**Uranium Recovery from Seawater: Development of Fiber Adsorbents Prepared via Atom-Transfer Radical Polymerization**

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Uranium Recovery from Seawater: Development of Fiber Adsorbents Prepared via Atom-Transfer Radical Polymerization

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**Author Contributions:**
T.S. conceived the scope of work and directed the research with the guidance of S.D.. T.S wrote the manuscript with input from all coauthors, especially from S.B., S.C., and C.T.. Y.O. and C.J.
prepared the precursor fiber, i.e. performed RIGP on hollow-gear PE fiber. T.S. and S.B. performed the synthesis of fiber adsorbents. S.B., J.K., C.T., and R.M. conducted uranium adsorption experiment with simulated seawater and real seawater in a batch mode. L.K. and G.G performed a marine testing, uranium adsorption experiment with a continuous flow from Sequim Bay.

**Graphical Contents Entry**

![Novel Fiber Adsorbent](image)

Fiber adsorbents synthesized via ATRP
Summary (Abstract)

A novel adsorbent preparation method using atom-transfer radical polymerization (ATRP) combined with radiation-induced graft polymerization (RIGP) was developed to synthesize an adsorbent for uranium recovery from seawater. The ATRP method allowed a much higher degree of grafting on the adsorbent fibers (595–2818%) than that allowed by RIGP alone. The adsorbents were prepared with varied composition of amidoxime groups and hydrophilic acrylate groups. The successful preparation revealed that both ligand density and hydrophilicity were critical for optimal performance of the adsorbents. Adsorbents synthesized in this study showed a relatively high performance (141–179 mg/g at 49–62 % adsorption) in laboratory screening tests using a uranium concentration of ~6 ppm. This performance is much higher than that of known commercial adsorbents. However, actual seawater experiment showed impeded performance compared to the recently reported high-surface-area-fiber adsorbents, due to slow adsorption kinetics. The impeded performance motivated an investigation of the effect of hydrophilic block addition on the graft chain terminus. The addition of hydrophilic block on the graft chain terminus nearly doubled the uranium adsorption capacity in seawater, from 1.56 mg/g to 3.02 mg/g. The investigation revealed the importance of polymer chain conformation, in addition to ligand and hydrophilic group ratio, for advanced adsorbent synthesis for uranium recovery from seawater.

1. Introduction

Uranium (U) exists uniformly as uranyl carbonates (primarily as [UO$_2$(CO$_3$)$_3$]$^+$) at a concentration of ~3.3 ppb in seawater. Because of the vast volume of the oceans, the total amount of uranium in seawater is 4.5×10$^9$ tonnes, approximately 1000 times larger than the
A nuclear power plant is typically designed to operate for a long period of time, beyond 60 years. The reserves of uranium in conventional terrestrial mining will eventually deplete, and scarcity of uranium might become a significant issue in the foreseeable future, even for currently operating nuclear plants. Additionally, the environmental and human health impact for the conventional terrestrial mining is always a big concern. To resolve these issues associated with the conventional terrestrial mining of uranium, the extraction of uranium from seawater presents a very attractive alternative route to obtain uranium for our nuclear fuel needs. However, a significant challenge remains for making the extraction of uranium from seawater a commercially viable alternative technology. The biggest challenge for this technology to overcome is the development of adsorbents with increased uranium adsorption capacity.

A recent estimate of a polymer adsorbent for uranium recovery from seawater indicated that a polymer fiber adsorbent with 6 mg/g uranium adsorption capacity at 3% capacity loss per use with 10 uses or one with 30 mg/g uranium adsorption capacity at single use would give $290/kg-Uranium, a comparable uranium price to that ($100-335/kg-Uranium) from conventional terrestrial resources. In order to achieve increased uranium adsorption capacity, the adsorbent performance has to be optimized and new technological developments have to happen, especially as this technology requires a highly selective extraction from such a low concentration of uranium in seawater.

Over the last 30 years, many efforts had been devoted to this topic and one of the most successful strategies among them was polymer fiber adsorbents synthesized via radiation-induced graft polymerization (RIGP). Over the years, the Japanese team developed polymeric fiber adsorbents, which contained polyethylene or polypropylene as a trunk polymer and amidoximated polyacrylonitrile (PAN) copolymerized with hydrophilic groups (e.g.,...
poly(methacrylic acid)) as a graft chain. The incorporation of hydrophilic groups is crucial to allow seawater to access the amidoxime group on the graft chain. Japanese researchers also performed marine tests with stacked unwoven fabrics and braided fibers for different periods of time and at different locations. Their study has established a good foundation to this research field.

Recent efforts at the Oak Ridge National Laboratory (ORNL) employed the same strategy (i.e., using RIGP) but with different geometry polyethylene fibers, which provided a high surface area, and demonstrated an improved uranium adsorption capacity. Polymeric fiber adsorbents for uranium adsorption have several advantages: 1) already proven to be deployable in seawater, 2) light weight, 3) easy to fabricate to various shapes and lengths. However, polymeric fiber adsorbents prepared solely via conventional RIGP have some limitations such as inability to tune its composition, degree of grafting (d.g.), conformation, and morphology due to its ill-controlled polymerization mechanism. Therefore in this study, we utilized a hybrid approach of using RIGP and controlled radical polymerization, atom-transfer radical polymerization (ATRP) to prepare polymeric fiber adsorbents for uranium recovery from seawater. Although a hybrid approach of RIGP and ATRP was previously reported, an application to fiber adsorbents has never been implemented to the best of our knowledge. Moreover, our strategy used RIGP-grafted poly(vinylbenzyl chloride) (PVBC) in the first step, where VBC is a readily available commercial monomer. First, polymer chains containing ATRP initiation sites were grafted via conventional RIGP (Figure 1), then the ATRP initiation site was utilized for subsequent ATRP. The use of controlled radical polymerization method offers several tunabilities including controllable composition and controllable degree of polymerization (length of graft chains), which ATRP can either increase to a much higher d.g. or prepare the
exact d.g. for the best performance. Additionally, this strategy creates brushes on a brush (Figure 1) and the unique polymer architectures, i.e., three-dimensional morphology, can also elucidate characteristics of the dense brush conformation for adsorption in aqueous systems.

This manuscript focuses on the demonstration of the novel RIGP-ATRP hybrid approach to prepare polymeric fiber adsorbents for uranium recovery from seawater. Since the balance between ligand forming groups and hydrophilic groups is the key for the optimum composition of graft chains, this study investigates various ratios of amidoxime groups to acrylic acid groups, with similar reaction conditions. The d.g. was aimed to be sufficiently high, so that the effect of graft chain length was minimal. The influence of d.g., i.e. graft chain length, to the uranium adsorption capacity is not a focus of this manuscript, although it is another important study to be pursued in near future. Moreover, we investigated the effect of graft chain conformation for further improvement of the uranium adsorption capacity. Although the current study focuses only on the recovery of uranium from seawater, this novel strategy for the preparation of polymeric fiber adsorbents is expected to be applicable to adsorbent synthesis for other applications, including the extraction of precious or toxic metals, proteins, and organic pollutants.

2. Results and Discussion

2.1 Synthesis of Fiber Adsorbents via a Combination of RIGP and ATRP

Hollow-gear-shaped polyethylene (PE) fibers were prepared via bicomponent melt-extrusion spinning of linear low density polyethylene (LLDPE) and polylactic acid (PLA) followed by washing with tetrahydrofuran (THF).24 The resulting hollow-gear fiber tow was subsequently modified via radiation-induced graft polymerization of 4-vinylbenzyl chloride.
(VBC) in dimethylsulfoxide (DMSO) (Fig. 1). The resulting d.g. of poly(4-vinylbenzyl chloride) (PVBC) on the hollow-gear polyethylene (PE-g-PVBC) was 96.4%, where d.g. is defined as $100 \times \frac{\text{mass of PVBC}}{\text{mass of PE}}$. The series of ATRP of acrylonitrile (AN) and tert-butyl acrylate (tBA) were performed on the PE-g-PVBC. After many trials of various reaction conditions, the following ATRP conditions were used to prepare grafted fibers to give a sufficiently high d.g.: PE-g-PVBC (1; molar ratio of VBC), CuCl (1.2), CuCl$_2$ (0.05), tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN) (1.5), DMSO as a solvent (~50 vol%) at 65 °C. The reaction time was set for 24 h for all the reactions. The feed ratio of AN and tBA (Table 1) was systematically varied to prepare varied incorporation of hydrophilic group, i.e. acrylic acid, by subsequent hydrolysis of tBA. The chemical composition of the resulting fibers includes PE-g-PVBC-g-PAN or PE-g-PVBC-g-(PAN-co-tBA). The d.g. was calculated using $100 \times \frac{\text{mass of PAN-co-tBA}}{\text{mass of PE-g-PVBC}}$.

All the samples showed a d.g. of at least 600%/PE-g-PVBC, which was most likely sufficient to minimize the difference of the mass ratio in graft chains (PAN, PAN-co-tBA) to the trunk polymer (PE-g-PVBC), i.e., graft chains weighed $> \sim 85$ wt% of total adsorbent weight. The length of graft chains (i.e., molecular weight of grafted PAN and PAN-co-tBA) was estimated from the gravimetric weight gain (g) and the number of initiation cites (mol) with the assumption that all the benzyl chloride initiation cites on PVBC were initiated by ATRP (Table 1). It should be noted that it is not possible to cleave these immobilized graft polymers without destroying other components, thus the molecular weight was estimated with the above assumption. The graft chain molecular weights ranged from 1850 – 8760 g/mol, indicating that dense short chain brushes were attached on a PVBC graft chain brush.
The addition of \( tBA \) (samples 2–7) as a comonomer increased the resulting d.g. as compared to AN alone (sample 1). The elemental analysis of these samples (C, H, N, O) permitted the calculation of PAN:PrBA molar ratios on the graft chain (Table 1). The trend of the resulting graft chain composition correlates well with the monomer feed ratio. All batches showed more incorporation of AN than \( tBA \), as compared to the feed ratio, indicating higher AN reactivity in the copolymerization. To provide a better understanding of the reactivity of AN and \( tBA \) in this system, the reactivity ratio was estimated using a linear method\(^{26} \) (Supporting Information). The estimated reactivity ratio was \( r_{AN} = 1.61 \) and \( r_{BA} = 0.88 \). It should be noted that the reactivity ratio value is an approximate estimation since the composition from the elemental analysis lacks high precision due to possibility of various errors in the analysis. The reactivity ratio of AN and \( tBA \) in ATRP condition was not found in the literature, but Brar et al.\(^{27} \) reported the reactivity ratio of a similar combination of monomers, acrylonitrile (AN) and 2-methoxyethyl acrylate (MEA) by ATRP as \( r_{AN} = 1.52 \) and \( r_{MEA} = 0.60 \). The estimated reactivity ratio for AN and \( tBA \) in this study is consistent with the higher reactivity of AN over MEA in their report.

Grafting \( tBA \) alone showed much higher d.g. (i.e., 14500%/PE-g-PVBC) in a similar reaction condition. The higher d.g. of \( tBA \) homopolymer grafting than that of AN alone indicates that \( tBA \) propagates better than AN, and the high incorporation of AN in the copolymers despite poor d.g. of AN alone suggests that AN might have more termination or side reactions in this ATRP condition.\(^{28, 29} \) Overall, this ATRP method provides much higher d.g. on the adsorbents than that from RIGP alone. Such high d.g. and tunability of the graft chain length and composition (e.g., block copolymers) suggest that this ATRP approach is a promising strategy.
2.2 Uranium Adsorption Capacity in Simulated and Real Seawater

PE-g-PVBC-g-PAN and PE-g-PVBC-g-(PAN-co-PrBA) fibers were reacted with hydroxylamine to generate the amidoxime ligand, and subsequent potassium hydroxide (KOH) treatment was performed to increase the hydrophilicity of the adsorbents. The resulting fiber adsorbents included PE-g-PVBC-g-poly(amidoxime) (PAO) and PE-g-PVBC-g-(PAO-co-poly(acrylic acid)) (PAA). Uranium adsorption tests in simulated seawater, spiked with 6-ppm uranium, were initially performed under the following conditions: ~15 mg sorbent in 250 mL or 750 mL of 6 ppm U, 10123 ppm Na\(^+\), 15529 ppm Cl\(^-\), 140 ppm HCO\(_3^-\), pH 8, 20–25 \(^\circ\)C, 24 h. Uranium analysis was performed by ICP-OES at \(\lambda_{U} 367.007\) nm. A 250-mL solution provides a quantitative evaluation of the performance of the synthesized adsorbents; however, for well-performing adsorbents, uranium uptake may be limited by uranium availability. Thus, it is also recommended to perform experiments using a larger solution volume, e.g., 750-mL, in order to increase the availability of uranium which is necessary for high-capacity adsorbents. The U adsorption capacity of these novel fiber adsorbents (samples 1-6), estimated from 250 mL U-spiked solution (Table 2), was much higher than that of conventional U adsorbents including JAEA-provided fiber adsorbent prepared by RIGP (~20 mg/g), METSORB 16/60 (25.2 mg/g), METSORB STP (12.3 mg/g), METSORB HMRP 50 (46.3 mg/g), and Dyna Aqua (21.2 mg/g). The high U adsorption capacity of these novel fiber adsorbents confirms this RIGP/ATRP hybrid strategy for preparation of adsorbents as a promising approach.

The U adsorption capacity from the U-spiked simulated seawater at 250 mL also showed two distinctive trends. One followed the U-adsorbing ligand density and the other corresponded to the hydrophilicity of the immobilized graft chains. When more AN is incorporated, the ligand density in the graft chains, i.e., density of amidoxime (AO) groups, becomes higher. Higher tBA
incorporation results in increasing hydrophilicity due to tBA conversion to acrylic acid (AA). In other words, lower numbered samples in Table 1 have higher ligand density and higher numbered samples have more hydrophilic groups with less ligand density. When samples 1–3 are compared, the U adsorption capacity for samples 1 and 2 is higher than the capacity of sample 3 due to the higher ligand density. Among samples 3–7, U adsorption capacity is the highest for sample 5. The increase of the hydrophilicity facilitated the increase of U adsorption capacity from samples 3 to 5. Further increase in hydrophilicity from samples 5 to 7 showed an adverse effect on the U adsorption capacity due to their decreased ligand density. The trend of U adsorption capacity was further confirmed in experiments with 750-mL solution volume. A minor difference between 250-mL and 750-mL scales is that samples 1 and 2 showed higher capacity than sample 5 in 750-mL volume, while sample 5 showed the highest U adsorption capacity in 250-mL volume.

Several of these high-capacity adsorbents (samples 1, 2, 5, 6) were selected for further real seawater testing in a continuous-flow system at the Marine Sciences Laboratory of the Pacific Northwest National Laboratory, at Sequim, WA. In these experiments, the adsorbent was packed in columns of 1-inch diameter and 6-inch height. Glass beads of 3-mm diameter were also packed in the columns to keep the adsorbent uniformly distributed along the columns. A flow rate of 250-300 mL/min seawater was typically used in these tests. The amount of uranium adsorbed after 42 days in seawater exposure was 1.52 mg/g (sample 1), 1.56 mg/g (sample 2), and 1.08 mg/g (sample 5). These values are comparable to the performance of fiber adsorbents previously reported by the Japanese team, but lower than values recently reported, high surface area fiber adsorbents. Considering the similar performance between adsorbents developed in this study and fiber adsorbents previously prepared by RIGP alone with both 250-
mL and 750-mL U-spiked simulated seawater, the lower performance of these adsorbents in seawater tests indicates that certain parameters of these fibers, including polymer conformation and morphology, are not optimized at low U-concentration conditions. Also, more hydrophilic adsorbents (samples 5 and 6) showed lower capacity than adsorbents with high ligand density (samples 1 and 2). Thus, hydrophilic groups in this graft chain conformation are not a dominant factor for adsorption performance, indicating that hydrophilic group interactions with other ions in this crowded brush conformation probably impede either interparticle diffusion of uranyl ions or amidoxime reaction with uranyl ions.\textsuperscript{20}

Due to its high capacity with a balance of hydrophilicity and ligand density, sample 5 was chosen for an adsorption kinetics study, which was conducted both in a continuous seawater-flow mode at Sequim Bay and in a batch mode with filtered coastal seawater collected from Charleston, SC, USA. In the continuous-flow experiments at Sequim Bay, six columns of sample 5 adsorbent were placed in parallel in a multi-channel flow system, and over a period of eight weeks, a column was removed every week for the first four weeks and every other week for the remaining period. The adsorbent was collected from each column, and treated with 1 N hydrochloric acid to strip the adsorbed species and prepare samples for chemical analysis using ICP-OES. Results from ICP-OES analysis showed slow uranium adsorption kinetics (Figure 2). Using a one-site ligand-saturation-kinetics model, the half saturation time of the adsorbent upon U adsorption was estimated at 40 days, which is approximately twice that of previously reported fiber adsorbents.\textsuperscript{20, 21} The slow kinetic trend was further confirmed by a seawater batch experiment conducted with coastal gulfstream seawater. In this experiment, an amount of ~5-mg adsorbent was fluidized in a 5-gallon tank of seawater, which was sitting on a shaker operating at 100 rpm. Samples of seawater were removed periodically for uranium analysis using ICP-MS.
The amount of uranium adsorbed vs time was obtained from the uranium concentration of samples measured by ICP-MS. Results in Figure 3 show that the U adsorption history was similar to the one observed in continuous-flow experiments at the Marine Sciences Laboratory in Sequim, WA. At 80-day exposure time, a U adsorption capacity of 1.3 mg/g was observed. This not-so-high U-adsorption capacity with seawater does not correspond to the high capacity observed with simulated seawater, suggesting that the morphology or certain parameters of these adsorbents impede U uptake in real seawater.

2.3 Effect of Graft Chain Conformation

One of the reasons for the not-so-high U adsorption capacity for the adsorbent samples 1–7 in real seawater could be due to the graft chain conformation. Since PAN-co-PrBA was grafted onto each repeat unit of grafted PVBC chain, the density of ligand-containing brushes was significantly higher than that of regular adsorbents prepared solely by RIGP. The highly dense brushes on a brush conformation might prevent effective diffusion of U species to the amidoxime ligands. To further understand this hypothesis, chain extension of graft brushes via hydrophilic chains was performed. Use of ATRP method enables the preparation of a block copolymer architecture by reinitiating the end group of the graft chains.32, 33 The short chain of PrBA was added to the tip of the PE-g-PVBC-g-(PAN-co-PrBA) brush, and further hydrolysis resulted in PE-g-PVBC-g-(PAO-co-PAA)-b-PAA (Figure 4). Immobilized hydrophilic graft chains are known to stand and stretch in aqueous system.34, 35 Thus, the addition of hydrophilic PAA block at the graft chain terminus should aid standing and stretching graft chains, i.e., more spreading of each graft chain toward water, due to favorable interaction between hydrophilic groups and water (Figure 4, bottom).
The hydrophilic block addition was performed onto sample 2 via ATRP due to its highest U adsorption capacity in the continuous-flow seawater experiment (Table 2). The ATRP reaction time of tBA was varied from 0–5 h to prepare a varying degree of added PtBA block. The d.g. of PtBA ranged from 13.7 to 352% (Table 3, samples 2.1–2.4), where d.g. was calculated using 
\[100 \times (\text{mass of PtBA block}) / [\text{mass of sample 2 before amidoximation (i.e., PE-g-PVBC-g-(PAN-co-PtBA))}].\] The PtBA block was further hydrolyzed to form a PAA block via subsequent KOH treatment, resulting in PE-g-PVBC-g-(PAO-co-PAA)-b-PAA. The successful preparation of varied hydrophilic block length on the graft chain terminus allows us to investigate how much hydrophilic block is needed to enhance U adsorption.

In the 250-mL U-spiked simulated seawater test, U adsorption capacities constantly decreased from samples 2.1 to 2.4, corresponding to decreased ligand density (as observed in random copolymers, samples 2 to 7 in Table 2). A comparison between the original sample 2 adsorbent and the short-chain-grafted sample 2.1 adsorbent showed that they had high U adsorption capacities, on the order of 80 mg/g. Since sample 2.1 showed the highest U adsorption capacity and the highest % U adsorbed among all block copolymers (samples 2.1 to 2.4), sample 2.1 adsorbent was selected for a subsequent U-adsorption experiment with real seawater using the same method and conditions as previously used for random copolymers at the Marine Sciences Laboratory of the Pacific Northwest National Laboratory, in Sequim Bay, WA. The U-adsorption performance of sample 2.1 in the seawater experiment nearly doubled the capacity, from 1.56 mg/g to 3.02 mg/g. This increase in capacity indicates that graft chain conformation is as important as the ligand density and hydrophilicity. It should also be noted that sample 2.1 performed better than adsorbents with PAO-co-PAA random copolymer graft chains, samples 2–7. The importance of ligand density and hydrophilicity has been previously reported,
but the significance of chain conformation has not been investigated yet in this field. To the best of our knowledge, this work is the first demonstration of the effect of graft chain conformation to the U-adsorption capacity. Our novel approach of utilizing controlled radical polymerization enabled us to alter the graft chain composition, and demonstrated the importance of graft chain conformation in addition to ligand density and hydrophilicity.

3. Experimental

3.1 Materials

Acrylonitrile (AN, >99%, Alfa Aesar) and tert-butyl acrylate (tBA, 99%, Alfa Aesar) were deinhibited via passing through activated alumina column prior to use. Copper(II) chloride, (CuCl₂, anhydrous, 98% min, Alfa Aesar), copper(I) chloride, (CuCl, 99.999%, Alfa Aesar), tris(2-(dimethylamino)ethyl)amine (Me₆-TREN, >99%, Alfa Aesar), 4-vinylbenzyl chloride (VBC, 90%, Acros Organics), dimethylformamide (DMF, anhydrous, Alfa Aesar), dimethylsulfoxide (DMSO, >99%, Alfa Aesar), tetrahydrofuran (BDH), acetone (BDH), methanol (Fisher), and potassium hydroxide (Fisher) were used as received. Hydroxylamine solution (50 wt % in water, Aldrich) was used in the preparation of AO reaction mixture. Uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O, B&A Quality), sodium bicarbonate (Aldrich), and sodium chloride (>99%, Aldrich) were used for the preparation of U-spiked simulated seawater.

3.2 Synthesis of Fiber Adsorbents

Hollow-gear shaped fibers were prepared via bicomponent melt-extrusion spinning of linear low density polyethylene (LLDPE) and polylactic acid (PLA) at Hills Inc. Dissolving the fugitive PLA component by washing the bicomponent fibers in THF at 50 °C gives LLDPE hollow gear fibers. The hollow-gear fiber tow was subsequently grafted with VBC in DMSO.
via the radiation-induced graft polymerization technique. The detailed method is described elsewhere.\textsuperscript{18, 19, 25} The resulting degree of grafting (d.g.) of poly(4-vinylbenzyl chloride) (PVBC) on the hollow-gear polyethylene (PE-g-PVBC) was 96.4 %, where d.g. is defined as $100 \times \text{mass of PVBC/mass of PE}$.

The following optimum ATRP conditions were employed on the PE-g-PVBC: PE-g-PVBC (1; molar ratio of VBC), CuCl (1.2), CuCl\textsubscript{2} (0.05), tris(2-(dimethylamino)ethyl)amine (Me\textsubscript{6}-TREN) (1.5), DMSO as a solvent (~50 vol%), and reaction temperature 65 °C for 24 h. The feed ratio of AN and tBA (Table 1) was systematically varied to control the degree of incorporation of the hydrophilic group, i.e., acrylic acid. After the reaction, grafted fibers were isolated, washed with DMSO and acetone several times, and dried under vacuum at 40 °C for several hours. The chemical composition of the resulting fibers includes PE-g-PVBC-g-PAN or PE-g-PVBC-g-(PAN-co-tBA). The d.g. was calculated using $100 \times \text{mass of PAN-co-tBA/mass of PE-g-PVBC}$. The series of PE-g-PVBC-g-(PAN-co-tBA)-b-tBA was also synthesized via the following conditions (Figure 4): PE-g-PVBC-g-(PAN-co-tBA) (1; molar ratio of VBC), CuCl (2.0), CuCl\textsubscript{2} (0.1), Me\textsubscript{6}-TREN (2.4), tBA (2000), DMSO as a solvent (~50 vol %) and reaction temperature at 65 °C for 0–5 h. The experimental procedure is the same as above.

The third step involves the amidoximation (AO) of AN groups in the polymer brush, followed by KOH treatment. AO was performed twice to ensure complete conversion of AN groups in grafted polymer chains, and a large excess of hydroxylamine (HA) was used each time. A volume of 6.0 mL of HA mixture (10 wt % in 1:1 (w/w) methanol/water) was added to 15±1 mg of the fiber adsorbent. The first AO was performed for 48 h at 80 °C. The reaction mixture was then replaced by fresh HA mixture (6.0 mL), followed by the second AO (80 °C, 24 h). The fibers were then washed with deionized water until neutral pH was achieved and dried in a
vacuum oven at 40 °C overnight, yielding constant weights. Prior to each U adsorption test, KOH treatment of the fibers was performed by adding 15.0 mL of 2.5 wt% KOH solution to an accurate weight of a dry amidoximated fiber (15.0±1.0 mg). The mixture was heated to 80 °C and maintained for 3 h. The fibers were then filtered and washed with deionized water until neutral pH was observed. Care was taken to ensure that the fibers did not become dry, and no loss of fibers occurred at any step of the procedure.

3.3 Adsorbents Characterization

Elemental analyses of PE-g-PVBC-g-(PAN-co-PrBA) fibers for carbon, nitrogen, hydrogen, and oxygen (C, H, N, and O) were performed by Galbraith Laboratories, Inc. (Knoxville TN). U adsorption tests were performed on amidoximated, KOH-conditioned fiber adsorbents, which were kept wet until the test. For simulated seawater tests, the preparation of U-spiked (5–7 ppm U) simulated seawater was reported elsewhere. Briefly, 17 mg \( \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \), 25.6 g NaCl, and 193 mg NaHCO\(_3\) were dissolved in deionized water to make a 1 L solution. A mass of 15.0±1.0 mg fibers was shaken in 250 mL or 750 mL of simulated seawater solution (pH ~8) for 24 h at room temperature. The amount of uranyl ion uptake was determined from the concentration difference between the beginning and the end of the test on a Perkin–Elmer Optima 2000 DV ICP-OES at 367.007 nm. The uranium adsorption capacity (mg/g) was calculated from \( \left[ (C_i - C_f) \ [\text{mg/L}] \right] \times \left[ \frac{\text{volume of solution [L]}}{\text{mass of adsorbent [g]}} \right] \) and % adsorbed was calculated from \( \left[ \frac{(C_i - C_f)/C_i} \right] \times 100 \), where \( C_i \) and \( C_f \) represent the initial and final solution concentrations.

3.4 Uranium Adsorption in Seawater

The performance of fiber adsorbents was assessed in continuous-flow experiments with seawater at the Marine Sciences Laboratory of the Pacific Northwest National Laboratory in
Sequim Bay, WA. A mass of ~60 mg of adsorbent was packed in a flow-through column of 1-inch diameter and 6-inch height. The adsorbent was uniformly distributed in the column volume and help in place by adding glass beads of 3-mm diameter. Marine testing was performed using filtered (0.45 µm) seawater at a temperature of 20±2 °C and at flow rate of 250–300 mL/min) using an actively pumping through a multi-channel flow system. A detailed experimental setup and analytical methods are described elsewhere.4

Batch adsorption experiments were performed using 5-gallon polyethylene tanks filled with filtered coastal seawater collected from Charleston, SC, USA. A mass of 5-mg of the adsorbent was added into a 5-gallon tank, with the adsorbent fibers freely suspended in the seawater. An initial seawater sample of 10 mL was collected prior to the addition of the adsorbent. The containers were shaken constantly at 100 rpm at room temperature (∼23 °C). 10 mL samples were collected periodically, using a pipet, for a duration of 80 days. Collected seawater samples were acidified with Optima nitric acid for analysis. The adsorbent fibers were recovered after the experiment and treated with concentrated acid solution for uranium elution.20

4. Conclusions

This manuscript demonstrated a novel adsorbent preparation method for U recovery from seawater. The ATRP method provides a much higher d.g. on the adsorbents than that achieved by RIGP alone. Such a high d.g. and tunability of the graft-chain length and composition (e.g., block copolymers) suggest that this ATRP approach is a promising strategy. This work also demonstrated that both ligand density and hydrophilicity were critical for optimal performance and the optimum balance was adsorbents with high ligand density and sufficient hydrophilicity. Although these adsorbents showed high performance in concentrated simulated U solution,
actual seawater tests with low concentration of uranium showed impeded performance due to slow adsorption kinetics. This behavior is attributed to the hypothesis that the brushes on the brush structure might be too crowded to allow efficient uranyl ion diffusion to the ligand. The U adsorption performance in seawater, which is lower than expected considering the results from simulated seawater, motivated further investigation of the importance of graft-chain conformation. Use of the ATRP method allowed us to prepare different compositions of graft chains through synthesis of a block copolymer architecture. The addition of a hydrophilic block on the graft chain terminus nearly doubled the U adsorption capacity in seawater and the observed capacity (3.02 mg/g) is comparable to the previously demonstrated best capacity adsorbent for uranium from seawater. Further investigation of graft chain conformation (length, density, composition) to U adsorption performance will be pursued in future work.

Acknowledgments

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### Table 1  ATRP of AN and tBA on PE-g-PVBC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed ratio (AN/PE-Y)</th>
<th>d.g. (%/PE-g-PVBC)</th>
<th>Graft-chain composition molar ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PAN-co-PrBA graft chain molecular weight (g/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
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<td>0</td>
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<sup>a</sup> from elemental analysis  
<sup>b</sup> estimated from the gravimetric weight gain (g) and the number of initiation cites (mol)

### Table 2  Summary of U adsorption data

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<tr>
<th>Sample</th>
<th>U adsorption (250 mL) (mg/g)</th>
<th>% adsorbed</th>
<th>U adsorption (750 mL) (mg/g)</th>
<th>% adsorbed</th>
<th>U adsorption (seawater) (mg/g)</th>
<th>Exposure time (days)</th>
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### Table 3  Degree of grafting and U adsorption capacity of block copolymer adsorbents

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<tr>
<th>Sample</th>
<th>d.g. (%/Sample 2)</th>
<th>U adsorption (250 mL) (mg/g)</th>
<th>% adsorbed</th>
<th>U adsorption (seawater) (mg/g)</th>
<th>Exposure time (days)</th>
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<td>352</td>
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</table>
Figures

Fig. 1 Reaction scheme for the preparation of fiber adsorbents via ATRP.

Fig. 2 Uranium adsorption kinetic data for sample 5 adsorbent in continuous-flow experiments with seawater at the Marine Sciences Laboratory in Sequim Bay, WA.
Fig. 3  Uranium adsorption kinetic data for sample 5 adsorbent in a batch mode of filtered coastal seawater.

Fig. 4  Hydrophilic-group addition to the tip of graft chains by block copolymer synthesis.

References