Extracting Uranium from Seawater: Promising AI Series Adsorbents

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Abstract

A new series of adsorbents (AI10 through AI17) were successfully developed at ORNL by radiation induced graft polymerization (RIGP) of acrylonitrile (AN) and vinylphosphonic acid (VPA) (at different mole/mole ratios) onto high surface area polyethylene fiber, with high degrees of grafting (DOG) varying from 110 to 300%. The grafted nitrile groups were converted to amidoxime groups by reaction with 5 wt% hydroxylamine at 80 ºC for 72 hours. The amidoximated adsorbents were then conditioned with 0.44M KOH at 80ºC followed by screening at ORNL with simulated seawater spiked with 8 ppm uranium. Uranium adsorption capacities in simulated seawater screening ranged from 171-187 g-U/kg-ads irrespectively of %DOG. The performance of the adsorbents with respect to uranium adsorption in natural seawater was also investigated using flow-through-column testing at the Pacific Northwest National Laboratory (PNNL). Three hours KOH conditioning led to higher uranium uptake than one hour. The adsorbent AI11 containing AN and VPA at the mole ratio of 3.52, emerged as the potential candidate for the highest uranium adsorption (3.35 g-U/Kg-ads.) after 56 days of exposure in seawater flow-through-columns. The rate of vanadium adsorption over uranium linearly increased throughout the 56 days of exposure. The total mass of vanadium uptake was ~5 times greater than uranium after 56 days.

Key words: graft polymerization, amidoxime, uranium adsorption, seawater, KOH conditioning

Introduction

Seawater is considered a major source of uranium with an estimated quantity of around 4.5 billion metric tons, which is nearly 1000 times higher than that available in terrestrial ores.[1-2] The extraction of uranium from seawater has been explored since the first half of the last century, but it is still far from being an economically viable method of uranium production because of the fact that the concentration of uranium in seawater is of the order of 1.4×10^{-8} mol/L (3.3 ppb).[3] Uranium in seawater is present principally as the anionic tricarbonatouranate (VI) [UO2 $(CO_3)_3]^{4-}$ species under the prevailing conditions.[4] A recent study determined that the dominant uranium(VI) species in seawater is the neutral $[Ca_2UO_2(CO_3)_3](aq)$.[5] Functionalized polymeric adsorbents in the forms of resins, beads, gels, or membranes have potential applications in selective preconcentration or separation of target metal ions from multicomponent environmental aqueous samples from ground water, seawater ,process waste streams etc.[6,7] Development of polymeric sorbents having different functional groups for the removal of heavy metal ions is of great importance due to their potentially high ion selectivity and easy handling.[8,9] A variety of hydrogels with special characteristics have received increasing importance because of their wide ranging applications.[10-12] The extraction of uranyl ions by structured hydrogels composed of acrylamide-maleic acid and acrylamideacrylic systems has been studied by Akkas et al. and Ghanshyam et al.[13, 14] Mun et al. and Nursel Pekel et al. carried out adsorption studies of the uranyl ions by hydrogels based on polyethylene glycol and methacrylic acid copolymers and N-vinyl 2-pyrrolidone/acrylonitrile copolymers containing amidoxime groups.[15, 16] Acrylic acid-co-2-acrylamido-2-methylpropane-1-sulfonic acid hydrogels were evaluated for uranium recovery by Atta et al.[17] It is most likely that uranium may not saturate the adsorbent during its

preconcentration from lean aqueous feeds like seawater. In such a situation, it is likely that other ions may also be adsorbed in the adsorbent along with uranium.

Over the past few decades, polyamidoxime (PAO)-based adsorbents have been demonstrated to be the most promising candidates for uranium extraction from seawater.[18-23] Marine tests by Japanese researchers with PAO-braided fiber adsorbents showed 1.5 g-U/Kg-adsorbents after 30 days of exposure in the Okinawa area.[24] Inspiring from this preliminary success, a number of research works have been carried out to provide a better understanding of the effects of different factors and parameters on the uranium adsorption capacity of PAO from seawater.[25-31] Adsorption of U(VI) from seawater by the PAO adsorbent has been found to be highly dependent on the physical parameters of the sorbent matrix , such as free volume, pore structure, tortuosity, hydrophilicity etc.[23,32-34] The presence of an acidic co-monomer with appropriate p*K*a value in the active binding sites may trigger the adsorption kinetics of U(VI) from seawater in the PAO adsorbent.[20,32,33]

In this present work, a series of adsorbents (AI series) containing acrylonitrile (AN) along with vinylphosphonic acid (VPA) at different mole ratios were prepared by radiation induced graft polymerization (RIGP) onto high surface area polyethylene trunk fiber.[35,36] Conversion of poly(acrylonitrile) (PAN) to PAO in the grafted precursor fibers was done by reacting with hydroxylamine. The AF series adsorbents were conditioned with 0.44M KOH at 80 ºC for two time-periods, i.e., 1 hour and 3 hours before they were explored for their uranium uptake capability by: (i) uranium uptake capacity after 24 hours contact with simulated seawater screening solution (spiked with uranium nitrate) at ORNL and (ii) uptake of uranium and other metal ions from natural seawater from Sequim Bay, WA, after exposure for 56 days, at the

Marine Science Laboratory (MSL) of the Pacific Northwest National Laboratory (PNNL) located in Sequim, WA.

Materials and Methods

Materials

All chemicals were reagent-grade or higher. Acrylonitrile (AN), vinylphosphonic acid (VPA), tetrahydrofuran (THF), methanol, dimethylsulfoxide (DMSO), N,N- dimethylformamide (DMF), hydroxylamine hydrochloride (HA-HCl) and potassium hydroxide (KOH) were obtained from Sigma-Aldrich. Ultrapure water (18 MΩ cm^{-1}, Thermo scientific Nanopore) was used in the preparation of HA-HCl and KOH solutions. Hollow-gear, high-surface-area polyethylene fibers (PE) were prepared by melt-spinning at Hills, Inc. (Melbourne, FL), using polylactic acid (PLA) as the co-extrusion polymer. Uranyl nitrate hexahydrate ($UO_2(NO_3)_2.6H_2O$, B&A Quality), sodium bicarbonate ($NaHCO_3$, ACS Reagent, Aldrich) and sodium chloride (>99%, Aldrich) were used to prepare the simulated seawater, and a 1000 ppm uranium (U) standard solution (High Purity Standards, North Charleston, USA) was used to prepare the ICP standards.

Preparation of adsorbent

The adsorbent fibers were prepared by RIGP at the NEO Beam Electron Beam Cross-linking Facility (Middlefield, OH). Prior to irradiation, the PLA was removed by submerging the fibers in excess THF under reflux at 65-70 °C overnight followed by drying at 40 °C under vacuum. The pre-weighed dry fiber samples were placed inside double-layered plastic bags within a plastic glove bag and sealed under nitrogen. The fibers were irradiated in the presence of dry ice using a translation table cycling the fibers for 16 passes under the electron beam to a dose of approximately 200 ± 10 kGy using 4.4-4.8 MeV electrons and 1 mA current from an RDI

Dynamitron electron beam machine. The total irradiation time was approximately 22 minutes. After irradiation, the fibers were immersed in 300-mL flask containing previously de-gassed grafting solutions consisting of AN and VPA in DMSO. The flasks were then placed in an oven at 64 °C for 18 hours for grafting. After grafting, the fibers were drained from the solution and washed with DMF to remove unreacted monomers and homopolymers followed by methanol and dried at 40 °C under vacuum. The grafted fibers were weighed to gravimetrically determine the percent degree of grafting (%DOG) of co-polymers onto the trunk polymer from pre-irradiation and post-grafting weights by using Eq.1:

$$\%DOG = \frac{\left(wt_{AG} - wt_{BG}\right)}{wt_{BG}} x100 \quad (1)$$

where wt_{BG} = dry weight before grafting and wt_{AG} = dry weight after grafting.

The nitriles in the grafted fiber samples were converted to amidoxime (AO) groups by treating with 10 wt% hydroxylamine hydrochloride in 50/50 (w/w) water/methanol (previously neutralized with KOH) at 80 °C for 72 h. The samples were then washed under vacuum filtration with deionized water, followed by a methanol rinse and allowed to dry at 40 °C under vacuum.

KOH conditioning of AO'd AF series fiber adsorbents

The AI series adsorbents were conditioned with 0.44M KOH at 80 ºC for two time-periods i.e., 1 hour and 3 hours prior to exposing them in the simulated seawater screening solution, as well as natural seawater for testing the uranium uptake capacity and kinetics.

Simulated seawater screening for uranium adsorption determination

Uranium adsorption in simulated seawater was carried out at ORNL. The simulated seawater screening solution was prepared by dissolving 193 ppm sodium bicarbonate, 25,600 ppm sodium chloride, and 8 ppm uranium from uranyl nitrate hexahydrate in 18.2 MΩ cm^{-1} water. The pH of the test solution was approximately 8. The concentrations of sodium and bicarbonate were selected to be similar to those of seawater. An aliquot was taken before addition of the adsorbent to measure the initial uranium concentration. Each of the alkaline-conditioned adsorbent samples was equilibrated with 750 mL of simulated seawater solution for 24 hours at room temperature with constant shaking at 400 rpm. After contacting for 24 hours, an aliquot was collected and the initial and final solutions were analyzed by inductively coupled plasma-optical emission spectroscopy (Perkin Elmer Optima 2100DV ICP-OES) at 367 nm. The uranium adsorption capacity was calculated from the difference in uranium concentration in the aliquot samples using Eq 2. The ICP-OES was calibrated using 6 standard solutions ranging from 0-10 ppm, which were prepared from 1000 ppm uranium in 5 wt % nitric acid stock solution, and a linear calibration curve was obtained. A blank solution of 2–3 wt % nitric acid was also prepared, and washouts were monitored between samples to ensure no uranium was carried over into the next analysis. In addition, a solution of 5 ppm yttrium in 2 wt % nitric acid was used as an internal standard, which was prepared from 1000 ppm stock solution (High-Purity Standards, North Charleston, USA).

$$\text{Uranium (U) adsorption capacity} = \left[\frac{Initial\ [U]\left(\frac{mg}{L}\right) - Final\ [U]\left(\frac{mg}{L}\right)}{g\ of\ dry\ adsorbent}\right] \times \text{Soln. vol. (L)} \quad (2)$$

Field Adsorption Tests

The adsorbent performance in the natural seawater was carried out at the Marine Sciences Laboratory (MSL), Pacific Northwest National Laboratory (PNNL), for 56 days in a flow-through column system, to assess and characterize in terms of kinetics and adsorbent capacity within 8 weeks by varying KOH-conditioning parameters, such as temperature and time. The quality of seawater was quantitatively monitored for pH, temperature, salinity, and trace-metal concentrations over the experimental period. The average salinity and uranium concentration observed in this study was approximately 12% lower than the normal salinity of 35 practical salinity units (psu) and uranium concentration of 3.3 ppb in seawater. Marine testing was performed using filtered (0.45 μm) seawater at a temperature of 20 ± 2 °C and at a flow rate of 250 mL/min, using an active pumping system. The details of the natural seawater adsorption test at MSL has been described elsewhere.[26, 37]

The performance of adsorbents in real seawater was assessed at PNNL-MSL located in Sequim, Washington. AI series adsorbents (~50 mg each) were conditioned with 0.44 M KOH at 80ºC for two different periods, i.e., 1 and 3 hours. Right after conditioning, adsorbents were packed into columns (1" diameter, 6" long) fabricated from all plastic components, mostly PVC and polypropylene. Pre-cleaned glass wool and 5 mm glass beads were used to hold the adsorbents in place in the column. The columns were installed in a 24-column all-PVC manifold for seawater flow-through adsorption testing. Seawater was pumped from Sequim Bay, WA, and filtered through 0.45 μm polypropylene cartridges for the continuous-flow adsorption experiment. The seawater temperature was controlled at 20±1ºC using an all-titanium immersion-heater in the head tank. Temperature and flow rate in each column were continuously monitored (10 min interval) using a temperature logger equipped with a flexible hermetically

sealed RTD sensor probe (OMEGA Engineering, Stamford, CT, USA) and an in-line turbine-style flow sensor (Model DFS-2W, Digiflow Systems), respectively. During the course of the adsorption experiment, seawater salinity and pH were monitored daily using a hand-held salinometer (Model 30, YSI) and pH meter (Orion 3 STAR, Thermo). The seawater exposure time of the adsorption experiment in this field experiment was 56 days. After the seawater exposure was completed, the adsorbents were removed from the columns and desalted by thoroughly rinsing with DI water. The adsorbents were further dried using a heating block and weighed. Digestion of the adsorbents was conducted with a 50% aqua regia solution at 85 °C for 3 hours. Samples were further diluted with DI water to be in the desired concentration range before analysis. Analysis of uranium and other trace elements was conducted using a Perkin-Elmer Optima 4300DV ICP-OES.

Results and discussion

The AI series adsorbents containing different mole ratios of AN and VPA were successfully prepared by RIGP. A representative chemical structure of AI series adsorbent is shown in Figure 1. A summary of the chemical compositions of the AI series adsorbents and their degree of grafting (calculated using eq.1) is presented in Table1.

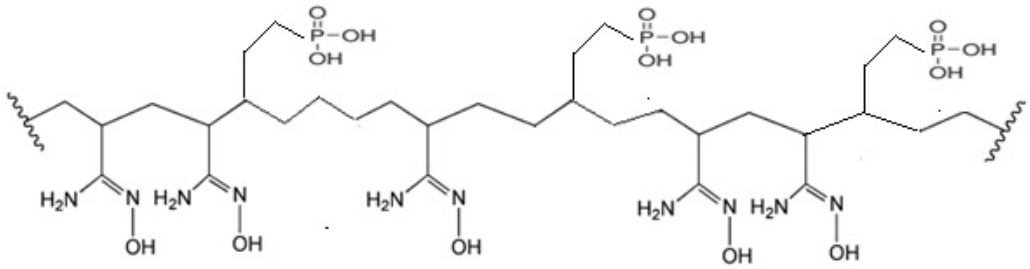

Figure 1. Chemical structure of amidoximated AI series adsorbents.

Table 1: Chemical compositions and degree of grafting of the AI series adsorbents

Adsorbent ID	AN/VPA mol/mol	% DOG
AI12	1.91	110
AI13	2.33	205
AI14	2.86	173
AI10	3.21	143
AI11	3.52	269
AI15	4.41	235
AI16	5.62	191
AI17	7.39	300

Fourier Transform Infrared (FTIR) spectrometry

FTIR spectra of the AI11fiber samples were recorded on a Perkin Elmer Frontier FTIR with a single-bounce diamond attenuated total reflectance (ATR) accessory at 2 cm^{-1} resolution and averaged over 16 scans. The spectra are shown in Figure 2. The stretching frequencies at 2247 cm^{-1}, 1376 cm^{-1} and 1094 cm^{-1} (Figure 2b) are corresponding to C≡N, free P=O and P-O-H groups,[20] respectively, and thus confirm grafting of acrylonitrile and vinylphosphonic acid onto the polyethylene. The disappearance of the nitrile stretch and appearance of N-H (3390 and 3230 cm^{-1}), C=N (1645cm^{-1}) and N-O (930 cm^{-1}) clearly indicates the conversion of the nitrile to amidoxime (AO). The appearance of the stretch at 1561 cm^{-1} (representative of COO^- group)represents the fact that some part of the amidoxime converted into carboxylate upon conditioning with 0.44M KOH at 80 ºC.

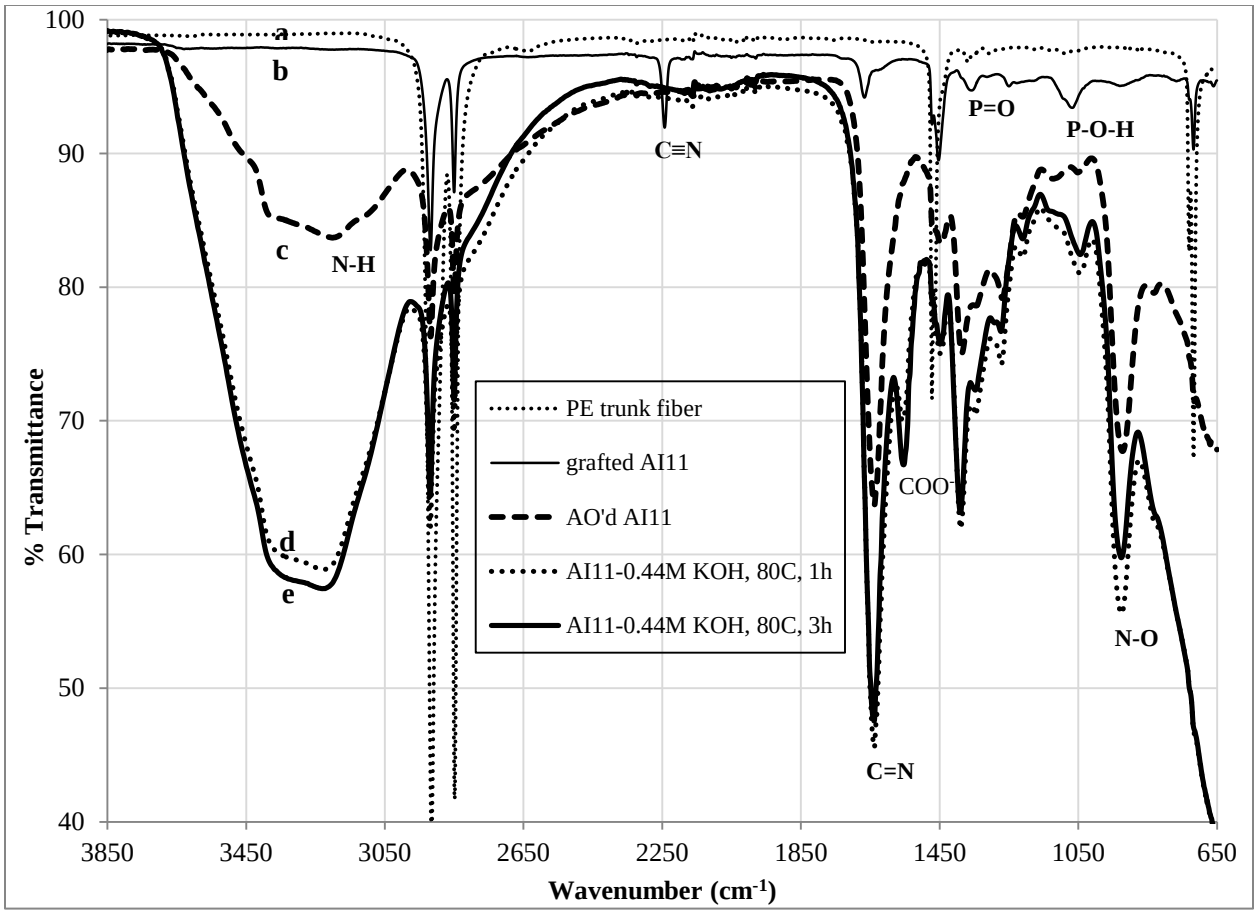

Figure 2. FTIR spectroscopy of (a) trunk PE fiber; AI11 adsorbent after (b) grafting, (c) amidoximation and (c, d) conditioning with 0.44M KOH at 80 C for 1hour and 3 hours, respectively.

Simulated seawater screening

Uranium adsorption studies with AI series samples for 24 hours of contact with the simulated seawater solution spiked with 8 ppm uranium were carried out after conditioning with 0.44M KOH at 80 ºC for 3 hours. As illustrated in Figure 3, the uranium adsorption capacity of the AI series adsorbents gradually increased with increasing AN/VPA mole ratio and reached a maximum at about 3.52. The uranium adsorption gradually decreased beyond the AN/VPA mole of 3.52 (i.e., AI11). Simulated seawater screening studies thus indicated that the adsorbent with

AN/VPA molar ratio in the range of 3.21-3.52 appears to be the optimum chemical composition for the highest uranium adsorption capacity from real seawater.

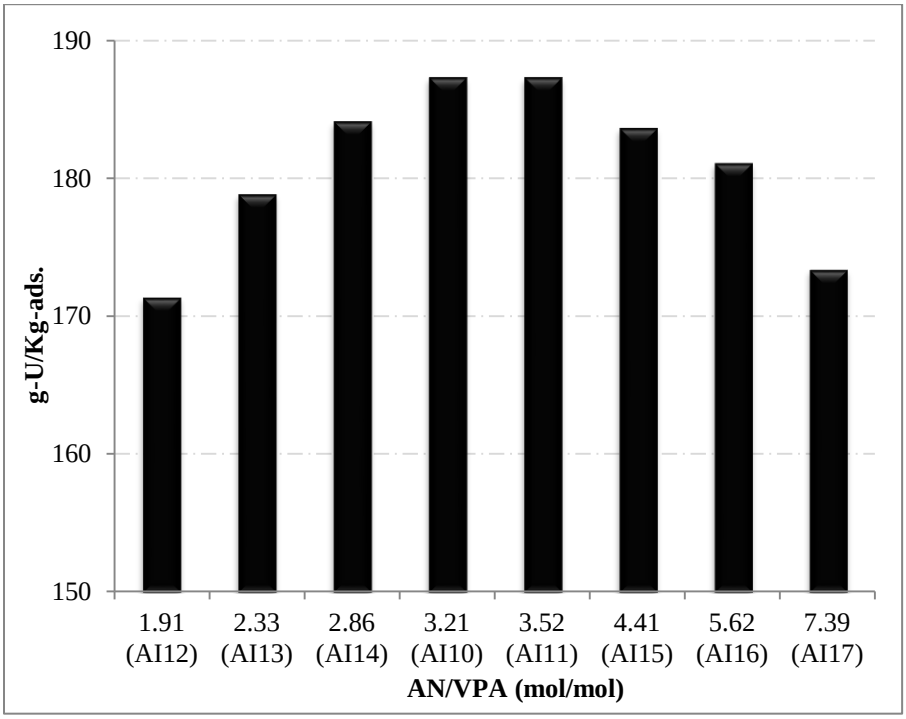

Figure 3. Uranium uptake capacities of AI series samples after 24 hours contact with simulated seawater screening solution spiked with uranyl ions at 7-8 ppm, after conditioning with 15 ml of 0.44M KOH at 80 ºC for 3 hours.

Field seawater testing

The performance of AI series adsorbents in natural seawater at PNNL-MSL was determined with filtered seawater from Sequim bay for 56 days contact in flow-through columns, carried out after treating with 0.44 M KOH at 80 ºC for 1 hour and 3 hours is shown in Figure 4. It appears that 3 hours KOH conditioning was slightly better than 1 hour with respect to uranium adsorption capacity by all the AI series adsorbents. Irrespective of the KOH conditioning time, the uranium adsorption gradually increased with increasing AN/VPA molar ratio in the adsorbents and reached a maximum at 3.52. It is also interesting to note that 3.52 (i.e., AI11 adsorbent), as

predicted from the simulated seawater screening study, was the optimum AN/VPA molar ratio providing the highest uranium adsorption capacity, including 3.35 g-U/Kg-ads and 3.25 g-U/Kg-ads after three hours and one hour KOH conditioning, respectively.

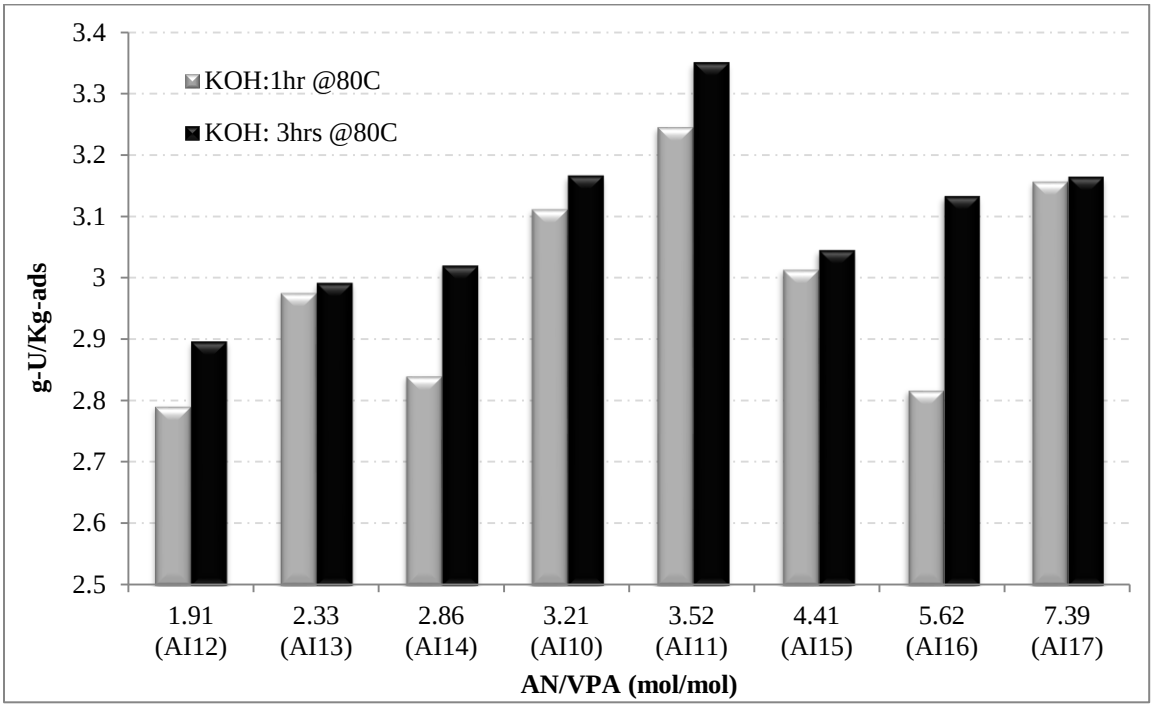

Figure 4. Uranium adsorption capacities of AI series samples after 56 days contact with Sequim Bay seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

Uranium adsorption selectivity over vanadium

The concentration of vanadium in seawater is quite low with an average level of ~1.9 ppb. One of the greatest drawbacks of PAO adsorbents is competition from vanadium.[38, 39] Adsorption of vanadium reduces the uranium capacity, and it also binds so strongly that eluting this metal may irreversibly damage the adsorbent.[27, 40] A comparison of the molar ratio of uranium over vanadium adsorption, after 56 days flow-through column testing in natural seawater is shown in Figure 5 after conditioning of the AI series adsorbent with 0.44M KOH at 80 ºC for 1 hour and 3

hours. Three hours of KOH conditioning, in general, favored adsorption of uranium more over vanadium as compared to one hour KOH conditioning. The adsorbent AI10 and AI11 (i.e., AN:VPA=3.21 and 3.52 mol/mol, respectively) treated with KOH for three hours, adsorbed more uranium over vanadium than the other candidates in the series. The AN/VPA molar ratio of 3.52, thus emerged as the optimum ratio for the highest and better selective adsorption of uranium from seawater.

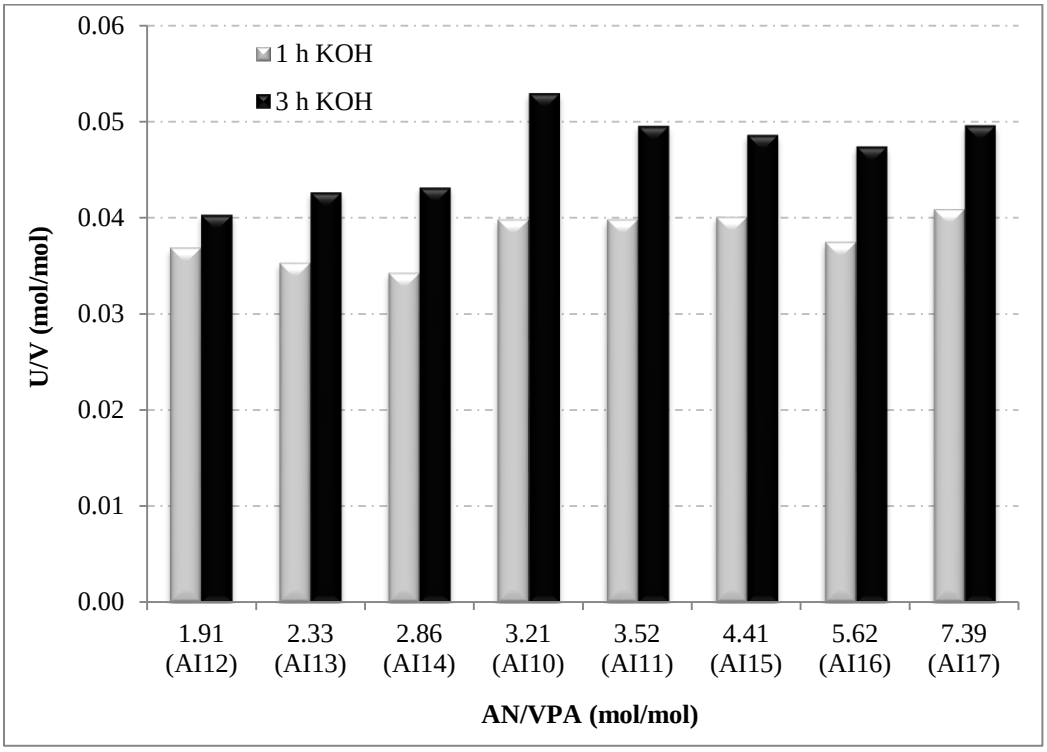

Figure 5. Adsorption of uranium over vanadium as a function of AN and VPA molar ratio of the AI series adsorbents after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

Kinetics of metal ions adsorption

The AI11 adsorbent was used to study the adsorption kinetics of uranium, vanadium and other metals from seawater, after conditioning with 0.44M KOH at 80 ºC for three hours. Around 50 mg of KOH-treated AI11 samples were packed in the respective columns through which filtered seawater from Sequim bay was passed at a flow rate of 250-300 $mL.min^{-1}$, at 20 ºC, over fixed durations, i.e., 7, 14, 21, 35, 42 and 56 days. The adsorption kinetics of uranium and some of the other metals (i.e., copper, zinc, iron, vanadium, calcium and magnesium) from seawater is illustrated in Figure 6. The rate of adsorption of the charge balancing ions of calcium and magnesium was very fast in the first 7 days and reached a plateau after 3 weeks. Uptake of copper and zinc is very low (< 1 g-U/Kg-ads) and reached equilibrium within a week. Uptake of uranium slowly increased with time and the uptake rate was maximum in the first week. The uptake rate of iron was the same as uranium up to 21 days but adsorbed at a higher rate afterwards. The most interesting part of this study was the very fast rate of vanadium adsorption. The vanadium adsorption linearly increased with time and did not reach equilibrium even after 56 days of exposure. A comparison of vanadium uptake over uranium (mole/mole) is shown in the inset of Figure 6. The adsorption of vanadium over uranium linearly increased throughout the 56 days of exposure. The total amount (g/Kg-ads.) of vanadium adsorbed by AI11 is ~5 times higher than that of uranium after 56 days of exposure in seawater in flow-through-column testing. The observed very high V/U ratio indirectly supports the fact that two adjacent amidoxime groups may be involved for coordination with one UO_2^{2+}, while VO_2^{+} most likely binds with one amidoxime group as well as imidazole nitrogen.[39]

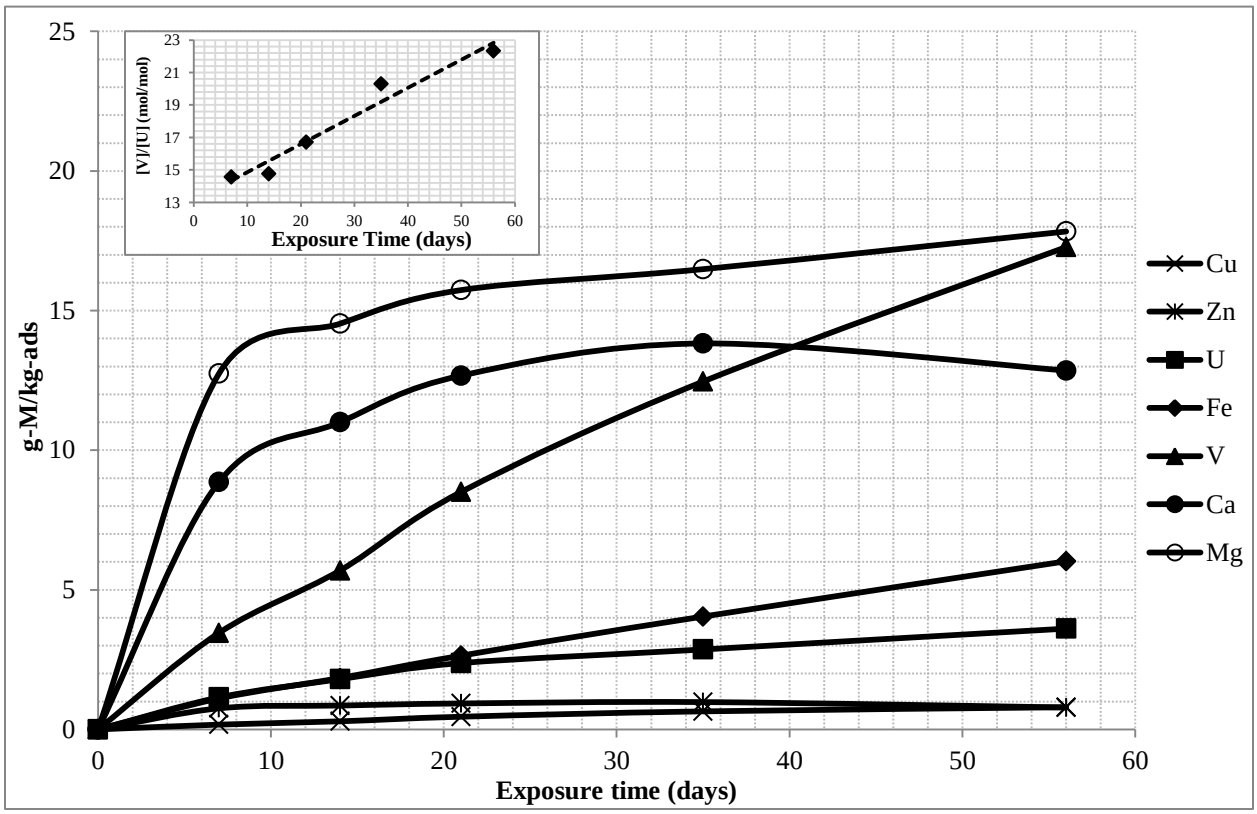

Figure 7. Adsorption kinetics of uranium, vanadium, iron, calcium and magnesium by the AF series adsorbents after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

Conclusions

The AI series adsorbents containing different mol ratios of acrylonitrile and vinylphosphonic acid were successfully prepared by electron beam induced graft polymerization onto high surface polyethylene fibers. The uranium adsorption performance of the AI series samples was investigated by two methods: 1) by contacting the adsorbent with simulated seawater spiked with 8 ppm uranium for 24 hours at ORNL and 2) in filtered natural seawater from Sequim Bay at

PNNL-MSL for 56 days exposure in flow-through columns. The AI11 adsorbent grafted with the molar ratio of 3.52 acrylonitrile to vinylphosphonic acid emerged as a promising candidate for high uranium adsorption efficiency from seawater as indicated in the adsorption studies performed using simulated seawater (at ORNL) and natural seawater (at PNNL). Three hours KOH conditioning (0.44M, at 80 ºC) was better than 1 hour with respect to uranium adsorption capacity by all the AI series adsorbents. The uranium adsorption capacities of the AI11 adsorbent after 56 days exposure in the flow-through columns were 3.25 g-U/Kg-ads and 3.35 g-U/Kg-ads after one hour and three hours KOH conditioning, respectively. The adsorption rate of uranium is faster than copper and zinc but slower than iron and vanadium. The adsorption of vanadium over uranium linearly increased throughout the 56 days of exposure. The total amount (g/Kg-ads.) of vanadium adsorbed by AI11 was ~5 times higher than uranium after 56 days of exposure in natural seawater in the flow-through-column test.

Acknowledgement

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