolymer. Scanning electron microscopy (SEM) performed on the fabrics revealed that the oxalate monomer, especially when grafted with or without solvent, did not result in surface morphologies which were optimal. The phosphate moieties had similar results. The most recent efforts to graft vinylbenzyl chloride precursor to the fabric prior to chemically adding the azo group however have shown morphologies closer to what would be considered optimal and now the irradiation conditions can be improved to reduce the size of the grafted modules. This sub-optimal morphology is what is most likely contributing to the disparity between the fabric and the charcoal extraction results.

The approach to improving the regeneration capacity of the adsorbent fabric was twofold. The first strategy employed was the use of monomer groups that would not require post irradiation treatment with harsh acids or bases unlike those required by the amidoxime groups[1]. All monomers used throughout the project required only grafting and washing for the grafted fabric to be ready for uranium extraction. Secondly, the use of ammonium oxalate as the eluent for the captured uranium on the surface of the grafted fabrics instead of harsher acids also improved the regeneration capacity of our fabrics as it avoided the degradation of the substrate polymer and resulted in reduced loss of uranium extracting groups after each regeneration cycle. The ability for the phosphate grafted fabric to regenerate 20 times with less than a 20% decrease in loading capacity demonstrates the success of this effort over the course of the project.

The use of “green chemistry” conditions was extensively explored for both the phosphate and the oxalate functional groups. Optimally, the phosphate group could be grafted using a 0.3% solution of polysorbate 20, which resulted in reduced degrees of grafting but a higher uranium loading and extraction efficiency. With the oxalate monomer, both surfactant and solvent-free grafting procedures were attempted. The surfactant grafting was not initially successful, as the uranium extraction efficiency was practically negligible. Oxalate monomer was also grafted to the surface of the fabric without the use of solvent which resulted in degrees of grafting greater than 100% and extraction efficiencies that reached 50% for 1 ppm uranium solutions and 35% for 0.2 ppm uranium solutions. These results however were not extremely reproducible and efforts have been made to determine sources of variance between fabrics grafted under similar conditions including the possibility of altering the fabric cleaning post-irradiation to ensure the removal of homopolymer. Finally, once the azo groups can be grafted to the surface of the fabric and can achieve an extraction efficiency approaching or exceeding that obtained through the charcoal experiments, the focus can be shifted to “green chemistry” conditions and optimized to match the results of the organic solvent grafting if possible.

Project Activities Summary

Over the course of this project numerous monomers and radiation grafting techniques were attempted in an effort to fulfill the listed objectives for the project. Testing involved the evaluation of a monomer repertoire that included eight organophosphorus compounds (including phosphates, phosphonates, and phosphine derivatives, three oxalates, four amines, one ketone, and four azo compounds. The preliminary studies in order to determine whether or not these compounds could actually remove uranium from seawater were performed by incorporating the compound onto the surface of activated carbon. These doped samples would then be exposed to a solution of uranium in seawater under different concentrations and exposure times. The compounds which had the best extraction performance would then be used in grafting experiments as possible candidates for a successful uranium extraction monomer.

Throughout this project, the substrate used for the majority of grafting experiments was a high surface area, polyamide 6 fabric purchased under the name Winged Nylon 6. An SEM image of this material next to a macroscale image of a sample piece of fabric in Fig. 1. This fabric was chosen for its high surface area and its chemical resilience, which would assist with increasing grafting densities and regenerability following extraction respectively.

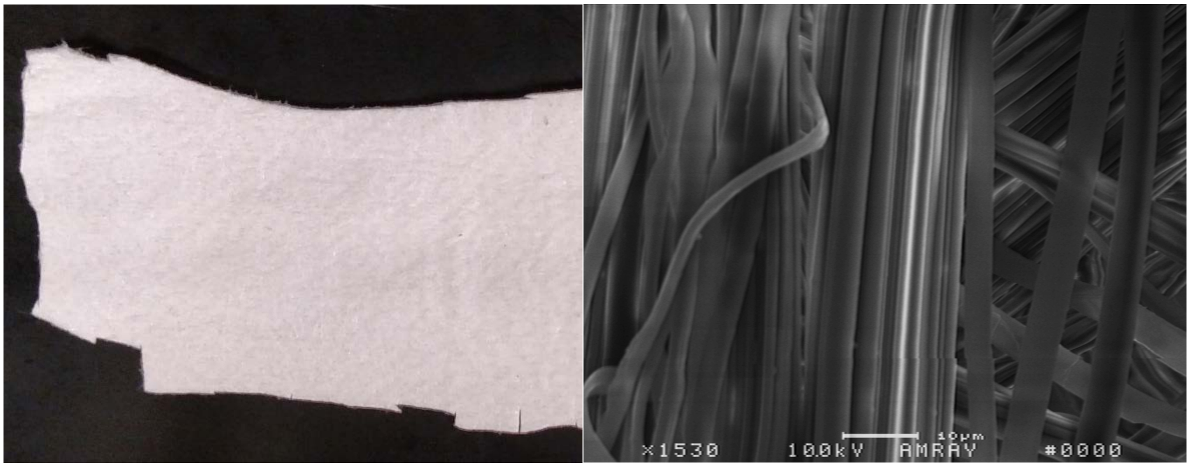


Figure 1 – Pictures of the polyamide 6 fabric prior to grafting (left) and an SEM image of the fibers that compose the fabric (right).

In order to better characterize the response of the fabric to irradiation, electron paramagnetic resonance (EPR) spectroscopy was performed on the polyamide fabric following irradiations. The study revealed that the lifetime of the radicals in the fabric was greater than 2.5 hours when not exposed to air, which verified the presence of radicals in the fabric during grafting, see Fig. 2.

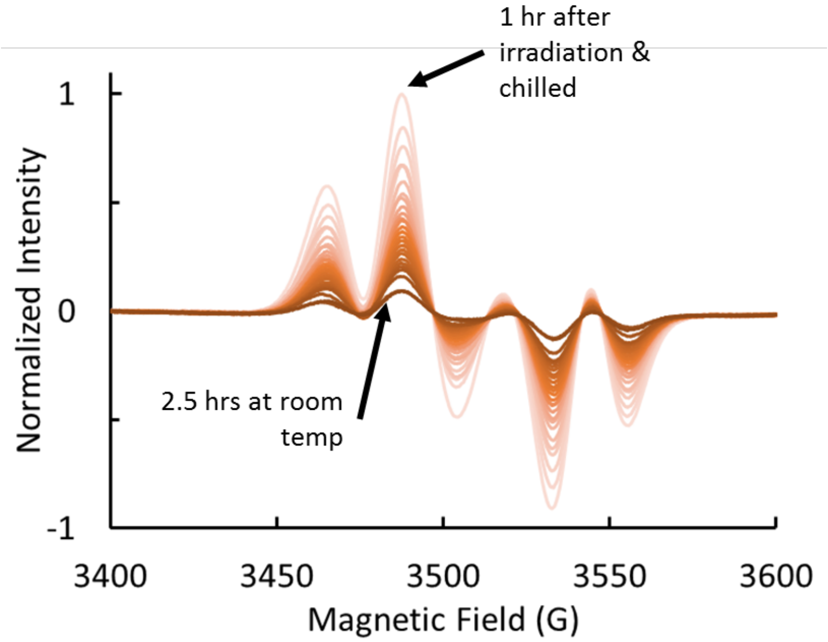
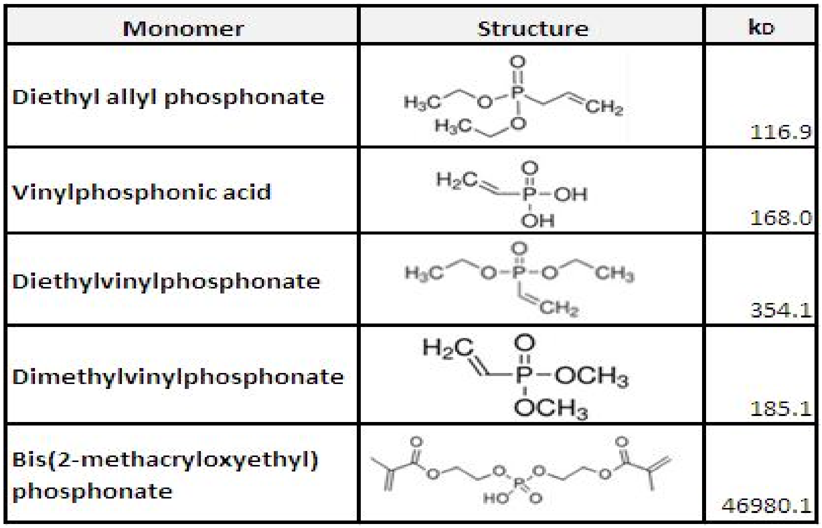


Figure 2 – The EPR spectrum of the radicals generated in the polyamide 6 fabric following a 150 kGy irradiation and their decay from 1 to 2.5 hours after the irradiation.

Phosphate Studies

The initial efforts to extract uranium from seawater were focused on obtaining allyl or vinyl functionalized phosphate derivatives. Phosphates have previously been used for the extraction of uranium from aqueous solutions and have been found complexed with uranium in natural ore deposits[2]. Commercially available ligands that matched these parameters were found and vetted using the activated carbon exposure method in order to determine which group was able to adsorb the most uranium from seawater in the shortest amount of time. The results of this initial experiment revealed bis-(2-methacryloxyethyl) phosphonate (B2MP) as the most successful candidate for extraction, see Fig. 3.



Monomer	Structure	kD
Diethyl allyl phosphonate		116.9
Vinylphosphonic acid		168.0
Diethylvinylphosphonate		354.1
Dimethylvinylphosphonate		185.1
Bis(2-methacryloxyethyl) phosphonate		46980.1

Figure 3 – All listed monomers were γ-irradiated at 5 kGy/hr for one hour onto Winged Nylon and tested for their ability to extract uranium which is exhibited by their K_D value (given in mL/g, K_D is equivalent to the mass of uranium adsorbed by the fabric per mass of the fabric given in g/g , divided by the concentration of uranium in the solution given in g/mL).

The radiation grafting of B2MP was then optimized using a Co-60 gamma irradiator, results of which are shown in Fig. 4. The optimal grafting density was found to be about 100% in relation to the amount of uranium extracted from solution.

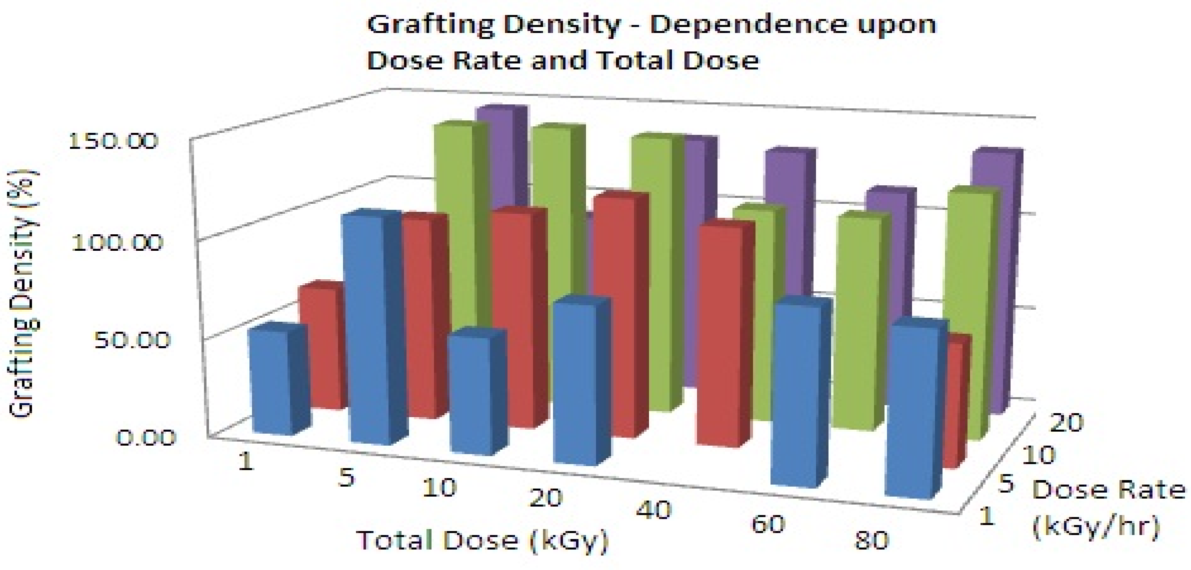


Figure 4 – Relationship between dose, dose rate, and grafting density for polyamide 6 fabrics grafted with B2MP irradiated by Co-60.

One important aspect of our approach is the reusability of the grafted fabrics. Current uranium extraction technologies, specifically the use of amidoxime grafted fabrics, require the use of base treatments in order to activate the uranium extracting groups[1]. These base treatments lead to a degradation of uranium extraction capacity and in order to regenerate the fabric following the removal of uranium would involve more base treatments[3]. The B2MP-based fabrics however not only do not require any pretreatment prior to being exposed to uranium in seawater, but they also exhibit excellent regenerative capacities, lose less than 20% of total capacity over 20 cycles of uranium adsorption as shown in Fig. 5.

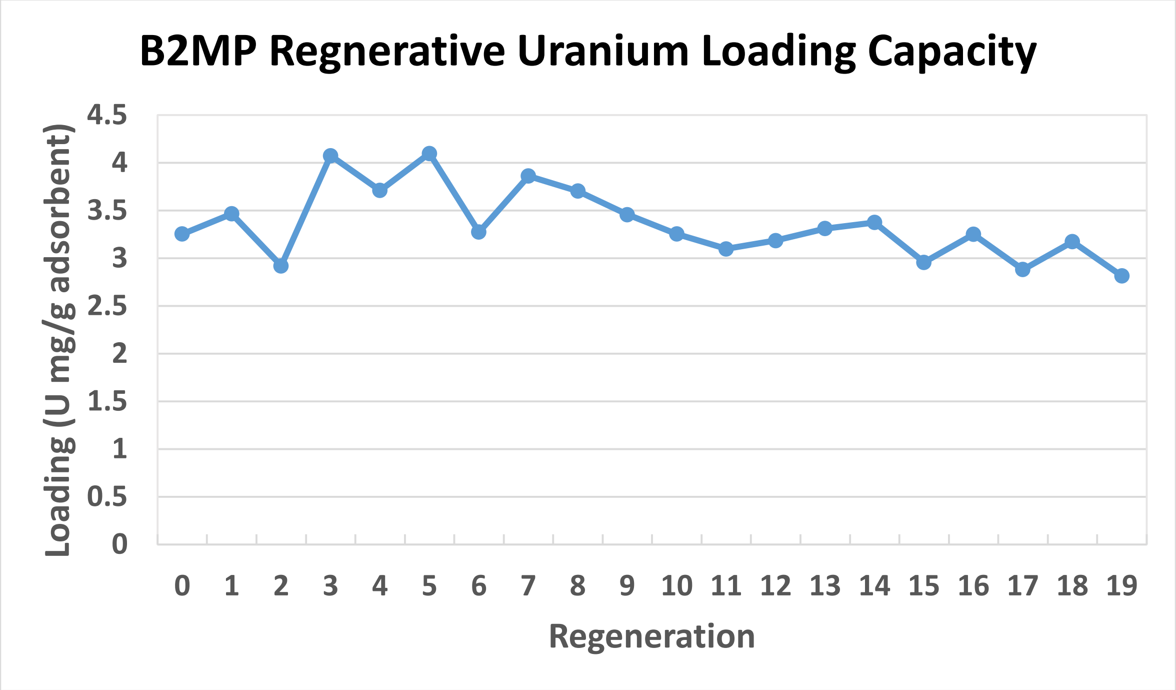


Figure 5 – Uranium loading for a B2MP fabric sample over 20 regeneration cycles.

Diallyl Oxalate (DAOx)

Oxalate salts were originally used to extract the uranium from the grafted fabric in order to improve the reusability of said fabric. It was theorized that the ability for the oxalate salt to remove the uranium could be translated to a grafted monomer. Starting with the requirements of a readily available and inexpensive monomer that contained both an oxalate group and at least one carbon-carbon double bond, diallyl oxalate was found as an optimal candidate.

The initial approach to grafting diallyl oxalate is shown schematically in Fig. 6 By dissolving either a small amount of diallyl oxalate in water or a larger amount in water in combination with a surfactant and irradiating said solution, the hydroxyl radicals produced by the radiation would be able to interact with both the monomer and the polymer substrate in order to prompt polymerization reactions. While numerous reactions are possible, three of the most important reactions are shown in the Fig. Reaction 1 and 2, substrate crosslinking and monomer homopolymerization respectively, are both undesired reactions as they do not result in the attachment of the uranium extracting, oxalate functional group to the surface of the fabric.

Reaction 3 is the most desired reaction as it results in the grafting and possible subsequent propagation of monomer grafting to the surface of the polymer.

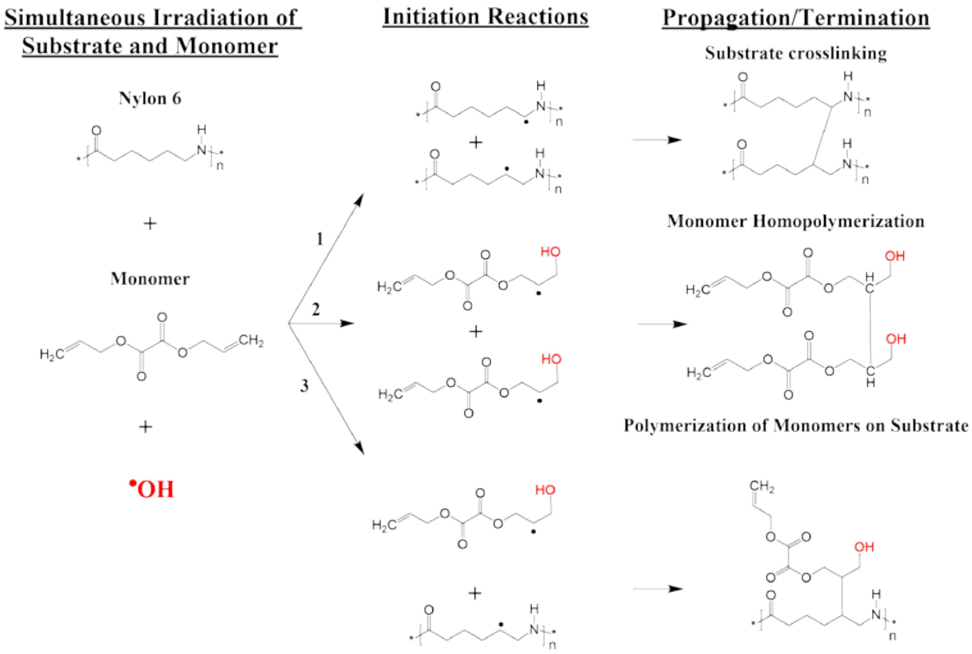


Figure 6 – Reaction mechanisms for three of the possible monomer-substrate reactions during DAOx grafting in surfactant solution. Substrate crosslinking and monomer homopolymerization, reactions 1 and 2 respectively, are undesired. Attachment of the monomer onto the substrate, reaction 3, is desired.

Unfortunately, the results of these grafting experiments did not lead to significant degrees of grafting, as shown in Fig. 7. Likewise, these low degrees of grafting resulted in low percentages of uranium removal from seawater. In order to improve upon these results with the oxalate monomer, a new approach was chosen.

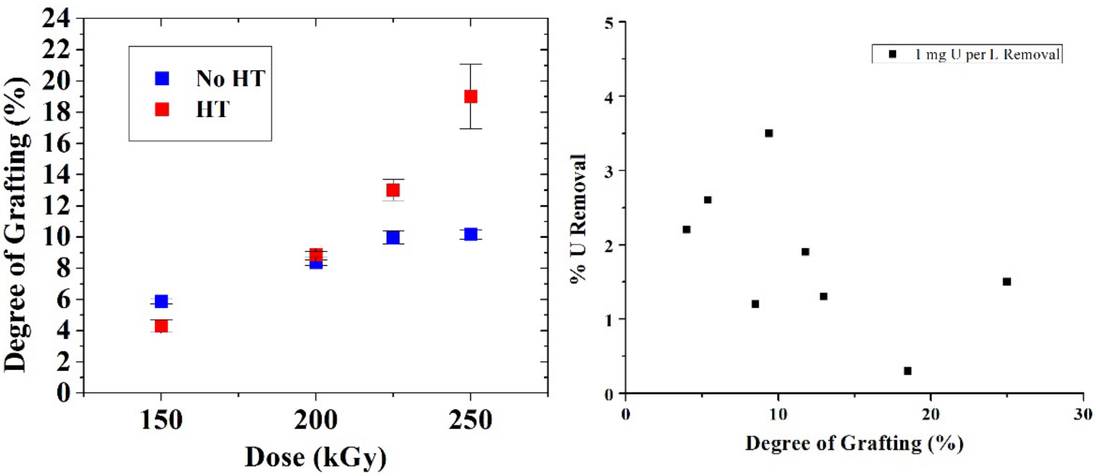


Figure 7 – Degrees of grafting (left) and uranium removal (right) for polyamide 6 fabrics grafted with DAOx using a surfactant based solution and electron beam radiation at a dose rate of about 230 kGy/hr.

DAOx at room temperature is a viscous liquid. As such, we believed that the monomer could be grafted effectively to the surface of the polyamide fabric without the use of a solvent. It was believe that the grafting and associated chemical reactions would proceed according to the mechanisms shown in Fig. 8.

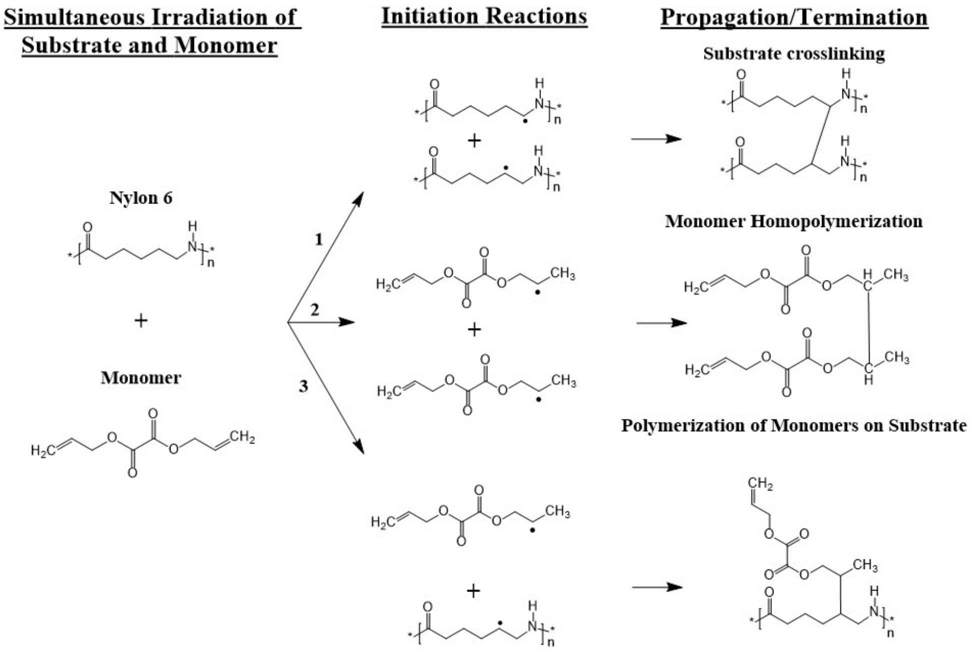


Figure 8 – Reaction mechanisms for three of the possible monomer-substrate reactions during DAOx grafting in pure DAOx. Substrate crosslinking and monomer homopolymerization, reactions 1 and 2 respectively, are undesired. Attachment of the monomer onto the substrate, reaction 3, is desired.

After extensive optimization of the “neat” grafting of DAOx, DoGs of almost 100% were obtained at doses of 250 kGy as shown in Fig. 9.

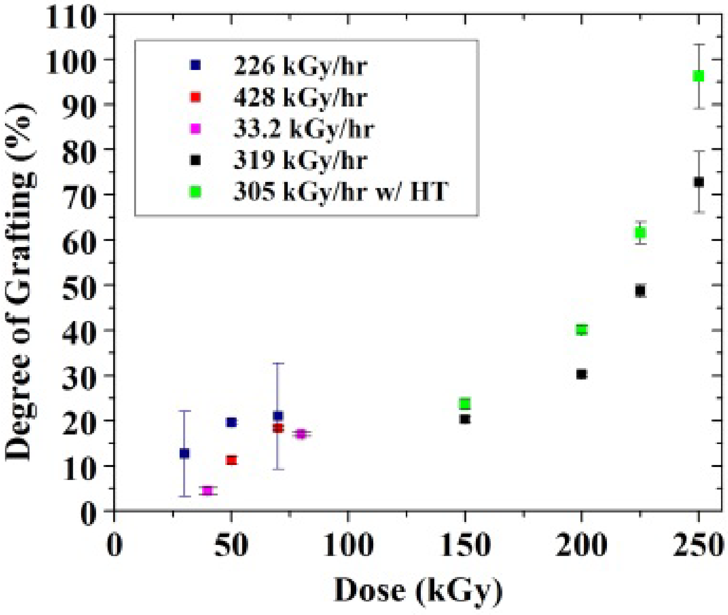


Figure 9 – Dependence of degree of grafting of DAOx monomer in pure DAOx solution on dose from electron beam irradiation.

In order to confirm that the attachment of diallyl oxalate to the surface of the polyamide was successful, x-ray photoelectron spectroscopy was used to evaluate the change in concentration of both the amount of ester and the amount of C-O bonds present at the surface of the fabric following both grafting and cleaning (in order to remove any excess oxalate that might be present at the surface). Both of these peaks within the C 1s peak of the spectrum are characteristic only of the oxalate group and not the polyamide backbone; this is reflected in the increase in both of these bond types following grafting in Fig. 10.

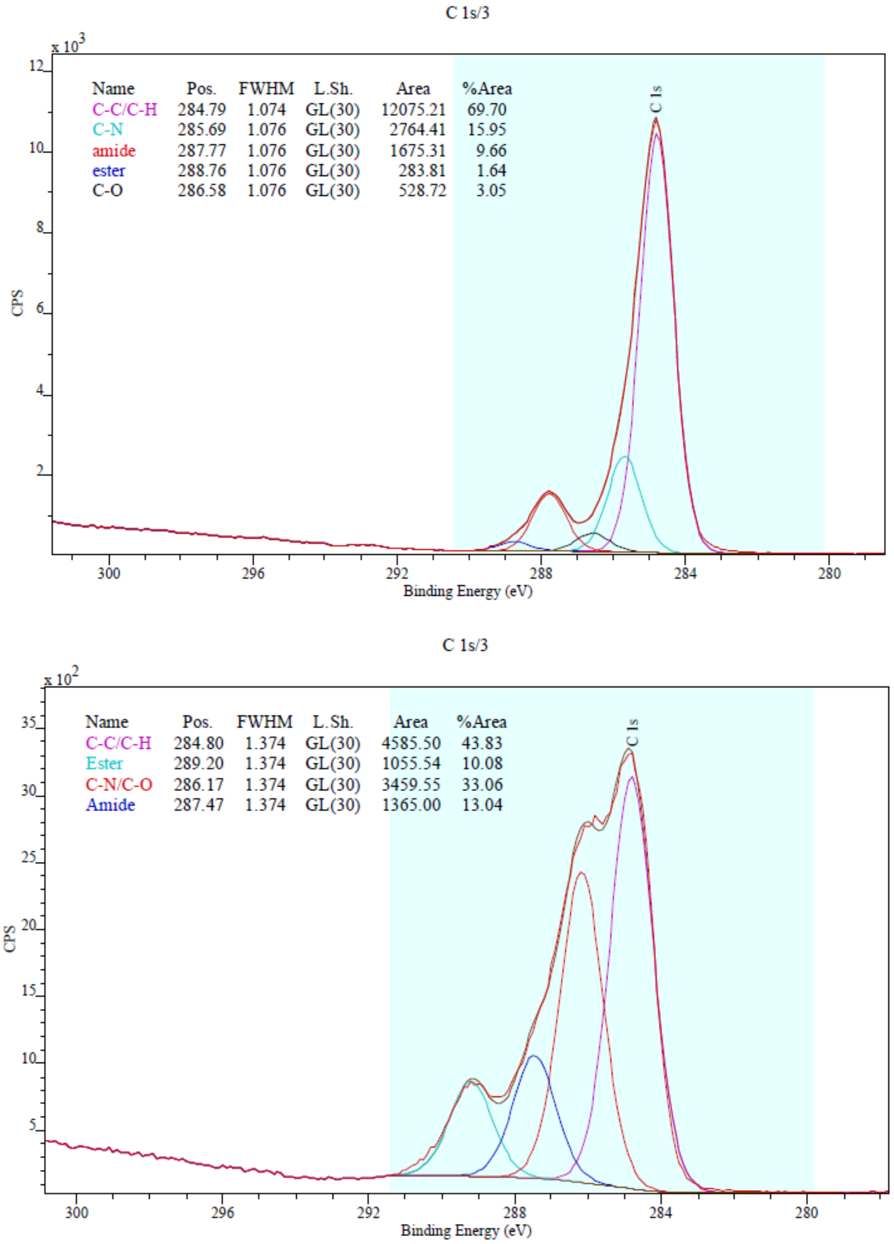


Figure 10 – The top figure shows the C 1s spectrum of ungrafted polyamide 6. The bottom figure shows the C 1s spectrum of DAOx grafted polyamide 6, which exhibits a noticeably larger ester and C-N/C-O peak due to the addition of the oxalate groups.

The ability for DAOx to adsorb uranium from seawater was then validated through laboratory testing in accordance with the previously described procedure. Testing was performed using solutions of both 0.2 and 1 mg U per L seawater. While there was not a clear trend correlating degree of grafting with % removal of uranium from solution, the best performing fabrics were able to extract greater than 50% of the total uranium in solution for 1 mg U per L seawater and greater than 30% for 0.2 mg U per L, see Fig. 11.

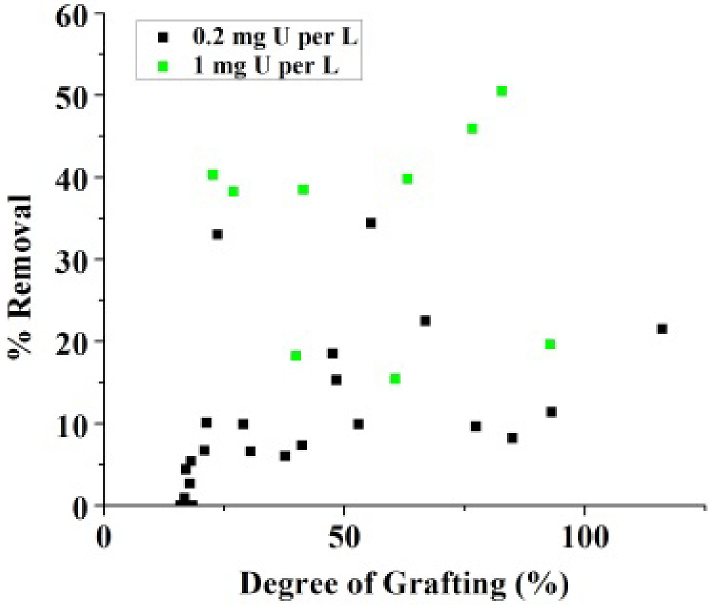


Figure 11 – Relationship between the degrees of grafting of DAOx grafted without the use of solvent and the uranium extraction efficiency for both 0.2 and 1 ppm concentrations.

Azo Compounds

Following the implementation of the spectrophotometric method for the determination of the amount of uranium removed from seawater, it was hypothesized that chemicals with similar functional groups to the one used in the spectrophotometric method would be able to extract uranium very efficiently. The monomer repertoire tested includes a number of pyridylazo compounds, such as those shown in Fig. 12.

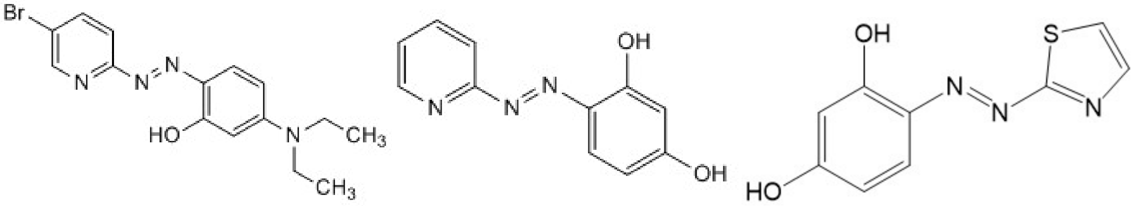


Figure 12 – The compounds shown are Bis[2-(methacryloyloxy-ethyl)] phosphate (B2MP, left), 4-(2-Pyridylazo)resorcinol (PAR, middle), and 4-(2-Thiazolylazo)resorcinol (TAR, right).

These commercially available derivatives of the azo group were found and tested initially by loading the chemicals on the surface of activated charcoal and then exposing the charcoal to different concentrations of uranium in seawater. The results from these tests are shown in Fig. 13 and 14. At only 50% ligand coverage, all of the tested compounds show greater than 80% removal of the total amount of uranium present in the 10 mL seawater sample across all concentrations. These results were very promising as previous compounds usually showed a decrease in the amount of uranium removed at lower concentrations. In order to distinguish between the different compounds more effectively, studies were done with only 5% ligand coverage on the activated charcoal. These results showed that PAN would be an optimal candidate for grafting to the surface of the substrate fabric.

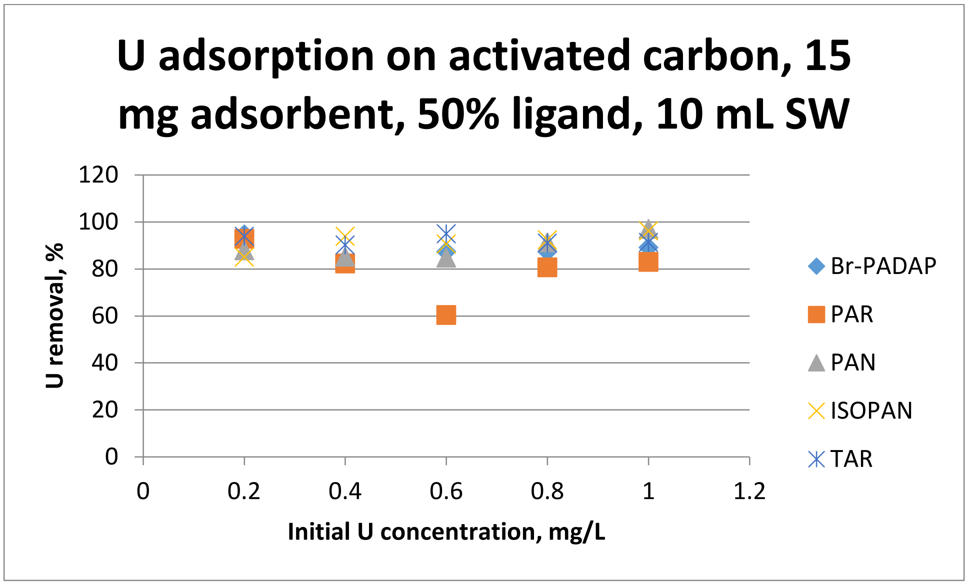


Figure 13- A comparison of the % uranium removal by activated carbon doped with 50% of ligand in 10 mL of seawater.

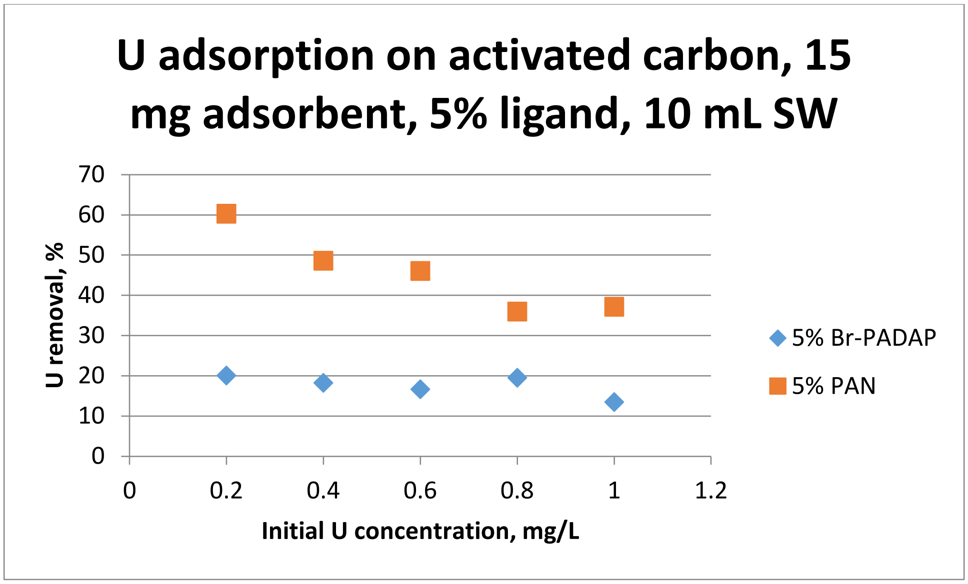


Figure 14 – A comparison of the % uranium removal by activated carbon doped with 5% of ligand in 10 mL of seawater.

Unfortunately, as delivered the compounds were not readily graftable as they contained no readily accessible allyl or vinyl functional groups. It was discovered however that the 4-(2-thiazolylazo) resorcinol compound could be chemically altered to include an allyl group without affecting the functional groups that are believed to contribute to the binding of uranium (the azo group, the nearest hydroxyl group, and the nitrogen in the thiazole ring). Through the reactions mechanism outlined in Fig. 15, two different allyl-functionalized compounds were created.

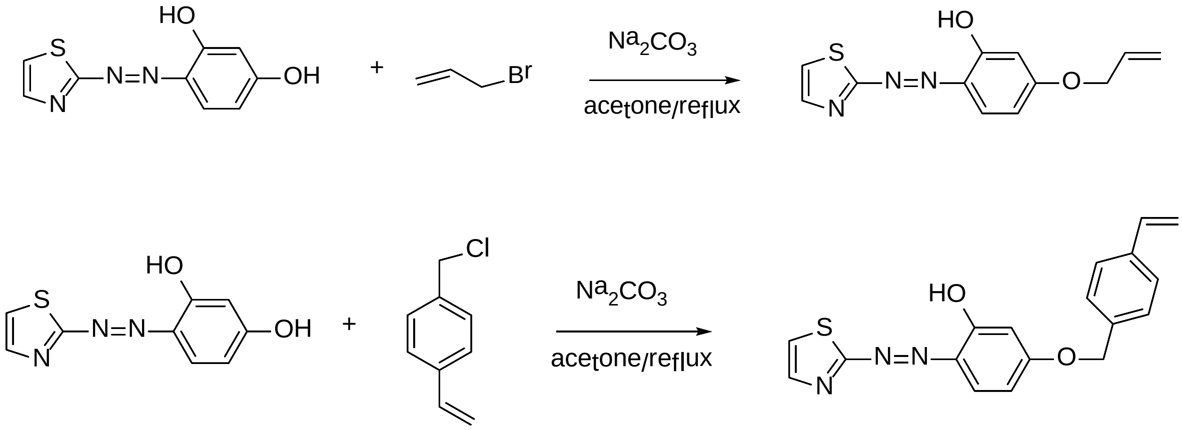


Figure 15 – The synthesis mechanisms for the allyl-functionalized azo monomers.

While numerous grafting techniques and parameters were attempted in an effort to graft these compounds, they were all mostly unsuccessful and the time and cost of synthesizing and purifying these two compounds made sample processing difficult. In order to improve on the economics and grafting density of the thiazolylazo compound on the surface of the polymer fabric, a new order was devised for processing samples. Instead of performing the chemical attachment of the allyl group to the TAR compound first, the vinylbenzyl chloride (VBC) precursor was grafted to the surface of polyamide fabric first. The resultant grafting was very high, reaching 150% DoG and higher, and much more homogeneous than previous experiments. The relationship between degree of grafting and dose for this compound is shown in Fig. 16.

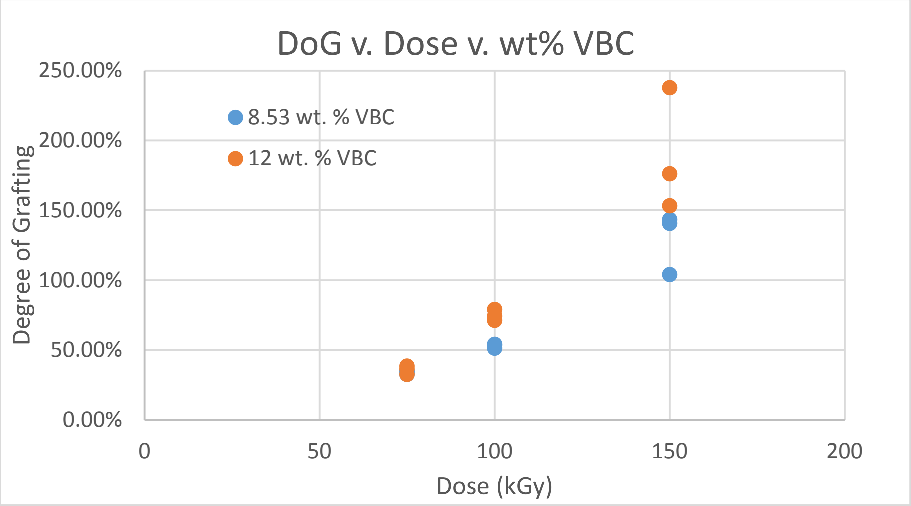


Figure 16 – The relationship between dose and degree of grafting of VBC on polyamide 6 under electron beam irradiation at a dose rate of 250 kGy/hr with two different concentrations of VBC in ethanol

After the grafting step of the chemical precursor to the surface of the polyamide fabric, the now chlorine functionalized fabric could have the TAR compound chemically attached to its surface. A scheme for this method of attaching TAR to the surface of the fabric is shown in Fig. 17. This method has several procedural improvements over the previous method. For example, the fabric grafting can be optimized prior to chemical attachment of the TAR groups, thereby reducing the amount of the more expensive TAR compound necessary to optimize the system. This method will also serve to improve the exposure of the TAR compound to the seawater environment, as the chemically attached TAR will only be attached at the surface of any homopolymer, versus being trapped inside homopolymer if the allyl-functionalized TAR had been grafted instead.

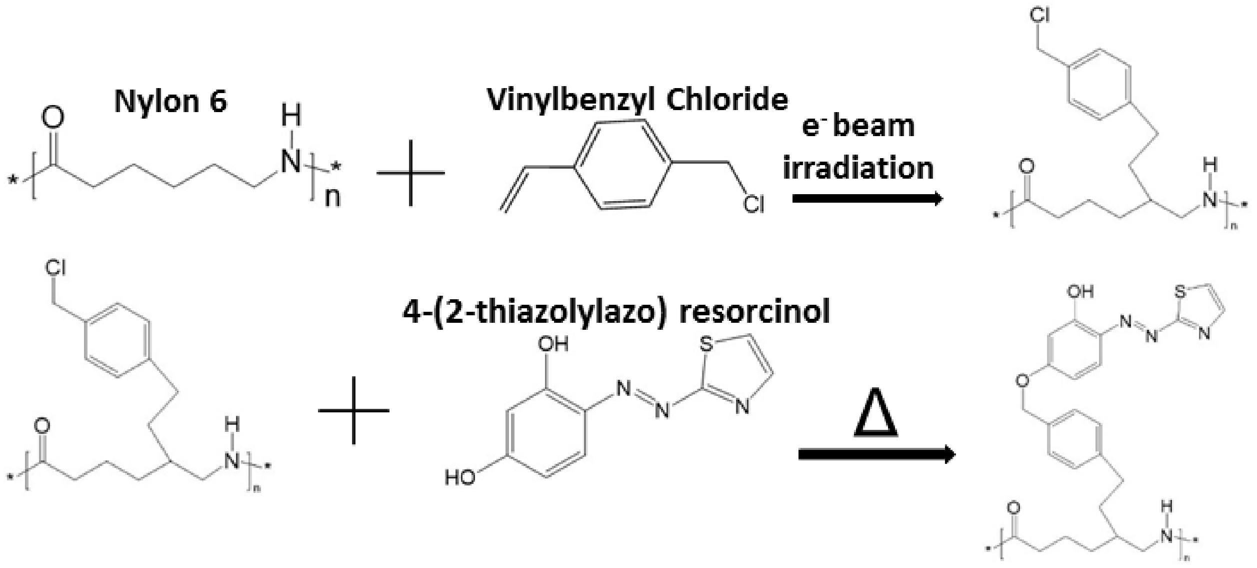


Figure 17 – The grafting and reaction mechanism for first attaching VBC to the surface of the polyamide 6 using electron beam irradiation and then chemically attaching TAR to the grafted VBC.

The preliminary results of the grafted TAR fabric are promising, as shown in Table 1. However the amount of uranium removal seen for 0.2 ppm U in 10 mL seawater is still far below what was expected based on the charcoal tests. It is believed that the potential seen in the charcoal tests can be obtained by improving the grafting density of the monomer and by increasing the surface area of the grafted polymer chains, which would in turn allow for a higher amount of TAR to be attached at their surface.

Sample	**Volume of 0.2 ppm U in seawater (mL)**	**Vinylbenyzl chloride Degree of Grafting (%)**	**% TAR Conversion from Vinylbenzyl chloride**	**% Uranium Removal**
TA1	10	146	7	27.5
TA4	10	75.0	13	18.9
TA6	10	34.1	9	18.2

Table 1 – A selection of samples produced by the irradiation grafting of VBC and then the chemical attachment of TAR with their % uranium removal from 10 mL of 0.2 ppm U in seawater solution.

References

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(2) Beltrami, D.; Cote, G.; Mokhtari, H.; Courtaud, B.; Moyer, B. A.; Chagnes, A. *Chem. Rev.* **2014**, *114* (24), 12002–12023.

(3) Seko, N.; Katakai, A.; Tamada, M.; Sugo, T.; Yoshii, F. *Sep. Sci. Technol.* **2004**, *39* (16), 3753–3767.

Award Products and Technology Transfer Activities

a. A list of the public releases of results is included below:
    i. Dietz, T. C.; Tomaszewski, C. E.; Tsinas, Z.; Poster, D.; Barkatt, A.; Adel-Hadadi, M.; Bateman, F. B.; Cumberland, L. T.; Schneider, E.; Gaskell, K.; LaVerne, J.; Al-Sheikhly, M. *Ind. Eng. Chem. Res.* **2015**.

b. A group website has been created, al-sheikhly.umd.edu, which has included announcements of events and publications surround the research associated with the project.

c. Throughout the term of the project, numerous collaborations were formed with other groups working on similar subject matter. Substrate materials, specifically the Winged nylon fabrics, were shared with Oak Ridge National Laboratory for testing of their effectiveness when grafted with other uranium extracting monomers. Samples were sent to Pacific Northwest National Laboratory for uranium extraction capacity testing in real seawater conditions. A large amount of collaboration was fostered with the National Institute of Standards and Technology, where we were able to use their radiation facilities for the monomer grafting. We also collaborated with faculty at the Catholic University of America for uranium extraction testing techniques as well as input into the possible coordination structures of uranium to our different monomers.

d. While none of the technologies or techniques used throughout this project were completely novel, they were advanced especially in regards to the creation of graft polymerized fabrics with the ability to remove solutes from solution. Specifically, the technique of irradiation grafting was improved through the study and improvement of grafting of different active functional groups to the surface of the polyamide fibers. The technique of chemically attaching uranium extraction monomers to the surface of a functionalized fabric was also not completely novel, but had not been done prior to this work with the thiazolylazo compounds on chloride functionalized polyamide fabric as far as the authors know.
e. None
f. No other products were generated as a result of this project.