

Uranium Removal from Seawater by Means of Polyamide 6 Fibers Directly Grafted with Diallyl Oxalate through a Single-Step, Solvent-Free Irradiation Process

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ABSTRACT: To test the effectiveness of oxalate-based polymeric adsorbents in the recovery of uranium from seawater, diallyl oxalate (DAOx) was grafted onto polyamide 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 γ radiation. After the fabrics were dried and weighed 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.

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 pretreatment 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 phosphates,³ 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 the logarithm of the stability constant of $[(\text{UO}_2)(\text{C}_2\text{O}_4)]^0$ ($\log \beta_{11}$) is approximately 6.3.⁶ This value significantly increases with increasing ionic strength but is only slightly affected by the pH.⁵ 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 $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2]^{2-}$, respectively.⁷ 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, respectively.⁸ 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 5.71.⁹ 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, 10.484, and 12.61, respectively, and for the complexes $[(\text{UO}_2)(\text{C}_2\text{O}_4)\text{OH}]^-$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{OH})_2]^{2-}$, $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2\text{OH}]^{3-}$, 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, respectively.¹⁰ On the basis of 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 is lowered to 3×10^{-4} M.¹⁰

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 $(\text{O}-\text{U}-\text{O})^{2+}$

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ion with five secondary oxygen atoms coordinated to it in a perpendicular plane.¹¹ 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 coordination.¹² 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 $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ layers.¹³ The structure reported by the aforementioned papers, including the existence of hydrogen-bonded chains, has been supported by XRD and IR studies.¹⁴ 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 chelate.¹⁵ 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 $[\text{UO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$, with 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 one.⁶ In summary, it has been demonstrated that oxalate forms a complex with uranyl that can be attributed to the coordination chemistry. The attraction of the anionic oxalate to the cationic uranyl complex marginally affects the binding between the two species.

The present study was aimed at studying the effectiveness of polymer-grafted diallyl oxalate in removing uranium from seawater environments. The selection of this fabric in addition to capacity is also subject to numerous other factors that could impact its ability to extract uranium in a real-world seawater environment, including long-term stability of the grafted monomer, efficiency of uranium desorption, and the amount of biofouling. The focus of this work was aimed at reducing the number of chemicals and steps required for fabrication that would maintain a considerable uranium capacity as compared to previous studies, such as those performed on amidoxime ligands. 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 the 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 Laboratories. 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 (N_2O , grade 6.0) were used as received. Winged Fibers composed of polyamide 6 were purchased from Allasso Industries, Inc. These fibers have an average surface area of about $14 \text{ m}^2/\text{g}$ or higher and a cross-sectional width and length between 1 and $100 \mu\text{m}$.¹⁶ An image of the cross sectional view of a representative fiber is shown in Figure 1.



Figure 1. An SEM image of a Winged Fiber cross section.

For extraction experiments, seawater was collected from the Atlantic Ocean ($34^\circ 42' \text{ N}$, $76^\circ 43' \text{ W}$). 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 2 describes the grafting polymerization of DAOx on polyamide 6 and the subsequent extraction testing. Pieces of Polyamide 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 1 h. Each vial was then purged for 20 min using either N_2O or an inert gas (Ar or N_2), respectively, for the surfactant and pure monomer samples, in order to eliminate oxygen from the system and, in the case of N_2O , 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 the limit the diffusion of oxygen into the vials.

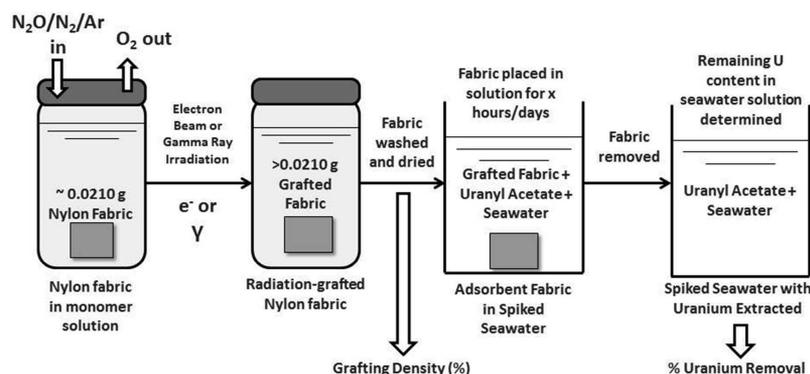


Figure 2. Detailed synthetic method for the single-step grafting process of the DAOx monomer to the surface of the Winged Polyamide 6 fabric and the subsequent extraction testing.

The DAOx monomer was grafted to the surface of the polyamide 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 1 week. Finally, samples were washed to remove excess monomer and homopolymer. Samples made with pure DAOx solution were rinsed with ethanol, placed in ethanol, and sonicated for about 10 min. Samples prepared in a solution of DAOx and surfactant were rinsed with DI water, placed in a solution of TWEEN 20 and water, and sonicated for about 10 min. Following this initial wash, both types of samples were rinsed and washed at least two more times with DI water with a 10 min 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.

The samples used to fabricate the polyamide 6 microparticles were initially grafted with DAOx through the use of a 5 kGy/h gamma irradiator. There was no subsequent heat treatment. The samples were washed and dried using the same method as that performed for samples prepared in a solution of DAOx and surfactant except the initial washing solution did not include TWEEN 20.

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. Owing to the insulating nature of the polyamide 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 were collected 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 polyamide 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 polyamide 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 reagent.¹⁷ 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 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 were exposed to Atlantic Ocean seawater during the adsorption experiments were dried overnight in a vacuum desiccator 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 polyamide 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 polyamide 6. Figure 3 shows that as the dose increases, the

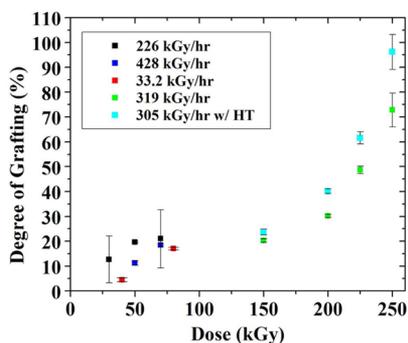


Figure 3. Grafting density of pure DAOx on polyamide 6 as a function of dose at various dose rates in the absence of oxygen. HT = heat treatment following irradiation.

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 polyamide[•] and DAOx[•]. These free radicals undergo various desired reactions (grafting through the formation of C–C bonds between DAOx and the polyamide 6), as well as undesired reactions, consisting of DAOx homopolymerization and the cross-linking reactions of polyamide[•].

Under our experimental conditions, the production of networks is unlikely, owing to the fact that during radiolysis, the concentrations of [DAOx] stay much higher than that of [DAOx[•]]. Therefore, the probability of the ionizing radiation interactions with DAOx to produce [DAOx[•]] is by far much

higher than the probability of interactions with DAOx[•] to produce •DAOx[•].

Certainly, there are H atoms produced during the radiolytic production of DAOx[•] and polyamide[•]. However, since the concentrations of [DAOx] monomer are much higher than the radiolytically produced [H], the probability of H reactions with DAOx through addition reactions to its double bond, producing another DAOx[•], would be much higher than H + H → H₂. H₂ can also be produced through the abstraction of H atoms from polyamide by the radiolytically-produced H; H + polyamide → polyamide[•] + H₂.

Therefore, under our experimental conditions, the decay reactions of the DAOx[•] and polyamide[•] can be represented as follows:

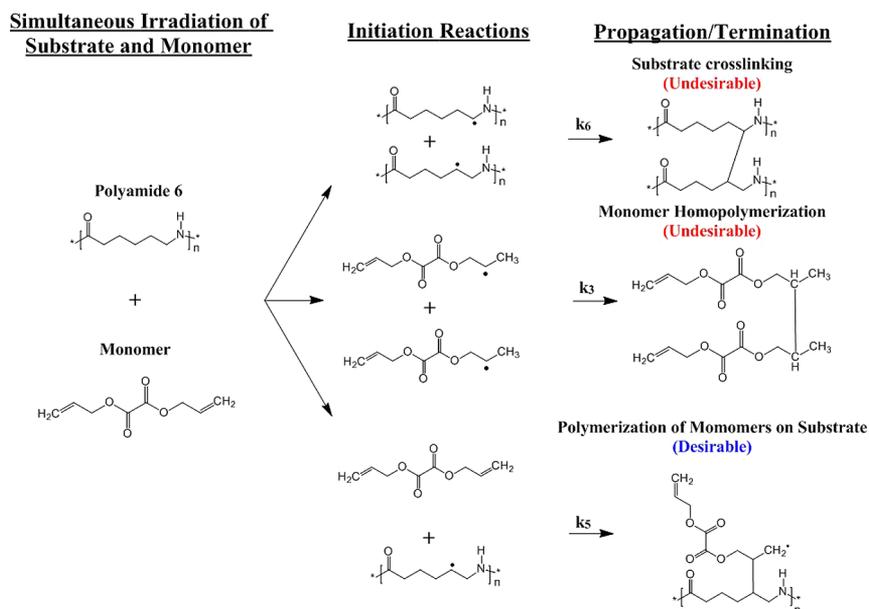
$$\begin{aligned} \frac{-d[\text{DAOx}^{\bullet}]}{dt} &= k_1[\text{nylon}^{\bullet}][\text{DAOx}^{\bullet}] + 2k_2[\text{DAOx}^{\bullet}]^2 \\ &+ k_3[\text{DAOx}^{\bullet}][\text{DAOx}] + k_4[\text{nylon} - (\text{DAOx})_n \\ &- \text{DAOx}^{\bullet}][\text{DAOx}^{\bullet}] \end{aligned}$$

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

where k_1 , k_2 , k_3 , k_4 , k_5 , and k_6 are the rate constants of the desired grafting reaction, the undesired termination reaction of the DAOx[•] radicals, the undesired homopolymerization reaction of the DAOx, the termination reaction of the growing grafted DAOx[•] radicals, the desired grafting-addition reaction of the DAOx on polyamide, and the undesired cross-linking reaction of the polyamide, respectively.

To cause desired reactions 1 and 5 to become the predominant reactions, dose rates as low as possible and high concentrations of the [DAOx] monomer were implemented. Although a higher dose rate (\dot{D}) enhances the desirable-grafting reaction 1, it also enhances the undesirable reaction 2. On the other hand, a lower dose rate enhances the desirable grafting

Scheme 1. Reaction of the Graft Polymerization Reactions of Neat Monomer on the Polyamide 6 Fabric in the Absence of Oxygen and Solvent



reaction 5 and the undesired homopolymerization reaction 3. Therefore, it is very crucial to optimize the dose rate and initial [DAOx] concentration to reach higher degrees of grafting. It should also be mentioned that in general, reaction rate constants k_1 and k_2 are very fast in comparison with the other reaction rate constants since they are radical–radical reactions. The reaction rate constants of the addition reactions k_3 and k_5 are much slower. However, the overall reaction rate of these addition reactions can be enhanced by increasing the initial [DAOx] concentration.

The symbol [polyamide•] does not represent a bulk concentration in solution, which can be expressed in units of mol L⁻¹, but an effective surface concentration representing the number of reactive radicals available for reaction with monomers in the surrounding solution. This number is particularly high in the present case since high surface area Winged Fibers are used.

Figure 3 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• radicals is slowed down, thus hindering the homopolymerization reactions and enhancing the grafting on the polyamide 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. In these experiments, the oxygen-free mixtures contain only DAOx and polyamide 6. The irradiation was carried out at room temperature at about the same dose rate. Figure 4 shows

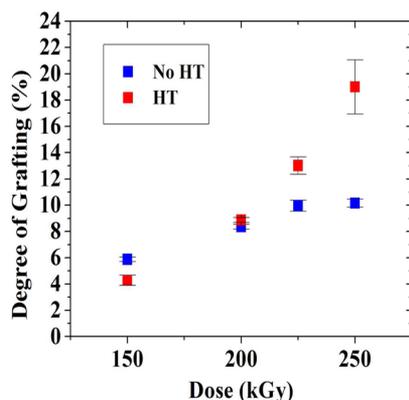


Figure 4. Grafting density of DAOx on polyamide 6 in an aqueous solution of TWEEN 20 surfactant as a function of dose at a dose rate of about 233 kGy/h in the absence of oxygen and via electron beam irradiation. HT = heat treatment following irradiation.

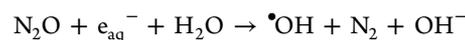
that as the dose increases, the degree of grafting increases, however the degrees of grafting are not as high as those achieved with neat DAOx monomer. This can be attributed to the difference in concentration of the DAOx monomer in contact with the surface of the polyamide 6 as well as less competition for radical sites on the surface of the fabric. 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:¹⁸

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

$$G(\bullet\text{H}) = 0.062, \quad G(\text{H}_2) = 0.042,$$

$$G(\text{H}_2\text{O}_2) = 0.082$$

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 DAOx• and polyamide• radicals upon reacting with polyamide 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 $k = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ Hence, saturating the system with N₂O 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 polyamide and DAOx to produce DAOx• and polyamide•.

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 atoms from the backbone of the polymer substrate (polyamide) producing OH–DAOx•, and H–DAOx• radicals, and •polyamide (–H) radicals, respectively. It should be mentioned that $\bullet\text{OH}$ and $\bullet\text{H}$ are also scavenged by the TWEEN 20 surfactant, since the mixture contains, 4.2 × 10⁻³ M TWEEN, leading to a decrease in the concentrations of OH–DAOx•, H–DAOx•, and •polyamide (–H) radicals. This also leads to the possibility of TWEEN being grafted on polyamide 6. This can dramatically decrease the number of sites available for uranium adsorption.

Surface Characterization Using XPS and Zeta Potential. Figure 5 shows the XPS spectra of the ungrafted polyamide and of the polyamide radiation-grafted with DAOx. The XPS results demonstrate the presence of C–C/CH, oxalate, amide, C–N, and ester groups.

Zeta potential measurements were performed on grafted and ungrafted polyamide 6 fabric that had been chemically transformed into microparticles. The zeta potentials for both the grafted and ungrafted polyamide 6 fabric were measured and the results are summarized in Table 1. These results appear to indicate that at a pH of about 8 the surface of the oxalate grafted fabric may be more negatively charged than the ungrafted polyamide 6.

Uranium Removal from Spiked Seawater. The results obtained for the removal of uranium from spiked seawater by means of polyamide 6 fabrics grafted with neat diallyl oxalate are shown in Figure 6. 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. As shown in Figure 6, it appears that as the DoG increases the percent removal of uranium from both the 1.0-mg/L and 0.2-mg/L U solutions may increase. The large scatter in the data can be ascribed to the nonuniform distribution of the grafted material on the polyamide 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. It has

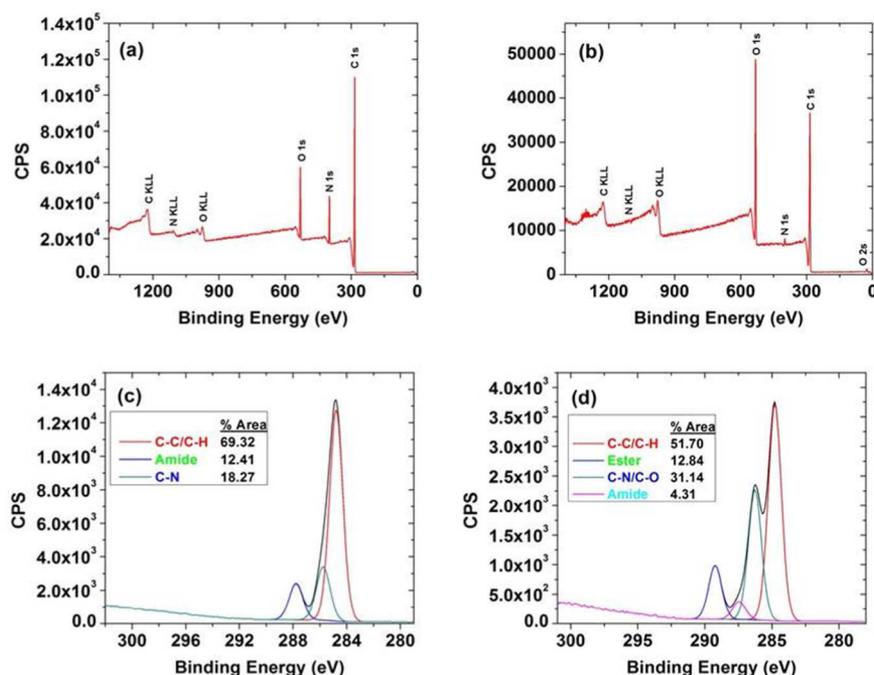


Figure 5. Comparison between the XPS spectra of ungrafted polyamide 6 (a,c) and DAOx grafted polyamide 6 (b,d). The presence of the ester peak in the grafted polyamide 6 can be attributed to the grafting of the oxalate group. The grafted sample was prepared by directly grafting neat DAOx by electron beam irradiation under argon to a dose of 200 kGy at a dose rate of 320 kGy/h. The sample achieved a grafting density of 29.7%.

Table 1. Average Sizes and Zeta Potentials of the Grafted and Nongrafted Polyamide 6 Microparticles^a

	particles from grafted polyamide 6	particles from nongrafted polyamide 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	$-6.1 \pm 0.9 \text{ mV}$	$-4.6 \pm 0.5 \text{ mV}$

^aThe grafted polyamide 6 fabric used for microparticle synthesis was fabricated using gamma radiation up to 40 kGy dose at a dose rate of about 5 kGy/h with a degree of grafting of 96.4%.

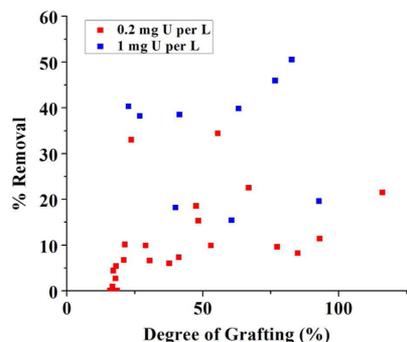


Figure 6. Percent uranium removal of the fabrics from uranyl acetate and seawater solutions doped to the respective levels. All samples were fabricated with electron beam irradiation, under argon, and in neat DAOx solution with dose rates of about 33 kGy/h and 320 kGy/h.

been reported that postirradiation heating can enhance the degree of grafting.²⁰ The mechanism behind this experimental observation is yet poorly understood. We speculate that the

high temperature enhances the diffusion of the monomeric materials into the substrate, since the T_g of polyamide 6 (polyamide should not be capitalized in this instance) is around 50 °C. Upon increasing the temperature above the T_g of polyamide the free radicals in the polymer will be available to a higher extent to react with the monomer molecules.

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 6 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 polyamide, which hinders the grafting of DAOx onto polyamide, since a large fraction of the $\cdot\text{OH}$ radicals may react with TWEEN, producing TWEEN \cdot radicals.

SEM/EDS Results. The SEM observations, see Figure 7, showed a nonuniform 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.

In conclusion, our results demonstrate that radiation grafting polymerization of DAOx on polyamide 6 through a solvent-

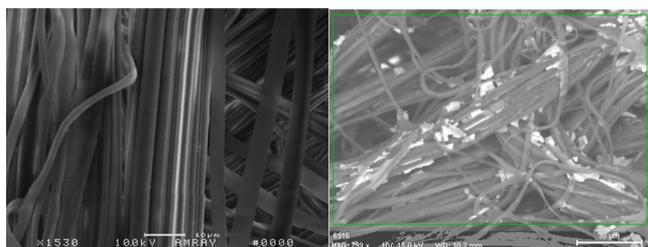


Figure 7. SEM images of both ungrafted (left) and grafted (right) fabrics. The grafted sample was fabricated with electron beam irradiation, under argon, and in neat DAOx solution to a dose of 250 kGy with a dose rate of about 320 kGy/h.

free, single-step-direct process can be accomplished in the absence of oxygen. In general, the degree of homopolymerization depends on the ratio of the radical yields of the monomer and the polymer, and is present in the case of indirect grafting as well, due to a chain transfer reaction between the polymer radicals and the monomer.²⁰ Direct grafting was preferred in this study because it gave rise to higher DoG. This can be attributed to the fact that the number of radicals on the surface of the polymer available for grafting of the monomer is higher, as indirect grafting always involves some decay of such radicals before the polymer is contacted with the solution of the monomer. EPR measurements of the radical concentrations on Winged Polyamide 6 fibers following electron beam irradiation showed rapid decay of the radicals within a time scale of minutes even in the absence of oxygen. This makes indirect grafting at room temperature impractical as a route of obtaining significant amounts of grafting. Grafting of DAOx onto the polyamide polymer is predominantly due to the reaction between the radiolytically produced polyamide[•] and DAOx monomer, as the concentration of the monomer greatly exceeds that of the radical species. Other reactions, namely, the desirable reaction between polyamide[•] and DAOx[•] radicals, and undesirable homopolymerization involving DAOx[•] radicals, are of secondary importance because they only involve radical species, which are present in a very low concentration at a steady-state radiolysis. These results also show that at radiation doses up to around 175 kGy, the undesirable homopolymerization is the predominant reaction. However, as the viscosity increases due to the homopolymerization reaction, the diffusion of the DAOx[•] C-centered radicals is retarded. This hinders the homopolymerization reaction and enhances the local grafting reaction, which allows the samples to reach a grafting density of 80–100% at a dose level of 250 kGy.

A further series of experiments employed direct radiation grafting of DAOx onto polyamide 6 using N₂O-saturated aqueous solutions containing DAOx and the surfactant TWEEN. These experiments showed that a degree of grafting

of 25% can be achieved at a dose of 250 kGy. This relatively low grafting density may be explained by the fact that the surfactant TWEEN also scavenges the [•]OH radicals. The concentration of TWEEN is much lower than that of DAOx in the solution. However, the rate constant for the scavenging of OH[•] by TWEEN may be much higher because the structure of TWEEN includes a large number of groups per molecule which can react with OH[•] radicals. In addition, TWEEN forms micellar aggregates at a critical micelle concentration (CMC) equal to 1.1 × 10⁻⁵ M. Therefore, at the concentration used in this study (4.5 × 10⁻³ M) a high portion of TWEEN in the solution exists as micellar structures that will enhance its ability to scavenge OH[•] radicals, causing a decrease in the radiolytic yields of polyamide[•] and DAOx[•] C-centered radicals, and thus its presence causes a decrease in the grafting density.

As expected, Figure 6 shows that as the grafting density increases, the extraction of uranyl from spiked seawater increases. The scattering of the results of the percentage extraction can be related to the nonuniformity of the grafting within the samples. This nonuniformity 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.

Overall, the capacity for industrial implementation for this specific copolymer system is high. The lack of use of organic solvents coupled with the degree of grafting and subsequent uranium extraction capacity from direct grafting methods will significantly simplify an industrial-level fabrication process. Unlike amidoxime-based fabrics, there would also be no requirement for postirradiation chemical treatment, even further limiting the quantity of extraneous solvents required for fabric manufacturing.

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Notes

The authors declare no competing financial interest.

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Table 2. Comparison of Different DAOx Grafted Polyamide 6 Samples in Terms of Their Selectivity for Uranium versus Sodium As Measured by EDS^a

dose (kGy)	degree of grafting	% U removal (from 0.2 mg U·L ⁻¹)	atomic % U on surface	atomic % Na on surface	atomic % Mg on surface	atomic % Ca on surface
150	21%	6.7	32.8	51.2	8.46	2.85
225	41%	18.5	26.7	58.9	9.78	1.50
250	77%	9.6	26.3	59.2	9.24	1.94
250	77%	45.9 ^b	28.4	55.0	9.17	2.90

^aAll samples were irradiated in neat DAOx solution under Ar using electron beam radiation at dose rates of about 320 kGy/h. ^b%U removal from 1 mg U·L⁻¹ conclusions.

dispersive X-ray spectroscopy was performed. The authors also acknowledge the support of Tim Mangel with the Laboratory for Biological Ultrastructure at the University of Maryland where scanning electron microscopy was also performed. Certain commercial equipment, instruments, or materials (or suppliers, or software, ...) are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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