Published in final edited form as:

Ind Eng Chem Res. 2016 April 20; 55(15): 4179–5214. doi:10.1021/acs.iecr.5b03401.

Uranium removal from seawater by means of polymeric fabrics grafted with diallyl oxalate through a single-step, solvent-free process

Travis C. Dietz¹, Claire E. Tomaszewski¹, Zois Tsinas², Dianne Poster³, Aaron Barkatt⁴, Mohammad Adel-Hadadi⁴, Fred B. Bateman³, Lonnie T. Cumberland³, Erich Schneider⁵, Karen Gaskell⁶, Jay LaVerne⁷, and Mohamad Al-Sheikhly^{1,*}

¹Department of Materials Science and Engineering, Univ. of Maryland, College Park, MD 20742, USA

²Department of Bioengineering, Univ. of Maryland, College Park, MD 20742, USA

³National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

⁴Department of Chemistry, The Catholic University of America, Washington, DC 20064, USA

⁵Department of Nuclear & Radiation Engineering, The University of Texas at Austin, Austin, TX 78712, USA

⁶Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, USA

⁷Department of Chemistry, Univ. of Maryland, College Park, MD 20742, USA

Abstract

In order to test the effectiveness of oxalate-based polymeric adsorbents in the recovery of uranium from seawater, diallyl oxalate (DAOx) was grafted onto nylon 6 fabrics by exposing the fabric, immersed in pure liquid DAOx or in a surfactant-stabilized dispersion of DAOx in water, to electron beam or gamma radiation. Following drying and weighing to determine the degree of grafting (DoG), the presence of oxalate in the fabrics was verified using XPS. Zeta potential measurements showed the fabric surfaces to be negatively charged. The fabrics were tested by rotating them for 7 days in a rotary agitator with actual seawater spiked with 0.2 or 1.0 mg·L⁻¹ uranium. The fraction of uranium in the solution which was removed due to uptake on the fabrics was found to rise with increasing DoG at both uranium concentrations. EDS measurements were used to map the distribution of adsorbed uranium on the polymeric fibers.

Synopsis

Pictorial representation of the radiation-induced grafting polymerization of allylic monomers on Winged Nylon 6 fabrics.

Corresponding Author: Professor Mohamad Al-Sheikhly, Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2215, mohamad@cua.edu, Phone: 301-405-5214, Fax: 301-314-2029.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Keywords

Single-step radiation graft polymerization; uranium extraction; seawater; nylon; acrylated oxalate

Introduction

Most of the work performed in recent decades on the extraction of uranium from seawater has been focused on polymer fabrics grafted with amidoxime groups^{1,2}. However, the problems associated with the use of such polymer fabrics have not yet been completely resolved. One such problem is the necessity for pre-treatment of the amidoxime-grafted polymer fabrics with alkali in order to make them hydrophilic. This results in reduced chemical and mechanical stability and prevents the adsorbent fabrics from being effectively regenerated after use without significant loss of capacity. In view of these problems, other active groups, such as phosphates³, have been considered as alternatives, but their effectiveness with respect to uranium adsorption within the pH range of seawater has been found to be limited.

The present study was intended to examine the possibility of using oxalates attached to solid surfaces as sorbents for uranium. The oxalate ion forms a variety of complexes with the uranyl ion^{4,5}. Early studies of the complexation constants showed that logarithm of the stability constant of $[(\text{UO}_2)(\text{C}_2\text{O}_4)]$ ($\log\beta_{11}$) is approximately 6.3⁶. This value significantly increases with increasing ionic strength but is only slightly affected by the pH⁵. Values of 6.77 and 12.00 were reported for the logarithms of the stability constants (β) in mildly acidic solutions for $[(\text{UO}_2)(\text{C}_2\text{O}_4)]^0$ and $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2]^{2-}$, respectively⁷. At a temperature of 25 °C and ionic strength of 3.0 M, the $\log\beta$ values of the complexes $[(\text{UO}_2)(\text{C}_2\text{O}_4)]^0$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2]^{2-}$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]^{4-}$, $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ and $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$ were found to be 6.31, 11.21, 13.8, 18.5, and 28.5, respectively⁸. At an ionic strength of 0.05 M, the $\log\beta$ value of $[(\text{UO}_2)(\text{C}_2\text{O}_4)]^0$ was reported to be 5.71⁹. An extensive study including both uranyl oxalate and uranyl oxalate hydroxide complexes at 25 °C and an ionic strength of 1.0 M, yielded, for the complexes $[(\text{UO}_2)(\text{C}_2\text{O}_4)]^0$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2]^{2-}$ and $[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]^{4-}$, $\log\beta$ values of 5.87, 190.484 and 12.61, respectively, and for the complexes $[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]\text{OH}^-$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{OH})_2]^{2-}$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2\text{OH}]^{3-}$ and $[(\text{UO}_2)(\text{C}_2\text{O}_4)_3\text{OH}]^{5-}$, $\log\beta$ values of 0.62, -6.25, 3.93 and 5.32, respectively¹⁰. Based on these values, at pH 8, an ionic strength of 1.0 M, a temperature of 25 °C, a uranyl ion concentration of 5×10^{-4} M, and a much higher oxalate concentration of 0.1 M, the majority species is $\text{UO}_2(\text{C}_2\text{O}_4)(\text{OH})_2^{2-}$ (about 65%), followed by $(\text{UO}_2)_3(\text{OH})_7^-$ (about 20%), $\text{UO}_2(\text{C}_2\text{O}_4)_2\text{OH}^{3-}$ (about 10%) and

$\text{UO}_2(\text{C}_2\text{O}_4)\text{OH}^-$ (about 5%). A roughly similar distribution is obtained under these conditions when the concentration of uranyl ion is lowered to 1×10^{-4} M and the concentration of oxalate to 3×10^{-4} M¹⁰.

Crystallographic measurements on $\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3$ have shown that each uranium atom exists as a linear $(\text{O}-\text{U}-\text{O})^{2+}$ ion with five secondary oxygen atoms coordinated to it in a perpendicular plane¹¹. According to this study, the oxalate groups have a tetradentate nature, with each oxalate group acting as a bridge between two uranyl ions using all four oxygen atoms for coordination. The oxalate groups occupy centrosymmetric positions and are planar. Further studies confirmed that the uranium atom has pentagonal bipyramidal coordination¹². The water molecules are hydrogen-bonded into zigzag chains. The resulting structure consists of $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$ chains^{12,13} with each third oxygen atom of the chain formed of water molecules coordinated to the uranium atom, with the uranyl oxalate chains linked into $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ layers¹³. The structural reported by the aforementioned papers, including the existence of hydrogen-bonded chains, have been supported by XRD and IR studies¹⁴. Furthermore, according to molecular dynamics simulations, the most stable form of the $\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3$ complex is a five-coordinate chelate¹⁵. It is reasonable to expect that the complex $\text{UO}_2(\text{C}_2\text{O}_4)(\text{OH})_2^{2-}$, which is probably the dominant form of uranyl under the conditions prevailing near the surface of an oxalate-grafted polymeric surface at pH 8 (see above) may have a similar structure to the five-coordinated $\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3$ with two of the water molecules replaced by hydroxide groups. This is compatible with the structural models described above, which represent the $\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3$ complex in the form of $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$, where two of the three water molecules being more amenable to change. Another finding that is compatible with this model is the observation that upon heating $\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3$ two of the three water molecules are lost at a much lower temperature than the third one⁶.

The present study was aimed at studying the effectiveness of polymer-grafted diallyl oxalate in removing uranium from seawater environments. Initial measurements performed with ammonium oxalate and dimethyl oxalate absorbed on active carbon showed these compounds to be largely ineffective in adsorbing uranium. However, diallyl oxalate (DAOx) was observed to have significant activity. In addition, the presence of double bonds in DAOx makes it possible to graft it onto polymeric substrates exposed to ionizing radiation. Accordingly, the study focused on measuring the uptake of uranium from seawater by polymeric fabrics grafted with diallyl oxalate under various conditions. A key objective of the study was to investigate the effects of grafting (direct or indirect), the medium (an aqueous or organic solution of DAOx or pure liquid DAOx), the radiation parameters (dose and dose rate), the dissolved gases present, etc., on the degree of grafting of the fabrics and on the effectiveness of these fabrics in removing uranium from seawater. Following the grafting process, the study was aimed at investigating the relationship between the degree of grafting and uranium uptake from seawater, as well as at characterization of the changes in chemical composition and morphology that take place during the grafting and the subsequent contact with seawater.

Experimental Section

Materials

Diallyl oxalate (DAOx) was purchased from Monomer-Polymer and Dajac Labs. Milli-Q (Millipore, Billerica, MA, USA) Type 3 water was used in all experiments. TWEEN® 20 (Sigma), Arsenazo III (Sigma-Aldrich), ethanol (Sigma-Aldrich and Pharmco-AAPER), argon gas (Ar, industrial grade), and nitrous oxide (N₂O, Grade 6.0) were used as received. Winged Fibers™ composed of nylon 6 were purchased from Allasso Industries®, Inc. For extraction experiments, seawater was collected from the Atlantic Ocean (34° 42' N, 76° 43' W). Uranyl acetate dihydrate (Fisher Scientific Company) was used in the preparation of U-spiked simulated seawater. The rotary agitator used to contact the fabrics with seawater was Model 3740-4-BRE, produced by Associated Design and Manufacturing Company.

Preparation of DAOx Grafted Fabrics

Figure 1 describes the grafting polymerization of DAOx on nylon 6 and the subsequent extraction testing. Pieces of Nylon 6 Winged Fiber fabric were cut into square pieces, each weighing approximately 20 mg. These pieces were then placed in vials along with either 10 mL of TWEEN® 20 food additive surfactant and DAOx solution or with 1-2 mL of pure DAOx monomer. The combined TWEEN® 20 and DAOx solutions were prepared by mixing and stirring quantities of TWEEN® 20, DAOx, and deionized water for at least one hour. Each vial was then purged for 20 minutes using either N₂O or Ar, respectively for the surfactant and pure monomer samples, in order to eliminate oxygen from the system and, in the case of N₂O, also to convert hydrated electrons produced by the irradiation into hydroxyl radicals. Finally, the vials were wrapped with paraffin film around the caps in order to limit the diffusion of oxygen into the vials.

The DAOx monomer was grafted to the surface of the nylon 6 fabric through the use of electron beam radiation at an energy of about 10.5 MeV, generated by the Medical-Industrial Radiation Facility at the National Institute of Standards and Technology. Up to 16 samples could be irradiated at one time using a mechanical turntable. Irradiation doses and dose rates were initially calibrated using NIST-traceable alanine dosimetry films on two sides of multiple vials on the turntable. The total dose was calculated using the average dose of the two sides, wherein a linear dose-depth profile was assumed, in conjunction with the counts obtained from a Faraday cup positioned behind the rotating samples. Following the irradiation, some samples were heat treated by placing them in an oven at 50°C for one week. Finally, samples were washed to remove excess monomer and homopolymer from the sample. Pure DAOx solution samples were rinsed with ethanol, placed in ethanol, and sonicated for about ten minutes. DAOx and surfactant solutions were rinsed with DI water, placed in a solution of TWEEN® 20 and water, and sonicated for about ten minutes. Following this initial wash, both types of samples were rinsed and washed at least two more times with DI water with a ten minute sonication between each wash. Finally, the fabric samples were rinsed with DI water and dried overnight in an oven at 60 °C. These dried samples were then weighed to determine their degree of grafting (DoG), which is calculated from $[(m_f - m_i)/m_i] \times 100$, where m_i and m_f represent the initial and final fabric masses, respectively.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos Axis 165 spectrometer using monochromatic Al radiation (at a power of 280 W) with a vacuum level at or below 5×10^{-8} torr throughout the data collection process. Due to the insulating nature of the nylon 6 samples, charge neutralization was required to minimize sample charging. All survey spectra were collected with a pass energy of 160 eV and all high resolution spectra with a pass energy of 20 eV. All spectra were calibrated to C-C/C-H bonding at 284.8 eV.

Microparticle Formulation and Zeta Potential Analysis

Microparticle solutions were prepared using pieces of nylon 6 grafted fabric via the “solvent in water” precipitation method. Samples were first dissolved in acetic acid at 80°C, at a concentration of 20 mg/mL to form the diffusing phase (organic phase). This phase was then added drop by drop into filtered deionized water (DI), which is the dispersing phase (aqueous phase), under moderate magnetic stirring. The formation of microparticles was instantaneous and the solution was kept under mild agitation for 4 h to allow for particle stabilization. Small aliquots from each microparticle solution were diluted in DI water and titrated to pH 8.3, pH 4.5, and pH 3 using sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions prior to surface charge characterization. The zeta potential of nylon 6 microparticles was assessed by means of electrophoretic light scattering (Zetasizer nano-ZS90; Malvern instruments; Westborough, MA).

Adsorption Experiments

Test solutions of uranium in seawater were prepared by dissolving a suitable quantity of uranyl acetate dihydrate in Atlantic Ocean Seawater. In each test, the adsorbent sample was added to a desired volume of a solution of uranium in seawater and the combination of test solution and solid adsorbent was rotated for a desired period of time at 30 rpm in a rotating agitator. At the end of this period, the solution was separated from the adsorbent and analyzed to determine the amount of uranium remaining in the solution by means of a spectrophotometric method based on the use of Arsenazo III as a color-forming reagent¹⁶. Arsenazo III forms a complex with uranium with an absorption peak at 651 nm. Each test was carried out 4 times under identical conditions. The fraction of the uranium taken up by the adsorbent was calculated from the difference in concentration of uranium in the test solution resulting from the contact with the adsorbent. The remaining solid adsorbent was dried in air and set aside for characterization by means of spectroscopic techniques such as XPS and SEM-EDS.

Scanning Electron Microscopy

A scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) detector was used to characterize the morphology of the adsorbent fabric and to identify the chemical species extracted by it. Adsorbent samples that have been exposed to Atlantic Ocean Seawater during the adsorption experiments were dried overnight in a vacuum dessicator and mounted on a SME aluminum stub for EDS analysis. The EDS detector was part of a Hitachi S-3400 variable pressure SEM.

Results and Discussion

Direct radiation grafting of DAOx onto nylon 6 was performed in the absence of oxygen in neat liquid DAOx and also in aqueous solutions in the presence of a surfactant.

Radiation grafting in the absence of solvents

In these experiments, the oxygen-free mixtures contain only DAOx and nylon 6. Figure 2 shows that as the dose increases, the degree of grafting increases. The irradiation was carried out at room temperature at varying dose rates. As shown in Scheme 1, radiation induces the formation of the C-centered free radicals of nylon $\bullet$ and DAOx $\bullet$. These free radicals undergo various desired reactions (grafting through the formation of C-C bonds between DAOx and the nylon 6), as well as undesired reactions, consisting of DAOx homopolymerization and the crosslinking reactions of nylon $\bullet$.

Therefore, under our experimental conditions, the decay rates of the DAOx $\bullet$ and nylon $\bullet$ can be expressed as follows:

$$\begin{aligned} \frac{-d[\text{DAOx}\bullet]}{dt} = & k_1[\text{nylon}\bullet][\text{DAOx}\bullet] + 2k_2[\text{DAOx}\bullet]^2 + k_3[\text{DAOx}\bullet][\text{DAOx}] \\ & + k_4[\text{nylon} - (\text{DAOx})_n - \text{DAOx}\bullet][\text{DAOx}\bullet] \end{aligned}$$

$$\frac{-d[\text{nylon}\bullet]}{dt} = k_1[\text{nylon}\bullet][\text{DAOx}\bullet] + k_5[\text{nylon}\bullet][\text{DAOx}] + 2k_6[\text{nylon}\bullet]^2$$

where k_1 , k_2 , k_3 , k_4 , k_5 , k_6 are the rate constants of the desired grafting reaction, the undesired termination reaction of the DAOx $\bullet$ radicals, the undesired homopolymerization reaction of the DAOx, the termination reaction of the growing grafted DAOx $\bullet$ radicals, the desired grafting-addition reaction of the DAOx on nylon, and the undesired crosslinking reaction of the nylon, respectively.

Figure 2 also shows that after receiving a dose of more than approximately 175 kGy, the grafting density increases much more sharply as a function of dose. This can be explained by the fact that as the viscosity of the medium increases with increasing dose, the diffusion of the DAOx $\bullet$ radicals is slowed down, thus hindering the homopolymerization reactions and enhancing the grafting on the nylon surface.

Radiation grafting in aqueous solutions and in the presence of a surfactant

Degrees of grafting as high as 25 % have been reached in the aqueous, N₂O-saturated mixtures containing 0.11 M DAOx and 4.5×10^{-3} M TWEEN® 20. Under these experimental conditions, water absorbed most of the electrons from the electron accelerator resulting in the formation of the following active species with their radiation chemical yields in micromole per joule:

$$G(\bullet\text{OH}) = G(e_{\text{aq}}^-) = G(\text{H}_3\text{O}^+) = 0.28, G(\bullet\text{H}) = 0.062, G(\text{H}_2) = 0.042, G(\text{H}_2\text{O}_2) = 0.082$$

Hydroxyl radicals ($\bullet\text{OH}$) constitute a powerful oxidant, and they are highly reactive (through addition, abstraction or electron transfer). The $\bullet\text{OH}$ radicals are responsible for initiating the grafting polymerization and other reactions in this system through the production of $\text{DAOx}\bullet$ and nylon $\bullet$ radicals upon reacting with nylon and DAOx. On the other hand, hydrated electrons (e_{aq}^-) are very strong reducing radicals and can be converted to $\bullet\text{OH}$ radicals through the following reactions:

The above reaction is very fast, having a reaction rate constant of $k = 8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ¹⁷. Hence, saturating the system with N_2O prior to irradiation, would double the $\bullet\text{OH}$ yield to $G(\bullet\text{OH}) = 0.56$ micromole per joules. In addition to $\bullet\text{OH}$, H-atoms ($\bullet\text{H}$) with $G(\bullet\text{H}) = 0.062$ micromole per joule, also react with nylon and DAOx to produce $\text{DAOx}\bullet$ and nylon $\bullet$.

Under these irradiation conditions and in the absence of oxygen, the radiolytically produced $\bullet\text{OH}$ radicals and H-atoms add to the unsaturation site of DAOx and abstract H-atom from the backbone of the polymer substrate (nylon) producing $\text{OH-DAOx}\bullet$, and $\text{H-DAOx}\bullet$ radicals, and nylon(-H) radicals, respectively. It should be mentioned that $\bullet\text{OH}$ and $\bullet\text{H}$ are also scavenged by the TWEEN surfactant, since the mixture contains, $4.2 \times 10^{-3} \text{ M}$ TWEEN, leading to a decrease in the concentrations of $\text{OH-DAOx}\bullet$, $\text{H-DAOx}\bullet$, and nylon(-H) radicals. This also leads to the possibility of TWEEN being grafted on nylon 6. This can dramatically decrease the number of sites available for uranium adsorption.

Surface characterization using XPS and Zeta Potential

Figure 3 shows the XPS spectra of the ungrafted nylon and of the nylon radiation-grafted with DAOx. The XPS results demonstrate the presence of C-C/CH, oxalate, amide, C-N, and ester groups.

In order to reinforce the hypothesis that the uranyl ion is binding to the negative oxalate group attached to the nylon 6 fabric, zeta potential measurements were performed on grafted and ungrafted nylon 6 fabric that had been chemically transformed into microparticles. The zeta potentials for both the grafted and ungrafted nylon 6 fabric were measured and the results are summarized in Table 1. These results show that at a pH of about 8 the surface of the oxalate-grafted fabric is negatively charged and thus suitable for extraction of UO_2^{2+} from the seawater.

Uranium Removal from Spiked Seawater

The results obtained for the removal of uranium from spiked seawater by means of nylon 6 fabrics grafted with neat diallyl oxalate are shown in Figure 4. The level of spiking was either 1.0 mg/L or 0.2 mg/L U (introduced as uranyl acetate). In each test, a sample weighing approximately 30 mg was rotated with 10 mL of the spiked seawater at 30 rpm for

7 days. The results show that significant removal of uranium from these solutions (>5%) took place when the degree of grafting exceeded approximately 18%, and, in general, the percent removal of uranium from both the 1.0-mg/L and 0.2-mg/L U solutions increased with increasing degree of grafting. The large scatter in the data can be ascribed to the non-uniform distribution of the grafted material on the nylon 6 fibers as observed by SEM (see below). Another reason for the scatter is associated with the fact that some of the adsorbent samples were subjected, following the radiation induced grafting, to heat treatment at 50°C for 7 days. The percent removal of uranium from the test solutions observed with these samples was generally higher than the corresponding percent removal observed with samples which did not undergo heat treatment. It should also be noted that the amounts of uranium in the test solutions were very small (0.01 or 0.002 mg, respectively) so that the results in Figure 4 cannot provide a realistic estimate of the maximum amount of uranium that can be removed by the fabric from large volumes of seawater.

On the other hand, the extent of extraction of uranyl ion from seawater by means of fibers grafted with DAOx in an aqueous environment in the presence of TWEEN was very low (<5%). This may be due to the grafting of TWEEN onto nylon, which hinders the grafting of DAOx onto nylon, since a large fraction of the $\bullet\text{OH}$ radicals may react with TWEEN, producing TWEEN $\bullet$ radicals.

SEM/EDS Results

The SEM observations showed a non-uniform distribution of the grafted material on the fibers, with some sections of the fibers coated with significant amounts of grafted material and other sections free of such coating. However, the EDS results (see Table 2) obtained for the fabrics following contact with the uranium-spiked seawater were remarkably similar for different regions of the fabrics, showing that the relative affinities of the adsorbent for the various ionic solutes in the seawater were consistent across the entire structure of the fabric.

Conclusions

In conclusion, our results demonstrate that radiation grafting polymerization of DAOx on nylon 6 through a solvent-free, single-step-direct process can be accomplished in the absence of oxygen. The desired reaction between the radiolytically produced nylon $\bullet$ and DAOx $\bullet$ C-centered radicals to form the grafting C-C bonds occurs despite the strong competition from the DAOx homo-polymerization reaction. These results also show that at radiation doses up to around 175 kGy, the undesirable homo-polymerization is the predominant reaction. However, as the viscosity increases due to the homo-polymerization reaction, the diffusion of the DAOx $\bullet$ C-centered radicals is slowed down. This hinders the homo-polymerization reaction and enhances the local grafting reaction, and this allows reaching a grafting density of 140% at a dose level of 250 kGy.

A further series of experiments employed direct radiation grafting of DAOx onto nylon 6 using N₂O-saturated aqueous solutions containing DAOx and the surfactant TWEEN. These experiments showed that a degree of grafting 25% can be achieved at dose of 250 kGy. This relatively low grafting density may be explained by the fact that the surfactant TWEEN also

scavenges the $\bullet\text{OH}$ radicals, causing a decrease in the radiolytic yields of nylon $\bullet$ and DAOx $\bullet$ C-centered radicals, and thus its presence causes a decrease in the grafting density.

As expected, Figure 4 shows that as the grafting density increases, the extraction of uranyl from spiked seawater increase. The scattering of the results of the percentage extraction can be related to the non-uniformity of the grafting within the samples. This non-uniformity in the grafting is the principal disadvantage of the solvent-free grafting. Notwithstanding this disadvantage, removal of as much as 50% of the uranium from the test solution was achieved using adsorbent fabrics produced using this method. In general, it was observed that the measured extent of uranium uptake from the seawater, whether spiked with 1 mg/L or 0.2 mg/L of uranium, increased with the degree of grafting of oxalate on the polymeric fabric.

Acknowledgments

The authors are indebted to the USA Department of Energy Nuclear Energy University Program (NEUP) for the financial support of this work through award number: DE-NE0000723.

ABBREVIATIONS

DAOx	diallyl oxalate
DoG	degree of grafting
XPS	X-ray photoelectron spectroscopy
EDS	energy-dispersive X-ray spectroscopy
DI	deionized water
SEM	scanning electron microscope

References

1. Kim J, Tsouris C, Mayes RT, Oyola Y, Saito T, Janke CJ, Dai S, Schneider E, Sachde D. Recovery of Uranium from Seawater: A Review of Current Status and Future Research Needs. *Sep Sci Technol.* 2013; 48(3):367–387.
2. Kim J, Tsouris C, Oyola Y, Janke CJ, Mayes RT, Dai S, Gill G, Kuo L-J, Wood J, Choe K-Y, Schneider E, Lindner H. Uptake of Uranium from Seawater by Amidoxime-Based Polymeric Adsorbent: Field Experiments, Modeling, and Updated Economic Assessment. *Ind Eng Chem Res.* 2014; 53(14):6076–6083.
3. Das S, Pandey AK, Athawale AA, Natarajan V, Manchanda VK. Uranium Preconcentration from Seawater Using Phosphate Functionalized Poly(propylene) Fibrous Membrane. *Desalination Water Treat.* 2012; 38(1–3):114–120.
4. Havel J. Spectrophotometric Study of Complex Formation of Uranyl with Oxalic Acid. *Collect Czechoslov Chem Commun.* 1969; 34(11):3248.
5. Erten H, Mohammed A, Choppin G. Variation of Stability-Constants of Thorium and Uranium Oxalate Complexes with Ionic-Strength. *Radiochim Acta.* 1994; 66–7:123–128.
6. Grinberg AA, Ptitsyn BV, Tekster EH. Physico-Chemical Properties of Aqueous Solutions of Complex Uranyl Oxalates. *Trans Radium Inst Acad Sci USSR.* 1956; 7:74–86.
7. Moskvina AI, Zakharova FA. Study of Formation of Uranyl Complex Ions in Oxalate Solutions by the Solubility Method. *Zhurnal Neorganicheskoi Khimii.* 1959; 4:2151–2160.

8. Havel J, Soto-Guerrero J, Lubal P. Spectrophotometric Study of Uranyl–oxalate Complexation in Solution. *Polyhedron*. 2002; 21(14–15):1411–1420.
9. Petit J, Geertsen V, Beaucaire C, Stambouli M. Metal Complexes Stability Constant Determination by Hyphenation of Capillary Electrophoresis with Inductively Coupled Plasma Mass Spectrometry: The Case of 1:1 Metal-to-Ligand Stoichiometry. *J Chromatogr A*. 2009; 1216(18):4113–4120. [PubMed: 19303078]
10. Crea F, De Robertis A, De Stefano C, Sammartano S. Dioxouranium(VI)–carboxylate Complexes: A Calorimetric and Potentiometric Investigation of Interaction with Oxalate at Infinite Dilution and in NaCl Aqueous Solution at $I = 1.0 \text{ Mol L}^{-1}$ and $T = 25 \text{ }^{\circ}\text{C}$. *Talanta*. 2007; 71(2):948–963. [PubMed: 19071399]
11. Jayadevan NC, Chackraburty. Crystal and Molecular-Structure of Uranyl Oxalate Trihydrate. *Acta Crystallogr Sect B-Struct Sci*. 1972; B 28(V15):3178–3182.
12. Mikhailov YN, Gorbunova YE, Shishkina OV, Serezhkina LB, Serezhkin VN. X-Ray Diffraction Study of the Crystals of $(\text{NH}_4)_6[(\text{UO}_2)_2(\text{C}_2\text{O}_4)(\text{SeO}_4)_4] \cdot 2\text{H}_2\text{O}$ and Refinement of the Crystal Structure of $[\text{UO}_2(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$. *Inorg Chem*. 1999; 44(9):1370–1375.
13. Artem'eva MY, Serezhkin VN, Smirnov OP, Plakhtii VP. Neutron Diffraction Study of Uranyl Oxalate $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{D}_2\text{O})] \cdot 2\text{D}_2\text{O}$. *Russ J. Inorg Chem*. 2006; 51(8):1307–1310.
14. Giesting PA, Porter NJ, Burns PC. Uranyl Oxalate Hydrates: Structures and IR Spectra. *Z Für Krist*. 2006; 221(4):252–259. 2006.
15. Bühl M, Grenthe I. Binding Modes of Oxalate in $\text{UO}_2(\text{oxalate})$ in Aqueous Solution Studied with First-Principles Molecular Dynamics Simulations. Implications for the Chelate Effect. *Dalton Trans*. 2011; 40(42):11192–11199. [PubMed: 21901192]
16. Strelow FWE, Van Der Walt TN. Comparative Study of the Masking Effect of Various Complexans in the Spectrophotometric Determination of Uranium with Arsenazo III and Chlorophosphonazo III. *Talanta*. 1979; 26(7):537–542. [PubMed: 18962484]
17. Dainton FS, Logan SR. Radiolysis of Aqueous Solutions Containing Nitrite Ions and Nitrous Oxide. *Trans Faraday Soc*. 1965; 61(0):715–722.

Figure 1.
Detailed synthetic method for the single- step grafting process of the DAOx monomer to the surface of the Winged Nylon 6 fabric and the subsequent extraction testing.

Figure 2. Grafting density of pure DAOx on nylon 6 as a function of dose at various dose rates in the absence of oxygen. HT = heat treatment following irradiation.

Figure 3.

Comparison between the XPS spectra of ungrafted nylon 6 (a,c) and DAOx-grafted nylon 6 (b,d). The presence of the ester peak in the grafted nylon 6 can be attributed to the grafting of the oxalate group.

Figure 4.
The percent uranium removal of the fabrics from uranyl acetate and seawater solutions doped to the respective levels.

Scheme 1.

Reaction of the graft polymerization reactions of neat monomer on the nylon 6 fabric in the absence of oxygen and solvent.

Table 1

The average sizes and zeta potentials of the grafted and non-grafted nylon 6 microparticles.

	Particles from grafted nylon 6	Particles from non-grafted nylon 6
Average Size	$5.6 \pm 1.6 \mu\text{m}$	$1.5 \pm 0.12 \mu\text{m}$
Zeta Potential in acidified DI Water (pH ~ 3)	$26.4 \pm 0.5 \text{ mV}$	$40.1 \pm 3.1 \text{ mV}$
Zeta Potential in acidified Seawater (pH ~ 4.5)	$-3.9 \pm 0.3 \text{ mV}$	$-3.9 \pm 0.4 \text{ mV}$
Zeta Potential in Seawater with pH adjusted to ~8.3	$-6.1 \pm 0.9 \text{ mV}$	$-4.6 \pm 0.5 \text{ mV}$

Table 2

Comparison of different DAOx grafted nylon 6 samples in terms of their selectivity for uranium versus sodium as measured by EDS.

Sample	Degree of Grafting	% U Removal (from 0.2 mg U*L ⁻¹)	Atomic % U on Surface	Atomic % Na on Surface
DA310	20.96%	6.7	32.8	51.2
DA318	47.60%	18.5	26.7	58.9
DA321	77.39%	9.6	26.3	59.2
DA324	76.69%	45.9 [†]	28.4	55.0

[†] - % U Removal from 1 mg U*L⁻¹