

# Enhancement of the Extraction of the Uranium from Seawater

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## Fuel Cycle R&D

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## Summary

An advanced polymeric adsorbent for extracting uranium from seawater has been developed through radiation grafting of bis(2-methacryloxyethyl)phosphate onto Winged™ nylon fabric. This adsorbent, prepared using “green” chemistry in aqueous solution, was tested in Atlantic Ocean seawater doped with uranium for adsorption capacity and reusability. The grafted adsorbent has exhibited distribution coefficients exceeding  $2 \times 10^4$  mL/g, a maximum loading of at least 4.4% uranium, and at least 21 cycles of effective reusability.

## 1. Introduction

The amount of dissolved uranium in seawater is estimated at  $4.3 \times 10^9$  tons,<sup>1,2</sup> approximately 1000 times the amount present in conventional ores that can be economically recovered<sup>1,3</sup>. The latter amount is estimated to be sufficient for only about another century of the operation of nuclear power plants at present-day capacity.<sup>2</sup> In addition, mining and processing of uranium ore pose serious environmental issues, in particular those related to mining wastes<sup>4</sup> and mill tailings<sup>5</sup>. These issues are avoided in the recovery of uranium from seawater. Interest in extracting uranium from seawater has spanned several decades and has led to studies of adsorbents such as hydrous titanium oxide, ion exchange resins and, more recently, polymeric adsorbents containing amidoxime groups<sup>6</sup> fabricated through radiation-induced grafting<sup>7</sup>. Typically, such adsorbents are prepared by exposing a polymer, such as polyethylene-coated polypropylene fiber, to electron beam irradiation in a nitrogen atmosphere, and then contacting the irradiated polymer with a de-aerated solution of acrylonitrile and methacrylic acid in dimethylsulfoxide. The product is subsequently treated with a hydroxylamine solution at 350 K in order to reduce the cyano groups to amidoxime groups.<sup>3,8</sup> Over the course of a full-scale, in-ocean extraction experiment, an amount of 1.1 kg of uranium was recovered from seawater over a period of 240 days using adsorption cages containing stacks of nonwoven fabrics of such amidoxime fibers.<sup>9</sup> The overall loading was 0.3 %<sup>10</sup>, while the average loading during 30 days of immersion was 0.05%<sup>9</sup>. The use of anchored braids of the amidoxime-grafted adsorbent fabric in seawater at a temperature of 30 °C rather than 20 °C resulted in raising the 30-day loading from 0.05% to 0.15%.<sup>8</sup>

If seawater is to be considered a practical source of uranium, the adsorbent has to meet several requirements including

- High distribution coefficient for uranium
- High maximum loading
- High selectivity for uranium in a seawater environment
- Rapid adsorption kinetics
- Multiple cycles of effective reusability
- Chemical and mechanical stability in ocean conditions
- Cost-effective production
- Compatibility with marine ecosystems

The current study has been intended to improve the performance of polymeric adsorbents in recovery of uranium from seawater through the use of phosphate-based adsorbing groups instead of amidoxime groups, the use of Winged™ fibers<sup>11,12</sup> with high surface area, and enhancement of the retention of the capacity of the adsorbents for uranium during multiple cycles of adsorption and elution. In addition to improvements in capacity, it has also been intended to make the synthesis of the new polymer adsorbents simpler and more environmentally friendly through the use of direct grafting in an aqueous environment without the need for a chemical treatment step following the grafting.

## 2. Experimental section

### 2.1 Monomers and polymeric supports

Five phosphate monomers, each containing at least one C=C bond in the form of a terminal vinyl, allyl or acrylic group, were selected for grafting onto polymeric fabrics and subsequent testing for uranium adsorption. These monomers included diethylallyl phosphonate, vinylphosphonic acid, diethylvinyl phosphonate, dimethylvinyl phosphonate, and bis(2-methacryloxyethyl) phosphate (B2MP). The fabrics included in the study were either nonwoven polymers, including nonwoven polypropylene and nylon 6 (The 3M Company), or Winged™ polymers<sup>11,12</sup> with ultra-high surface area (10-90 m<sup>2</sup>/g) (Allasso Industries), again including polypropylene and nylon 6. Since the grafting densities obtained with various polymeric supports depend on the concentration of radicals obtained upon their irradiation, an electron paramagnetic resonance (EPR) spectrometer (Bruker x-band) was used to measure the spin concentrations obtained upon irradiation (in the absence of oxygen and B2MP) of the candidate polymers used in the study.

### 2.2 Adsorbent preparation through grafting

Two types of grafting were used in order to attach the phosphate monomers to the polymeric supports. The indirect grafting route consisted of irradiating the polymeric support in the absence of oxygen and then placing it in an oxygen-free solution of the phosphate monomer in de-ionized water. The direct grafting route consisted of keeping the polymer immersed in a nitrogen-purged solution of the phosphate monomer (0.093 M in the case of B2MP) in de-ionized water during the irradiation. It should be noted that at this concentration the B2MP monomer was not completely dissolved in water and some of it remained in the form of fine suspension. One radiation source used in the grafting experiments was a Co-60 gamma radiation source (1.8 TBq). The accumulated gamma doses used in the study were between 5 and 60 kGy. The other radiation source was a 1-9 MeV electron beam linear accelerator with a variable pulse repetition rate (50-300 Hz, 3- $\mu$ s pulse). The dose rates were determined using radiochromic film dosimetry (Far West Technology, Inc.) Following the grafting operation, the adsorbents were allowed to sit overnight in the monomer solution, and were then removed from the solution, sonicated twice in de-ionized water to remove homopolymerized material, and dried in air to constant weight. The weight gain was used to calculate the degree of grafting, which is given by the ratio  $(W_f - W_i)/W_i$ , where  $W_i$  and  $W_f$  are the weights of the sample of the fiber fabric before and after grafting, respectively.

In order to explain the differences in extent of grafting between indirectly grafted and directly grafted samples, the decay of the free radicals produced upon irradiation of the polymer was investigated. Measurements of spin concentration were performed on Winged™ nylon 6 samples irradiated under nitrogen in the absence of oxygen and B2MP using 1.9-Gy, 3- $\mu$ s, 6.8-MeV pulses produced by the electron beam accelerator at various total doses (100-350 kGy). The spin concentrations were measured as a function of time following the irradiation by means of an EPR spectrometer (see Section 2.1). The high doses used in these experiments were intended to allow monitoring of the decay of the radicals.

### 2.3 Adsorption experiments

In each adsorption experiment, a piece of dry adsorbent fabric, weighing between 10 and 50 mg, was placed in a volume of between 5 and 100 mL of Atlantic Ocean seawater (34° 42' N, 76° 43' W) doped with 10-20 mg/L uranium. The uranium was introduced in the form of uranyl nitrate by diluting a 1000-mg/L uranium standard solution (Spex CertiPrep PLU2-2Y) with seawater. The solution was then rotated with the adsorbent sample at 30 rpm for a period of time of between 1 and 168 hours. At the end of the testing period, the adsorbent sample was removed and air dried. The solution was analyzed by means of a Perkin Elmer inductively coupled plasma atomic emission spectrometer (ICP-AES), with a sample of the original solution run in parallel. Measurements of the concentration of uranium in the original solution ( $C_0$ ) and in the solution contacted with the adsorbent ( $C$ ), respectively, were used to calculate the fraction of uranium removed from the solution  $(C_0 - C)/C_0$ , the loading (g U adsorbed/g adsorbent), and the apparent distribution coefficient  $K_d' = (\text{loading, g} \cdot \text{g}^{-1}/C, \text{g} \cdot \text{mL}^{-1})$ . For instance, under testing conditions involving a 15-mg adsorbent sample immersed in 10 mL of seawater doped with 10  $\text{mg} \cdot \text{L}^{-1}$  uranium, a distribution coefficient,  $K_d'$ , of  $1 \times 10^4 \text{ mL} \cdot \text{g}^{-1}$  corresponds to a loading of 6.25 mg U/g adsorbent or 0.625% and to removal of 96.9% of the uranium from the seawater.  $K_d'$  is the apparent distribution coefficient which is not truly constant because it is subject to variation with time, until equilibrium between the adsorbent and the solution is established and the value of  $K_d'$  reaches the true distribution coefficient,  $K_d$ .

### 2.4 Regeneration

Following the adsorption experiment, the adsorbent sample is rotated at 30 rpm with an eluant solution. Following the elution period (in most cases, 20 hours) the eluate is analyzed by means of ICP-AES to determine the concentration of desorbed uranium, and then the adsorbent is rinsed with de-ionized water, air-dried, and rotated at 30 rpm with a fresh volume (typically 10 or 20 mL) of the original solution of uranium in seawater. As described above in the case of the initial adsorption experiment, the solution is removed for uranium analysis and the adsorbent is rinsed with de-ionized water and air-dried prior to further elution and adsorption steps. The apparent distribution coefficient,  $K_d'$ , is determined for each adsorption step.

### 2.5 Analytical uncertainties

Based on analysis of the results of the AES-ICP measurements on solutions of uranium in seawater, the smallest difference in uranium concentration between two samples which could be detected at a 95% confidence level was  $0.2 \text{ mg} \cdot \text{L}^{-1}$ . Under typical conditions used in the testing,

involving a 15-mg adsorbent sample contacted with 10 mL of a solution of  $10 \text{ mg}\cdot\text{L}^{-1}$  of uranium in seawater, such an effective detection limit implies that only loadings between 0.13 and 6.5 mg U/g adsorbent (corresponding to removal of between 2% and 98% of the uranium from the solution, respectively) could be measured with statistical significance. These limits correspond to apparent distribution coefficients between  $1.4 \times 10^1$  and  $3.3 \times 10^4 \text{ mL}\cdot\text{g}^{-1}$ .

### 3. Results

#### 3.1 Selection of adsorbing molecule, polymeric support and grafting technique

Fiber fabrics consisting of Winged™ nylon 6 were subjected to direct grafting with various organic phosphates or phosphonates containing C=C bonds using Co-60 gamma irradiation at a dose rate of  $5 \text{ kGy}\cdot\text{hr}^{-1}$  for 10 hours, amounting to a total dose of 5 kGy. A sample weighing 15 mg was cut out of each grafted fabric and rotated with 10 mL of a solution of  $10 \text{ mg}\cdot\text{L}^{-1}$  uranium in seawater for 1 hour. The results of the experiment, expressed in terms of the apparent distribution coefficient ( $K_d'$ ), are shown in Table 1.

Monomer	Distribution Coefficient ( $\text{mL/g}$ ) <sup>[i]</sup>
Diethylallyl phosphonate	$1.2 \times 10^2$
Vinylphosphonic acid	$1.7 \times 10^2$
Diethylvinyl phosphonate	$3.5 \times 10^2$
Dimethylvinyl phosphonate	$1.9 \times 10^2$
Bis(2-methacryloxyethyl) phosphate (B2MP)	$\geq 3.3 \times 10^4$

**Table 1** Distribution coefficients after one hour of contact with seawater doped with 10 mg/L U, 15 mg adsorbent. Each monomer grafted onto Winged™ nylon, Co-60 irradiation to 5 kGy total dose; 5 kGy/hr.

The results in Table 1 show that bis(2-methacryloxyethyl) phosphate (B2MP) was far superior to the other phosphate or phosphonate monomers. Accordingly, B2MP was selected for use in all the following experiments.

Experiments under similar conditions were conducted on the other polymeric supports (Winged™ and nonwoven propylene as well as nonwoven nylon 6) grafted with B2MP. It was observed that the  $K_d'$  values for uranium using grafted nonwoven nylon 6 were lower by a factor of 2.5 than those obtained using nonwoven nylon 6. In addition, Winged™ nylon samples exhibited the best retention of mechanical integrity and flexibility during and after irradiation. In contrast, the nonwoven nylon samples showed poor retention of mechanical properties, while the polypropylene samples were the least resistant to radiation.

Samples of Winged™ nylon 6 grafted with B2MP were prepared using both indirect grafting

(irradiation of the nylon support, followed by reaction with B2MP) and direct grafting (irradiation while the nylon is immersed in the B2MP solution). Indirect grafting generally resulted in low degrees of grafting (<50%) and low  $K_d'$  values obtained in tests of uranium adsorption. Accordingly, direct grafting was adopted as the preferred grafting procedure.

Measurements of the initial spin concentrations in the various polymers showed that the number of free radical sites available for grafting was higher in the cases of Winged™ nylon 6 and polypropylene than in the cases of the corresponding nonwoven fabrics.

### *3.2 Uranium loading*

An adsorbent fabric was produced by irradiating Winged™ nylon in the presence of a de-aerated B2MP solution using a Co-60 gamma source at a dose rate of  $10 \text{ kGy}\cdot\text{hr}^{-1}$  over a period of 4 hours (corresponding to a total dose of 40 kGy). The irradiated nylon was cut to provide several 15-mg samples. Each sample was rotated at 30 rpm for 20 hours with a volume of between 10 and 100 mL of a solution of  $20 \text{ mg}\cdot\text{L}^{-1}$  uranium in seawater, and the remaining concentration of uranium in the solution was determined using ICP-AES. The results are shown in Figure 1. They show that the loading was proportional to the mass of uranium in the solution in contact with the adsorbent, which was in turn controlled by the volume of the solution. The highest loading observed was 4.4% U or 44 mg U/g of adsorbent. However, since the dependence of the loading on the mass of uranium at this point is still linear, the ultimate loading can be expected to be substantially higher.

### *3.3 Effects of grafting parameters on the degree of grafting and distribution coefficient of uranium*

Adsorbent samples were produced by irradiating Winged™ nylon 6 in the presence of de-aerated B2MP solutions at different concentrations in de-ionized water, using a Co-60 gamma source at a dose rate of  $10 \text{ kGy}\cdot\text{hr}^{-1}$  over a period of 4 hours (corresponding to a total dose of 40 kGy). Subsequently, the samples of the grafted B2MP were sonicated in de-ionized water, air-dried, weighed, and tested by rotating each sample with 10 mL of a solution of  $20 \text{ mg}\cdot\text{L}^{-1}$  uranium in water for 20 hours as described above. The relationship between the concentration of B2MP in the aqueous phase during the grafting process, the degree of grafting, and the apparent distribution coefficient,  $K_d'$ , for uranium is shown in Figure 2. It can be seen that both the degree of grafting and the distribution coefficient for uranium increased with increasing concentration of B2MP in the aqueous medium during grafting, but at the highest concentration of B2MP the degree of grafting still rises (to above 200%) while  $K_d'$  appears to reach a plateau. (As mentioned above, part of the B2MP remains in fine dispersion rather than in true solution, especially at high overall concentrations of B2MP in water.)

Additional experiments on the effects of the grafting parameters on the performance of the adsorbent have shown that high distribution coefficients were obtained upon grafting B2MP onto Winged™ nylon 6 at intermediate dose rates of between  $1$  and  $10 \text{ kGy}\cdot\text{hr}^{-1}$  and high total doses of  $>30 \text{ kGy}$ .

### 3.4 Adsorption kinetics

Adsorbent samples were produced according to the procedure detailed in Section 3.2. One of them was placed in a stationary volume of 50 mL of seawater doped with  $20 \text{ mg}\cdot\text{L}^{-1}$  uranium. The other one was placed in a similar volume of uranium-doped seawater and continuously rotated at 30 rpm. At certain intervals, 2-mL samples of the solution in each of the two experiments were removed, diluted with de-ionized water, and analyzed. The concentrations of uranium remaining in solution were used to calculate the values of  $K_d'$  as a function of contact time. The results are shown in Figure 3. It can be seen that extent of adsorption grows very rapidly during the first 10 hours, moderately rapidly during the next 40 hours, and slowly thereafter. The extent of adsorption in the dynamic experiment is consistently larger than the extent of adsorption in the static experiment throughout the duration of the experiments.

### 3.5 Adsorbent regeneration

Regeneration of the B2MP-grafted nylon 6 adsorbents was studied using adsorbent samples prepared according to the procedure detailed in Section 3.2. Various eluants were used, including aqueous solutions of HCl,  $\text{HNO}_3$ , citric acid, ethylenediamine and ammonium oxalate. Of these eluants, the strong acids HCl and  $\text{HNO}_3$  were found to cause degradation of the adsorption capacity of the adsorbent over several cycles of adsorption/elution. Citric acid and ethylenediamine were less damaging, but still gave rise to deterioration in the performance of the adsorbent from cycle to cycle. In contrast, regeneration with a saturated solution (approximately 0.4 M) of ammonium oxalate in water was observed to be highly effective in restoring the capacity of the adsorbent to remove uranium from seawater without causing degradation of the adsorbent. Although there was a small loss in the adsorption capacity during the first adsorption/desorption cycle, no significant further loss occurred during at least 20 subsequent cycles (Figure 4). It should be noted that the drop in  $K_d' = C_a/C_s$  during the first cycle is associated with a small decrease in loading, since in cases where  $C_s \ll C_a$  a small rise in  $C_s$  can cause a large decrease in  $K_d'$ . In regard to the time scale of the elution step with saturated solutions of ammonium oxalate, it was noted that the desorption was typically about 90% complete within a period of 20 hours.

## 4. Discussion

### 4.1 Adsorbing molecules and polymeric supports

Among nylon fabrics grafted with the five phosphonates and phosphates explored in the present study, those grafted with B2MP were found to be far more efficient in adsorbing uranium than those grafted with the other four substances. It should be noted that of the five molecules investigated, only B2MP has two C=C bonds, while the other molecules contain only one double bond. The presence of a second double bond may contribute to the formation of stable covalent attachment of the complexing species to the polymer. In addition, B2MP, having the longest chain, is the most likely to enfold uranium ions and thus form highly stable complexes.

Among the polymeric supports, Winged™ nylon 6 is by far the most effective, owing to its very large surface area as well as to its retention of its mechanical integrity and rigidity during

irradiation and during the following exposure to seawater.

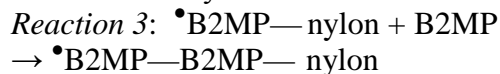
#### 4.2 Radiation-induced grafting in water - a "green chemistry" synthetic route

Radiation grafting<sup>7</sup> eliminates the need for using catalysts, which are retained as impurities in the product. Radiation-induced grafting in aqueous media is relatively rare,<sup>13-15</sup> but it has significant advantages in eliminating the use of organic solvents, thus minimizing the generation of hazardous wastes.

As detailed in the previous sections, two grafting methods were used in the present study. Indirect grafting involves irradiation of the supporting polymer, followed by bringing it in contact with the solution of the monomer under oxygen-free conditions. The second route, which is less commonly used, is direct grafting, where the supporting polymer is immersed in the solution of the monomer during irradiation.

##### 4.2.1 Indirect grafting

In the course of indirect grafting, the irradiation produces carbon-centered radicals ( $\bullet$ nylon) on the polymer, and these radicals undergo addition to double C=C bonds when the irradiated polymer is contacted with the de-aerated solution of the monomer. The relevant reactions are:



In order to suppress crosslinking due to reaction between two  $\bullet$ nylon radicals, the irradiation has to be carried out at very low temperatures and at low dose rates. These requirements, in addition to the need to transfer the irradiated nylon to the B2MP solution in the absence of oxygen, complicate the process. In the present experiments, indirect grafting was found to result in low grafting densities (<50%) and low distribution coefficients for uranium.

##### 4.2.2 Direct grafting

Much better results have been obtained using direct grafting, where the nylon is immersed in the B2MP solution during irradiation. The proposed set of reactions for direct grafting is based on the fact that under the irradiation conditions being used and in the absence of oxygen, the  $\bullet$ OH radicals, which are produced upon radiolysis of the aqueous medium, add to the unsaturation sites of the B2MP and abstract H-atoms from the backbone of the nylon polymer, producing  $\bullet$ B2MP—OH radicals and  $\bullet$ nylon(-H) radicals, respectively (Figure 5).

The following are all the competing reactions of the B2MP monomer, nylon,  $\bullet$ B2MP—OH, and  $\bullet$ nylon(-H) radicals:

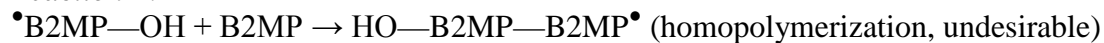
##### $\bullet$ B2MP—OH radical reactions:

Depending on the B2MP concentration, polymer concentration, dose rate, and total dose,

$\bullet$ B2MP—OH radicals undergo the following competing reactions:



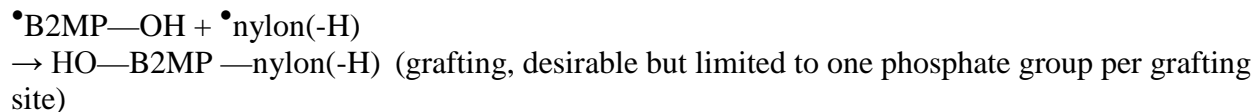
*Reaction 1:*



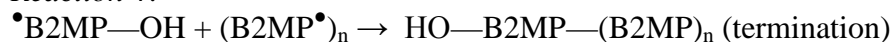
*Reaction 2:*



*Reaction 3:*

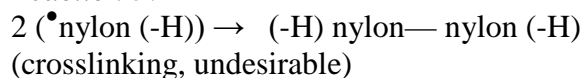


*Reaction 4:*

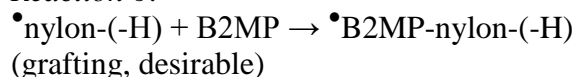


*Nylon(-H) radical reactions:*

*Reaction 5:*



*Reaction 6:*



Reaction 6 is the most important and most desirable process since it produces grafting polymerization and formation of brush-like structures (Figure 6). Reactions 2, 4 and 5 are enhanced at high dose rates while reactions 1 and 6 are enhanced at low dose rates. High monomer concentrations enhance reaction 1. Large surface areas of the polymer enhance reaction 6 and suppress reaction 2. Based on this set of reactions, maximum grafting densities are expected at intermediate dose rates since at very low dose rates Reaction 1 becomes predominant while at very high dose rates Reaction 2 becomes predominant, in both cases enhancing the competition of these undesirable reactions against the desirable Reaction 6. As detailed above, experiments on the effects of dose rate on the degree of grafting and the distribution coefficients for uranium have indeed showed that the best adsorbents were produced at dose rates between 1 and 10 kGy·hr<sup>-1</sup>. Some homopolymerization (Reaction 1) can take place even under these conditions, resulting in reduced distribution coefficients for uranium due to blocking of the adsorption sites, but the homopolymerized material is effectively removed by sonicating the grafting product in de-ionized water.

In general, direct grafting produced adsorbents with much higher grafting densities than indirect grafting (up to 200% compared with <50%) and high distribution coefficients for uranium. In addition, direct grafting is a single-step rather than two-step process, and it eliminates the need to perform the irradiation at very low temperatures and to transfer the irradiated nylon into the B2MP solution rapidly under oxygen-free conditions. EPR measurements showed that even in the absence of oxygen considerable decay of the  $\bullet\text{nylon}$  radicals takes place over short periods of time, with radical half-lives of the order of  $1 \times 10^3$  s at room temperature. The use of direct grafting eliminates these problems.

### 4.3 Uranium adsorption

The achievable loading of uranium on a given adsorbent depends not only on the density of the adsorbing sites but also on selectivity for the ion of interest in the presence of other ions in the aqueous matrix. It has been shown that in the case of the "traditional" amidoxime-based adsorbents many ions can give rise to significant competition against uranium for the adsorption sites, and this leads to reduction in the uranium loading. Some of these ions, such as Na, have very small distribution coefficients on amidoxime-based adsorbents but are present in seawater at very large concentrations, while others, such as Fe, Pb, Ni and Co are present in low concentrations but have high distribution coefficients.<sup>9</sup> The high loading observed on the B2MP-grafted Winged™ nylon 6 adsorbents reflects high selectivity to uranium as well as high density of adsorbing sites.

In seawater, uranium is predominantly present in the form of the  $\text{UO}_2(\text{CO}_3)_3^{4-}$  anionic complex and to a smaller extent as the  $\text{UO}_2(\text{OH})_3^-$  complex.<sup>16</sup> Carbonate complexes of uranium have been removed from seawater using anion exchange resins<sup>17</sup> or extracted into organic solvents, including organic derivatives of phosphoric acid such as bis-(2-ethylhexyl)-*o*-phosphoric acid (HDEHP)<sup>18</sup>. It is likely that the chemical interactions involved in the adsorption of uranium from seawater on nylon-immobilized B2MP are similar to those that take place in the solvent extraction process with HDEHP.

### 4.4 Regeneration

Regenerability of adsorbents for uranium from seawater is a key to establishing the viability of this process, since a single-use process, at the end of which the spent adsorbent has to be discarded, is not economically viable.<sup>9</sup> The current study shows ammonium oxalate to be a very effective regenerant for the B2MP-based adsorbent. Previous work on polymeric adsorbents produced by radiation grafting of amidoxime group on polymers<sup>3,19</sup> showed that 0.5 M HCl is effective in removing the adsorbed uranium from the loaded adsorbent. However, upon re-use it is observed that the capacity of the regenerated adsorbent becomes considerably lower, and at the end of five adsorption-elution cycles this capacity is completely destroyed. It was shown that alkali treatment following elution with acid can reduce, but not eliminate, the decay in adsorbent performance,<sup>3,20</sup> but such treatment adds another step and generates a large volume of waste, in addition to having limited effectiveness. In contrast, regeneration of the B2MP-based adsorbent using a saturated ( $\approx 0.4$  M) aqueous solution of ammonium oxalate provides more than 20 regeneration cycles without significant loss of capacity and without the need for an additional chemical treatment between the adsorption and elution steps. The slight decrease in capacity during the first cycle may be attributed to the presence of a small amount of B2MP, possibly present as a homopolymer, which is weakly bound to the polymer. The effectiveness of the ammonium oxalate regenerant can be attributed, on one hand, to the complexing of uranium by oxalate, and, on the other, to the near-neutral pH of the regenerant, which prevents hydrolytic damage to the B2MP-grafted adsorbent.

### 4.5 Sample Variability

We have observed considerable variations in performance from one batch of B2MP-grafted nylon 6 adsorbent to another. We postulate that one of the important factors leading to

variability in adsorbent properties is the fact that the solubility of B2MP in water is very limited and, as a result, it is difficult to maintain uniform distribution of B2MP in the aqueous phase during the grafting operation. Sample variability is reflected in a large scatter in the values of the grafting density and also in large discrepancies among results obtained upon testing the grafted samples to determine their effectiveness in adsorbing uranium from seawater. Irreproducibility has also been observed when several slices of a single sample were tested to determine the extent of uranium adsorption. This, too, may also be attributed to the fact that B2MP is non-uniformly dispersed in the aqueous phase during the grafting step. Stirring the dispersion inside the irradiation cell, while not completely impossible, poses very difficult problems due to the effects of high doses of gamma radiation on electronic equipment. Accordingly, we investigated the possible advantages of addition of phase-merging agents. Addition of large amounts of methanol (>50 % by volume) can lead to formation of a clear uniform liquid phase, but it results in low grafting densities (< 20 %) because methanol effectively scavenges the  $\bullet\text{OH}$  radicals and prevents them from reacting with the C=C bonds of B2MP. The introduction of very high percentages of methanol also thwarts the intention of making the process environmentally friendly. In view of these shortcomings of the use of methanol, we studied the effects of introducing small amounts of surfactants. The two surfactants investigated so far were Tween 20 (polyoxyethylene (20) sorbitan monolaurate and Span 80 (sorbitan monooleate). Tween 20 was found to be more effective in forming a clear aqueous phase, and was therefore selected for further use. Grafting of B2MP in Nylon 6 took place in a gamma cell using concentrations of up to 0.6 % of Tween 20. This concentration was found to be sufficient to form a clear aqueous phase, in agreement with predictions based on calculations of the CMC (critical micelle concentration). The grafting density obtained upon testing four samples of Nylon 6 grafted with B2MP in the presence of 0.6 % Tween 20, as well as upon four samples grafted in the presence of 0.13 % Tween 20 and seven samples grafted in the absence of Tween 20, was found to be approximately 50 %. Tests of uranium adsorption on 13-mg slices of these samples in 20-mL volumes of a solution of  $10 \text{ mg}\cdot\text{L}^{-1}$  U in Atlantic Ocean seawater, showed the extent of uranium removal from the seawater to be  $(69 \pm 22)$  % for the samples grafted in the presence 0.6 % Tween 20,  $(82 \pm 8)$  for the samples grafted in the presence of 0.3 % Tween 20, and  $(85 \pm 8)$  % for the samples grafted in the absence of Tween 20. It was concluded that the presence of Tween 20 during the grafting process did not result in improving the extent of uranium adsorption or in a smaller scatter among the results. This may be due to some hydroxyl scavenging by Tween 20. We are considering the use of alternative surfactants.

#### *4.6 Stability of Adsorbent against Loss of Phosphate*

In a previous experiment on adsorption of uranium on Nylon 6 grafted with B2MP followed by a repeated elution and regeneration step using a 0.4-M aqueous solution of ammonium oxalate, it was observed that the value of the distribution coefficient,  $K_d$ , for the initial adsorption step was approximately  $18000 \text{ mL}\cdot\text{g}^{-1}$ . Following elution of the uranium with 0.4 M aqueous solution of ammonium oxalate,  $K_d$  for the second adsorption of uranium was observed to be about  $1000 \text{ mL}\cdot\text{g}^{-1}$  and it remained at this level for more than 20 subsequent adsorption/regeneration cycles. In the past, we tentatively attributed the drop in  $K_d$  during the from the first cycle to the second cycle to loss of weakly bound B2MP which had contributed to uranium attachment during the first cycle only. In order to check this possibility, we measured the amount of phosphorus extracted from 8-mg samples of B2MP-grafted Nylon 6 into 10 mL, 20 mL, 50 mL and 100-mL

volumes of seawater upon stirring for periods of 1 day and 2 days. The extent of P extraction in all cases corresponded to a loss of <2 % of B2MP. Therefore, loss of B2MP cannot be considered to have a significant effect on the performance of the adsorbent. An alternative interpretation of the decrease of  $K_d$  from the first cycle to subsequent cycles of the regeneration experiment is detailed below.

#### *4.7 Limits on Uranium Loading - Saturation of Adsorption Sites or Competition by Other Solutes?*

In previous tests of 15-mg samples of adsorbent with seawater samples containing between 0.2 and 2 mg of uranium, it was observed that the loading (amount of adsorbed uranium per unit weight of adsorbent) increased with increasing amount of uranium in the solution and reached approximately 45 mg U/g adsorbent (corresponding to 4.5 % by weight) when the uranium content of the solution reached 2 mg. The correlation between the amount of uranium present in the aqueous phase and the amount adsorbed was verified in recent experiments. It is important to find out if the loading is limited by the number of active sites on the adsorbent or by competition by other solutes present in seawater. According to Tamada (2009) other solutes, such as Fe, Pb, and Ni have  $K_d$  values larger than those of U and their concentrations in seawater are sufficiently high to predict that competition is a major capacity-limiting factor when amidoxime-grafted polyethylene is used to recover uranium from seawater. We compared the  $K_d$  values obtained upon contacting B2MP-grafted Nylon 6 samples weighing 12 mg each with 100 mL of simulated seawater containing only the major solutes (16502 mg NaCl + 6841 mg  $MgSO_4 \cdot 7H_2O$  + 5647 mg  $MgCl_2 \cdot 6H_2O$  + 1467 mg  $CaCl_2 \cdot 2H_2O$  + 725 mg KCl + 196 mg  $NaHCO_3$  in 1 L of de-ionized water) on one hand and with actual Atlantic Ocean seawater on the other. The pH was 8 in all experiments. The results indicated that the  $K_d$  value obtained in the actual seawater was lower by only 28 % than the corresponding value in the simulated seawater. This indicates that competition by transition elements is not a major capacity-limiting factor in the case of B2MP, as opposed to the case of amidoxime. Further experiments on leaching in fully and partially simulated seawater are in progress.

#### *4.8 pH Effects*

It is well-known that the adsorption of uranium on various sorbents is sensitive to relatively small changes in pH because of changes in the speciation of uranium ions. In particular, at above-neutral pH uranium in seawater is mostly present in the form of one of several carbonate complex. In our adsorption experiments, we have prepared the starting solution by adding uranium to seawater to bring the uranium concentration to a desired level (usually 10 or 20  $mg \cdot L^{-1}$  U) and then adjusting the pH to around 8 using  $NaHCO_3$ . However, we have observed that during the contact with the adsorbent the pH decreases, and that the extent of the decrease is larger the larger is the ratio of the weight of the adsorbent to the volume of solution. This decrease may be attributed to ion exchange between  $Na^+$  ions in the seawater, which are present at a high concentration of approximately 0.4 M, and  $H^+$  ions originating from the  $P(=O)-OH$  groups of B2MP. This observation provides an alternative explanation for the drop of  $K_d$  from the first adsorption step to the second and subsequent steps in the ammonium oxalate regeneration experiments mentioned above. This explanation assumes that during the first step, the pH drops upon contact between the fresh B2MP-grafted adsorbent and the  $Na^+$ -rich seawater, resulting in a higher  $K_d$ . (Separate experiments have shown that a decrease in pH results in an increase of  $K_d$  for the adsorption of uranium.) Following treatment with 0.4 M ammonium

oxalate, the speciation of the surface sites on the adsorbent becomes constant, with these sites being occupied by  $\text{Na}^+$  and  $\text{NH}_4^+$  ions, and the pH of subsequent U-doped seawater brought in contact with the adsorbent no longer drops. Thus, the  $K_d$  observed during the second and subsequent regeneration cycles is the "true"  $K_d$  for the pH of seawater. We intend to verify this explanation in upcoming experiments and to make sure that the procedures to be used in future adsorption tests maintain the pH of seawater at 8 throughout the test duration. Of course, maintaining the pH at this level cannot be achieved simply by introducing a high concentration of pH 8 buffer without verifying that such a high buffer concentration will not have its own specific effects on the adsorption of uranium.

## 5. Conclusions

We have demonstrated that effective adsorbents for uranium from seawater can be fabricated through radiation-induced grafting of phosphate-containing monomers onto ultra-high surface area Winged™ fabrics in an aqueous medium. Grafted bis(2-methacryloxyethyl)phosphate (B2MP), which has two C=C groups, has been found to provide much higher distribution coefficients for uranium than other organic phosphates and phosphonates. Winged™ nylon 6 has been observed to be preferred to Winged™ nylon polypropylene as well as to nonwoven nylon 6 and polypropylene because it combines high surface area and good retention of mechanical properties upon irradiation. We have found that direct grafting, which eliminates the delay between irradiation and introduction of the organic phosphate and thus prevents decay of the radiation-produced radicals on the polymer, can produce higher grafting densities and higher distribution coefficients for uranium than indirect grafting. Uranium loadings of up to 4.4% and distribution coefficients of the order of  $10^4$  mL/g have been obtained with Winged™ nylon 6 directly grafted with B2MP upon contact with actual seawater doped with uranium. This adsorbent, regenerated with a saturated aqueous solution of ammonium oxalate, has exhibited at least 21 cycles of reusability with negligible degeneration of adsorptive capacity following the first cycle.

Several issues which are related to the performance of the adsorbent on a large scale in the ocean require further research and are currently under active study. These issues include variability in performance among various batches of adsorbent, the stability of the adsorbent against phosphate loss, the nature of the limits on uranium loading (saturation of adsorption sites vs. competition by other solutes), and pH effects. Significant progress has already been made on these issues. For instance, it has been shown that phosphate loss in seawater is extremely small. Additional issues, such as the effect of the temperature of the seawater on uranium adsorption, will have to be studied.

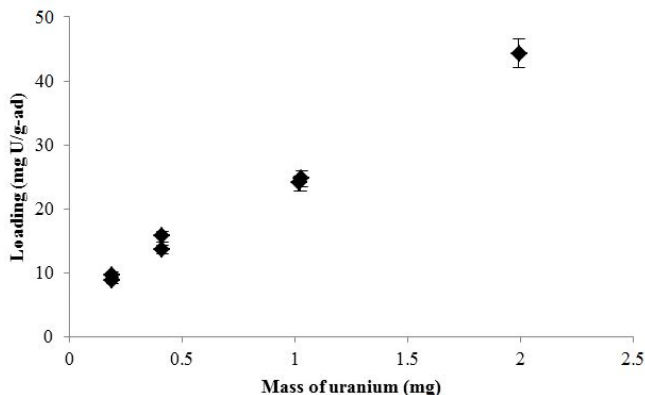
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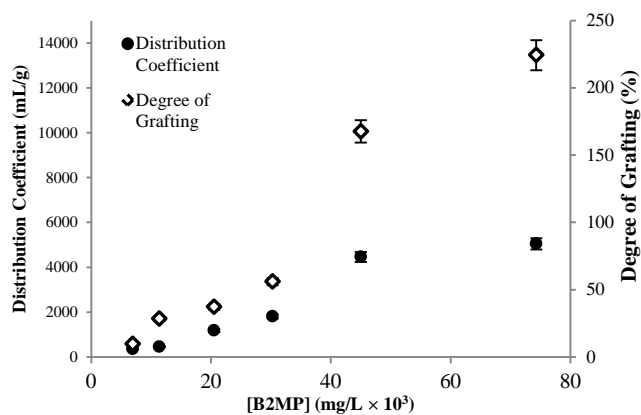
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## Figures

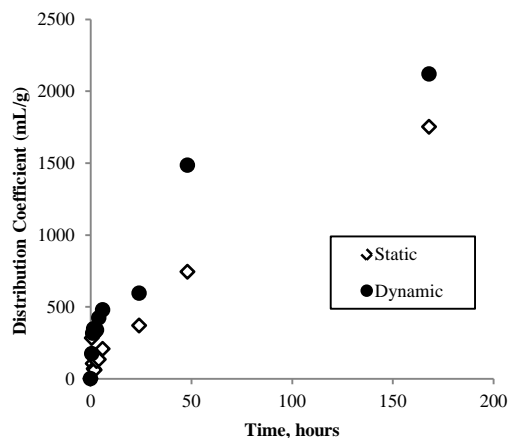


**Figure 1.** Loading of uranium on adsorbent with increasing mass of uranium in solution for B2MP grafted onto Winged™ nylon, Co-60 irradiation to 40 kGy total dose, 10 kGy/hr dose rate. Testing with 15 mg adsorbent, 10-100 mL of 20 mg/L U in seawater for 24 hours

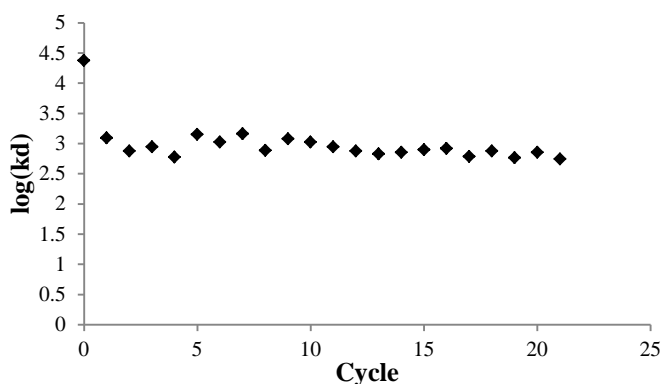


**Figure 2.** Relationship between degree of grafting and  $k_d$  for B2MP directly-grafted onto Winged nylon to 40 kGy, 10 kGy/hr. Testing with 10 mL of 20 mg/L U in seawater for 20 hours

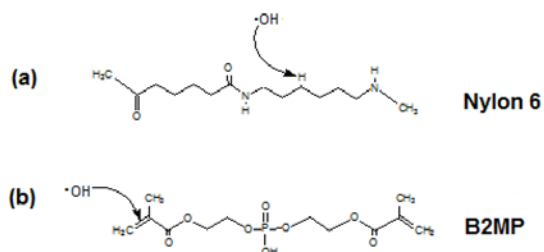




**Figure 3.** Preliminary kinetics of uranium loaded on an adsorbent based on B2MP grafting onto Winged nylon in both a static and dynamic (rotated) system. Measurements performed in real seawater doped to 20 mg U/L



**Figure 4.** Regeneration of adsorbent in 1 M ammonium oxalate solution. Adsorbent based on B2MP grafted onto Winged nylon, kd's determined in real seawater doped to 10 mg U/L.



**Figure 5.** The reaction between the hydroxyl radical produced by irradiation of the solvent and (a) the polymeric substrate, nylon 6 and (b) the monomer, B2MP