Extracting Uranium from Seawater: Promising AF Series Adsorbents

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Abstract

A new family of high-surface-area polyethylene fiber adsorbents named as AF series, was recently developed at the Oak Ridge National Laboratory (ORNL). The AF series adsorbents were synthesized by radiation-induced graft polymerization of acrylonitrile and itaconic acid (at different monomer/co-monomer mol ratios) onto high surface area polyethylene fibers. The degree of grafting (%DOG) of AF series adsorbents was found to be 154 – 354%. The grafted nitrile groups were converted to amidoxime groups by treating with hydroxylamine. 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. The uranium adsorption capacity in simulated seawater screening ranged from 170-200 g-U/kg-ads irrespective of %DOG. A monomer/co-monomer mol ratio in the range of 7.57-10.14 seemed to be optimum for highest uranium loading capacity. Subsequently, the adsorbents were also tested with natural seawater at Pacific Northwest National Laboratory (PNNL) using flow-through column experiments to determine uranium loading capacity with varying KOH conditioning time at 80ºC. The highest adsorption capacity of AF1 measured after 56 days of marine testing was demonstrated as 3.9 g-U/kg-adsorbent and 3.2 g-U/kg-adsorbent for 1hr and 3hrs of KOH conditioning at 80ºC, respectively. Based on capacity values of several AF1 samples, it was observed that changing KOH conditioning from 3hrs to 1hr at 80ºC resulted in 22-27% increase in uranium loading capacity in seawater.

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

Introduction

As estimated by IAEA, the total identified conventional uranium resources can only last for about a century.[1] Hence it is of great importance to exploit some new and sustainable uranium sources at affordable cost. The concentration of uranium in seawater is of the order of 1.4x10^{-8} mol/L (3.3 ppb)[2] and is found to be present principally as the anionic tricarbonatouranato (VI) $[UO_2(CO_3)_3]^{4-}$ species.[3] A recent study claimed that the dominant uranium (VI) species in seawater is the neutral $[Ca_2UO_2(CO_3)_3](aq)$.[4] Although the concentration of uranium (VI) in seawater is low, the total amount of 4.5 billion tons of uranium locked in seawater[5] is much larger than the territorial sources. It can effectively supplement the shortage of uranium and satisfy the demand for uranium for nuclear power plants in the future. It is reported that if 1% of this amount of uranium can be recovered for use in nuclear power plants, the presently known resource will be multiplied by a factor of 10. $[UO_2(CO_3)_3]^{4-}$, the dissolved species of uranium in seawater makes its extraction chemically possible by conventional methods i.e., solvent extraction, co-precipitation, ion exchange, electrode deposition, membrane filtration, coagulation etc. Out of various separation technologies investigated for uranium recovery from seawater, however, solid phase extraction by chelating adsorbent polymers was found to be the most feasible preconcentration-separation process in terms of cost, adsorption capacity and environmental footprint.[6-8]

Development of polymeric adsorbents having different functional groups for the removal of heavy metal ions is of great importance due to their high ion selectivity and easy handling.[9,10] Poly(amidoxime) (PAO) has been found to be chemically viable for the uranium recovery from seawater[11]. One of the greatest drawbacks of PAO adsorbents is competition from vanadium[11-14] which is present in seawater at a mass concentration of ~1.9 ppb, which is lower than that of uranium. However, considering the molar concentration of vanadium in seawater i.e., 3.7×10^{-8}, which is a ~2.6 time higher than that of uranium. The physical and chemical structures of the PAO-sorbents play an important role in uranium sorption from seawater.[15,16-18] The presence of an acidic co-monomer with an appropriate pK_a value may enhance the adsorption kinetics and uptake capacity of uranium from seawater by the PAO-sorbent.[16, 17, 19] The objective of the present work is to study the effects of chemical compositions of PAO adsorbents on the uranium uptake capacity from seawater. A new family of high surface area polyethylene fiber adsorbents named as, AF series was recently developed at the Oak Ridge National Laboratory (ORNL).[20,21] The AF series of adsorbents that include AF1 through AF9 were synthesized by radiation-induced graft polymerization of acrylonitrile (AN) monomer and itaconic acid (ITA) co-monomer (at different monomer/co-monomer mol ratios) onto high surface area polyethylene fibers. Conversion of poly(acrylonitrile) (PAN) to PAO in the grafted precursor fibers was done by reacting with hydroxylamine. It is also a well-known fact that conditioning of PAO sorbent with KOH significantly enhances the uranium loading capacity from seawater.[7, 11, 15, 22] 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 from a simulated seawater screening solution (which was spiked with uranium nitrate) exposure for 24 hours in ORNL and (ii) uptake of uranium and other metal ions from real seawater (Sequim Bay, WA) exposure for 56 days, at the Pacific Northwest National Laboratory (PNNL).

Materials and Methods

Materials

All chemicals were reagent-grade or higher. Acrylonitrile (AN), itaconic acid (ITA), 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-extrustion 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 PE based adsorbent fibers were prepared by radiation-induced graft polymerization (RIGP) using the facility at the NEO Beam Electron Beam Cross-linking (Middlefield, OH). The co-extruded polylactic acid (PLA) was removed from PE by submerging the fibers in excess THF at 65-70 °C overnight, before the irradiation. 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 for a total period of ~22 minutes. The irradiated fibers were immediately immersed in 300-mL flask containing previously de-gassed grafting solutions consisting of AN and ITA in DMSO in the glove bag under nitrogen atmosphere. The flasks were then put in an oven at 64 °C for 18 hours for grafting. After grafting, the fibers were drained from the solution and thoroughly washed with DMF to remove unreacted monomers and homopolymers followed by methanol and dried at 40 °C under vacuum. The percentage degree of grafting (%DOG) was determined gravimetrically from pre-irradiation and post-grafting weights, of co-polymers onto the trunk polymer (Eq 1):

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

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

The conversion of the grafted nitriles in fiber samples into amidoxime (AO) groups was performed 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 amidoximated samples were then washed 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 AF 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 or real seawater for testing the uranium uptake capacity.

Simulated seawater screening for uranium adsorption determination

Batch experiments with synthetic seawater were conducted at ORNL. The simulated seawater screening solution consisting of 193 ppm sodium bicarbonate, 25,600 ppm sodium chloride, and

8 ppm uranium from uranyl nitrate hexahydrate was prepared 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. A sample of the solution was collected prior to adsorbent addition to determine the initial uranium concentration. Each of the KOH-conditioned adsorbent samples was then 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 taken and the initial and final solutions were analyzed using inductively coupled plasma-optical emission spectroscopy (Perkin Elmer Optima 2100DV ICP-OES) at 367 nm. From the difference in uranium concentration of the solution, the uranium adsorption capacity is determined, 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).

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

Field Adsorption Tests

The adsorbent performance, carried out at the Marine Sciences Laboratory, Pacific Northwest National Laboratory (PNNL) for 56 days in a flow-through column, was assessed and characterized in terms of kinetics and adsorbent capacity equilibrium using natural seawater 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 uranium concentration observed in this study was slightly lower than the normal uranium concentration in seawater of 3.3 ppb [for a salinity of 35 practical salinity units (psu)]. 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. Glass wool and glass beads were used as packing materials for the columns. The details of the natural seawater adsorption test at MSL has been described elsewhere.[23]

Sample Handling and Analytical Procedures at PNNL

The performance of adsorbents in real seawater was assessed at PNNL-MSL located in Sequim, Washington. AF series adsorbents (~50 mg each) were conditioned with 0.44 M KOH at 80ºC for different period i.e., 1 and 3 hours. The conditioned 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 is pumped filtered through 0.45 μm polypropylene cartridges before it flows through the manifold for the continuous-flow adsorption experiment. The seawater temperature is controlled at 20±1ºC using an all-titanium immersion-heater. The flow rate in each column is typically controlled at 250-300 mL/min. Temperature and flow rate are periodically monitored in every ten minutes 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 experiments, 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 was 56 days.

After the seawater exposure was completed, the adsorbent fibers were removed from the columns and desalted by thoroughly rinsing with DI water. The adsorbent fibers 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 performed using a Perkin-Elmer Optima 4300DV ICP-OES with quantification based on standard calibration curves.

Results and discussion

The AF series adsorbents having different mole ratios of AN and ITA were successfully synthesized by RIGP. The degree of grafting of the adsorbents calculated by using eq.1 ranged from 150-350%. The grafted acrylonitrile was converted to amidozime by reacting with 10 wt % hydroxylamine hydrochloride in 50/50 (w/w) water/methanol (previously neutralized with KOH) at 80 °C for 72 h. The chemical structure of an amidoximated AF adsorbent in represented in Figure1.

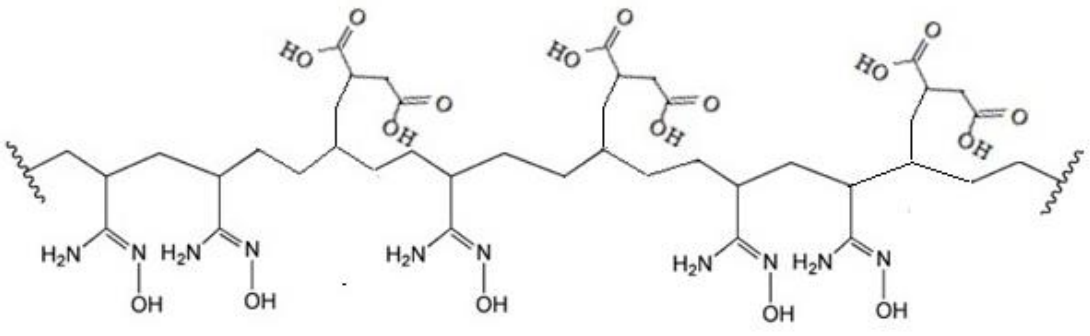

Figure 1. Representative chemical structure of AF series adsorbnets.

Elemental analysis

Two samples, i.e., AF1 and AF8 were selected for elemental analysis. The degree of grafting of AF1 and AF8 adsorbent calculated by eq.1 were ~354% and 348%, respectively. The weight gain after amidoximation with 10 wt% hydroxylamine at 80ºC for 72 hours was ~30%. The elemental analysis for carbon, hydrogen, nitrogen and oxygen was carried out by Galbraith Laboratories, Inc., Knoxville, TN. The results of elemental analysis are shown in Table 1. The nitrogen and oxygen percentage in the electron beam grafted material confirms that AN and ITA are grafted onto PE at an 85:15 and 93:7 weight percent ratio in AF1 and AF8, respectively. The percent weight increase of nitrogen and oxygen in the amidoximated samples indicates significant conversion of acrylonitrile into amidoxime. The difference in the total percentage of elements confirms deprotonation of the amidoxime functional groups on conditioning with KOH. It can also be postulated that loss of nitrogen with gain of oxygen indicates conversion amidoxime into another functional group (e.g. carboxylate) upon conditioning with 0.44 M KOH.

Table 1. Results of C, H, N, O elemental analysis

Sample ID	Elements (wt %)				
	C	H	N	O	Total
PE hollow fiber	84.88	15.77	< 0.5	< 0.5	~100
grafted AF1	67.08	8.16	18.54	6.12	~100
Amidoximated AF1	48.95	8.13	20.15	22.53	~100
AF1 – 0.44 M KOH @80 ºC for 3 hrs	45.43 (48.27)	7.6 (8.08)	16.88 (17.94)	24.27 (25.79)	~94* (100)
grafted AF8	69.14	7.57	19.45	2.72	~100
Amidoximated AF8	49.24	8.18	20.86	21.43	~100
AF8 – 0.44 M KOH @80 ºC for 3 hrs	45.67 (48.33)	7.22 (7.64)	18.42 (19.49)	23.19 (24.54)	~94* (100)

*The rest (6%) is potassium.

Scanning Electron Microscopy (SEM)

The crosses sectional images of the grafted, amidoximated and KOH-conditioned AF1 dried fibers, collected using a JOEL, JSM-6060 SEM at 10kV, demonstrated the hollow gear definition with good gear lengths and increase in fiber diameter after amidoximation. It is also interesting to note that i) the amidoximated fibers are further swelled on KOH conditioning and ii) the fibers retain their hollow gear definition even after 3 hours of KOH conditioning.

Fourier Transform Infrared (FTIR) spectrometry

FTIR spectra of the AF1 and AF8 fiber 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 frequency at ~ 2245 cm^{-1} is a representative of C≡N group and thus confirms grafting of acrylonitrile onto the polyethylene. The stretching frequencies at 1704 cm^{-1} (Figure 2a) and 1765 cm^{-1} (Figure 2b) represent the carbonyl group of itaconic acid in AF1 and AF8, respectively. The disappearance of the nitrile stretch and appearance of N-H (3400, 3250 cm^{-1}), C=N (1670 cm^{-1}), C-N (1245 cm^{-1}) and N-O (950 cm^{-1}) clearly indicates the conversion of the nitrile to amidoxime (AO). The appearance of the stretch at 1560 cm^{-1} represents the fact that some part of the amidoxime converted into carboxylate upon conditioning with 0.44M KOH at 80 ºC.

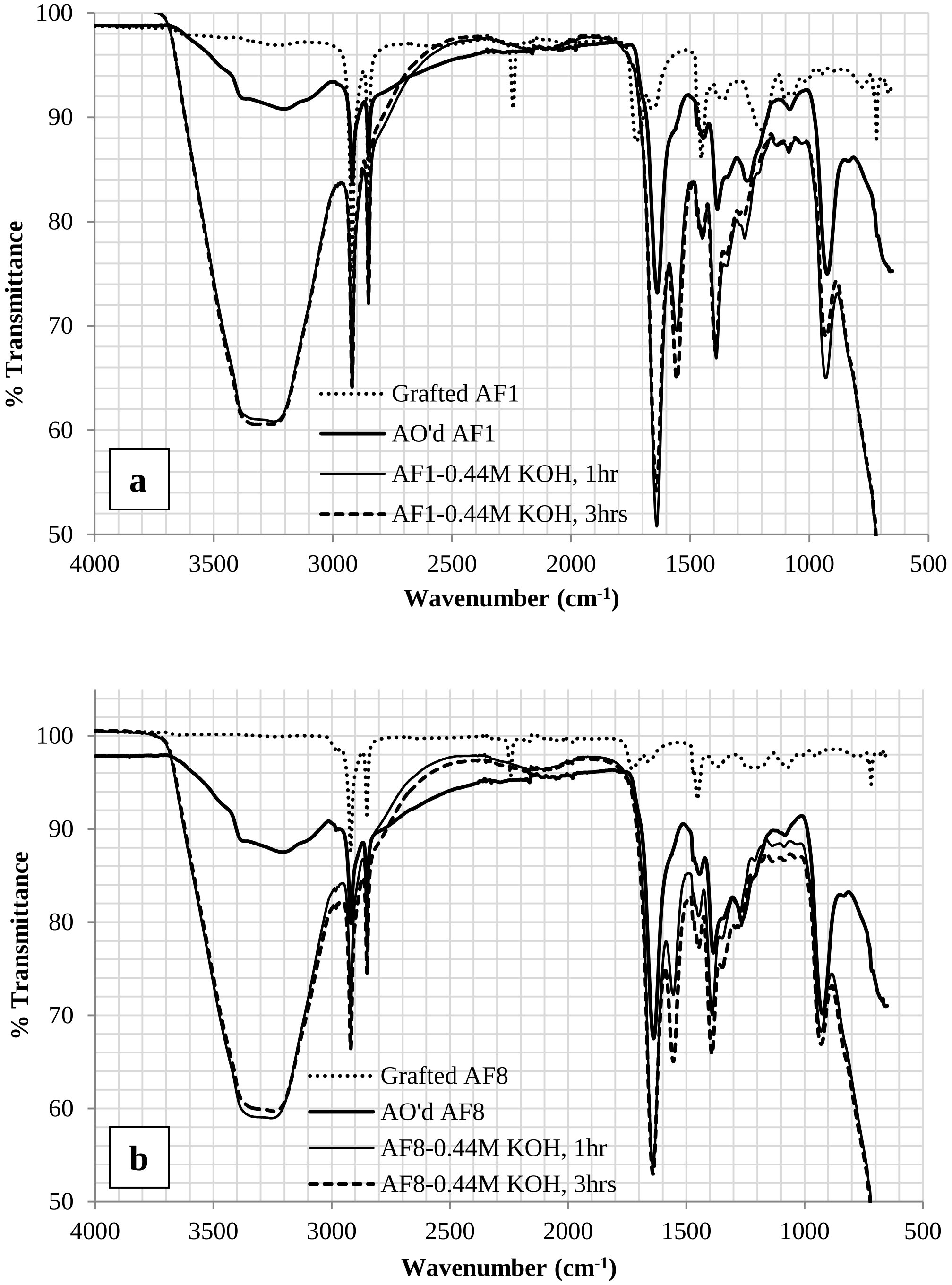

Figure 2. FTIR spectroscopy of AF1 (a) and AF8 (b) fiber after grafting, amidoximation and KOH conditioning.

Simulated seawater screening

The uranium adsorption studies of the AF series samples after 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 1 hour and 3 hours. As illustrated in Figure 3, the adsorption capacity of the AF series adsorbents are quite high for both 1 hour and 3 hours KOH conditioning and did not show a definite trend with AN and ITA mole ratio. However, simulated seawater screening studies did indicate that an adsorbent with AN/ITA molar ratio in the range of 7.57-14.50 might be the optimum chemical composition for the highest uranium adsorption capacity from real seawater.

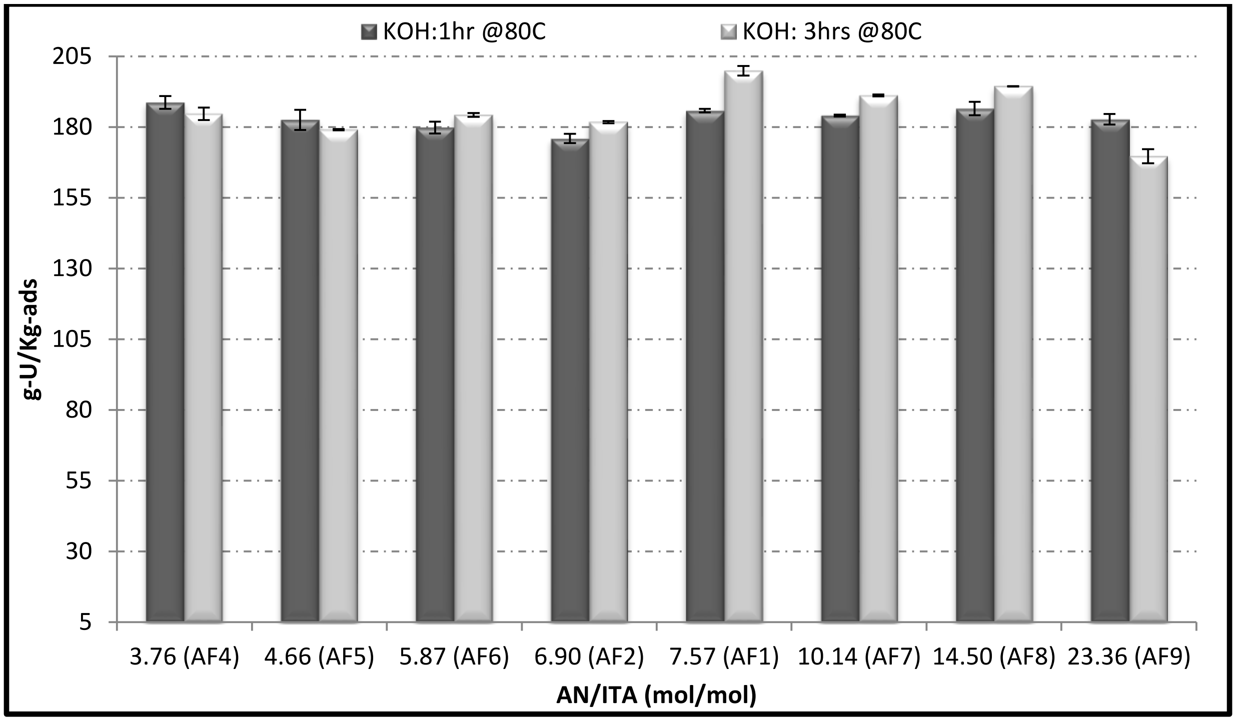

Figure 3. Uranium uptake capacities of AF series samples after 24 hours contact with simulated seawater screening solution spiked with uranyl ions at 7-8 ppm, after conditioning with 15 ml of 0.44M KOH at 80 ºC for 1hour and 3 hours.

Field seawater testing

The performance of AF series adsorbents in natural seawater at PNNL-MSL with filtered water from Sequim Bay for 56 days 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. As can be seen from the figure, one hour KOH conditioning was better than three hours with respect to uranium adsorption capacity by all the AF series adsorbents. Irrespective of the KOH conditioning time, the uranium adsorption gradually increases with increasing AN/ITA molar ratio in the adsorbents and reaches a maximum followed by a plateau region. It is also interesting to note that 10.14 and 7.57 are the

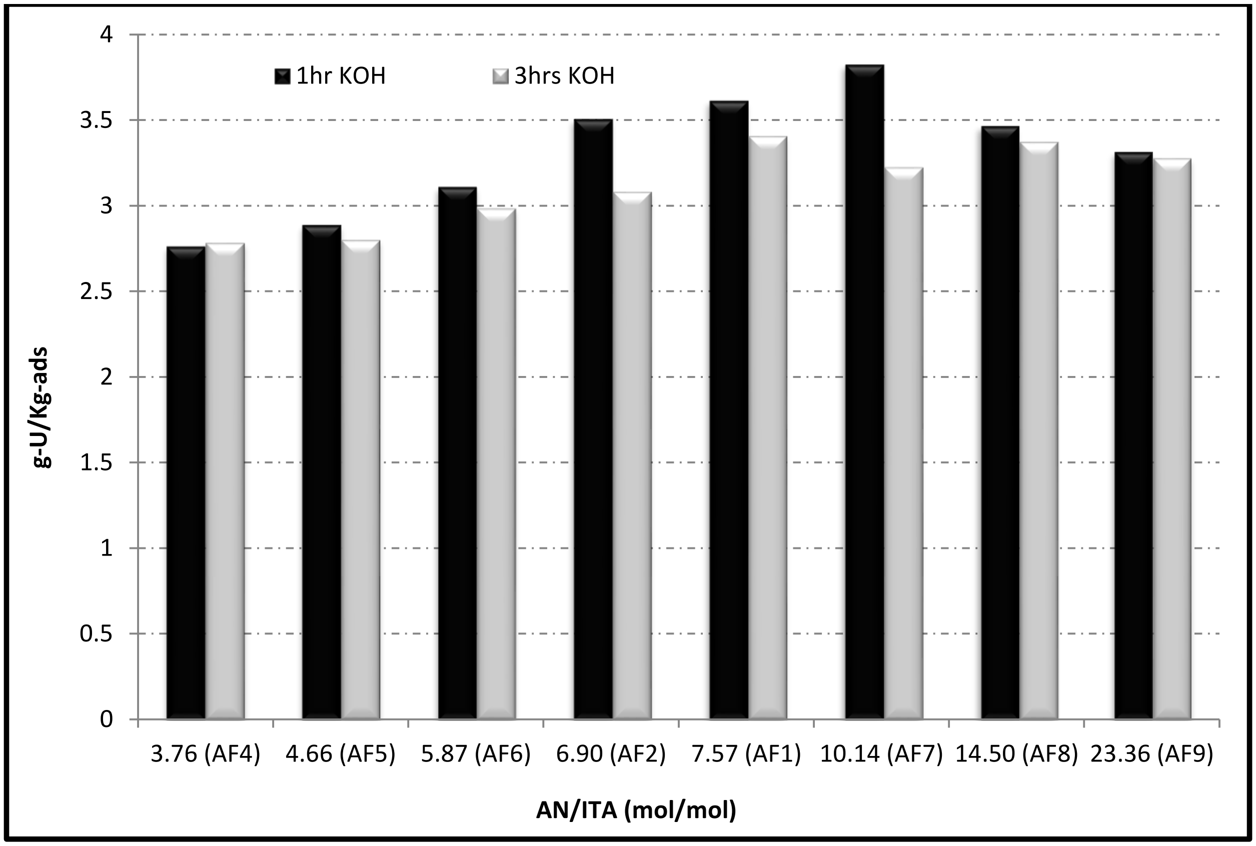

Figure 4. Uranium adsorption capacities of AF series samples after 56 days contact with Sequim Bay seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

optimum AN/ITA molar ratio in the case of one hour and three hours KOH conditioning, respectively toward the highest uranium adsorption capacity (i.e., 3.83 and 3.41 g-U.Kg^{-1}-ads, respectively). The results of the field seawater study are consistent with the simulated seawater screening.

Uranium adsorption selectivity over vanadium and iron

A comparison of the molar ratio of uranium over vanadium and iron adsorption, after 56 days of flow-through column testing in natural seawater is shown in Figure 5a&b after conditioning of the AF series adsorbent with 0.44M KOH at 80 ºC for one hour and three hours. Three hours of KOH conditioning, in general, favored adsorption of uranium over vanadium and iron as compared to one hour KOH conditioning. The adsorbent AF9 (i.e., AN:ITA=23.36 mol/mol) treated with KOH for three hours, uptakes more uranium over vanadium and iron than the other candidates in the series. On the other hand, the AF7 adsorbent (i.e., AN:ITA=10.14 mol/mol) treated with KOH for one hour, adsorbs more uranium over vanadium and iron than that for three hours. This observation indeed supports the fact that 10.14 is the optimum molar ratio between AN and ITA for obtaining the highest and most selective adsorption of uranium from seawater, upon conditioning with 0.44M KOH at 80 ºC for one hour.

Uptake of calcium and magnesium

A comparison of the molar ratio of uranium adsorption over the charge balancing ions, such as calcium and magnesium, after 56 days flow-through column testing in natural seawater is shown in Figure 6a&b after conditioning of the AF series adsorbent with 0.44M KOH at 80 ºC for one hour and three hours. The AF series adsorbents conditioned with KOH for one hour preferentially adsorbed more uranium over calcium and magnesium as compared to three hours

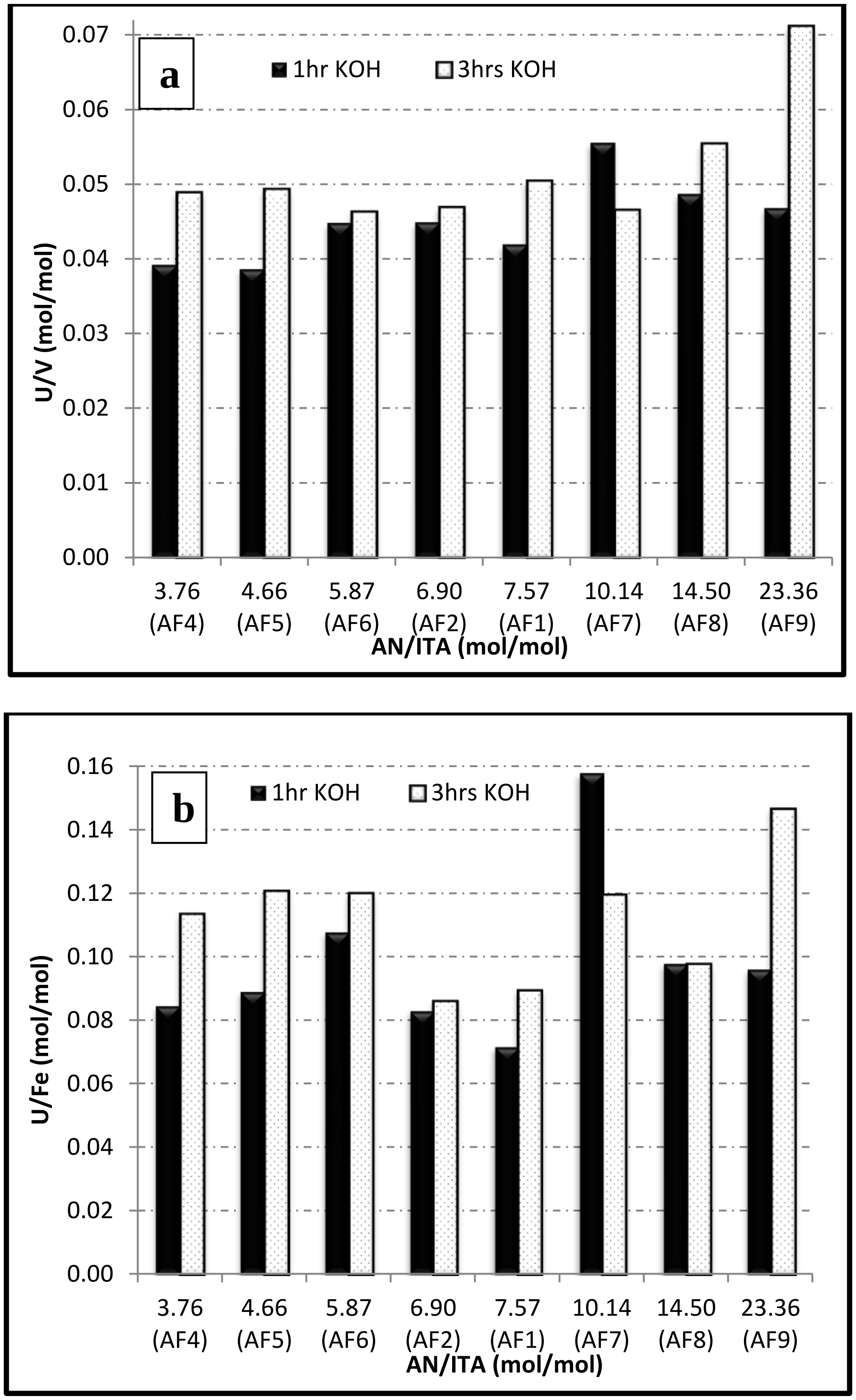

Figure 5. Adsorption of uranium over vanadium (a) and iron (b) as a function of AN and ITA molar ratio of the AF series adsorbents after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

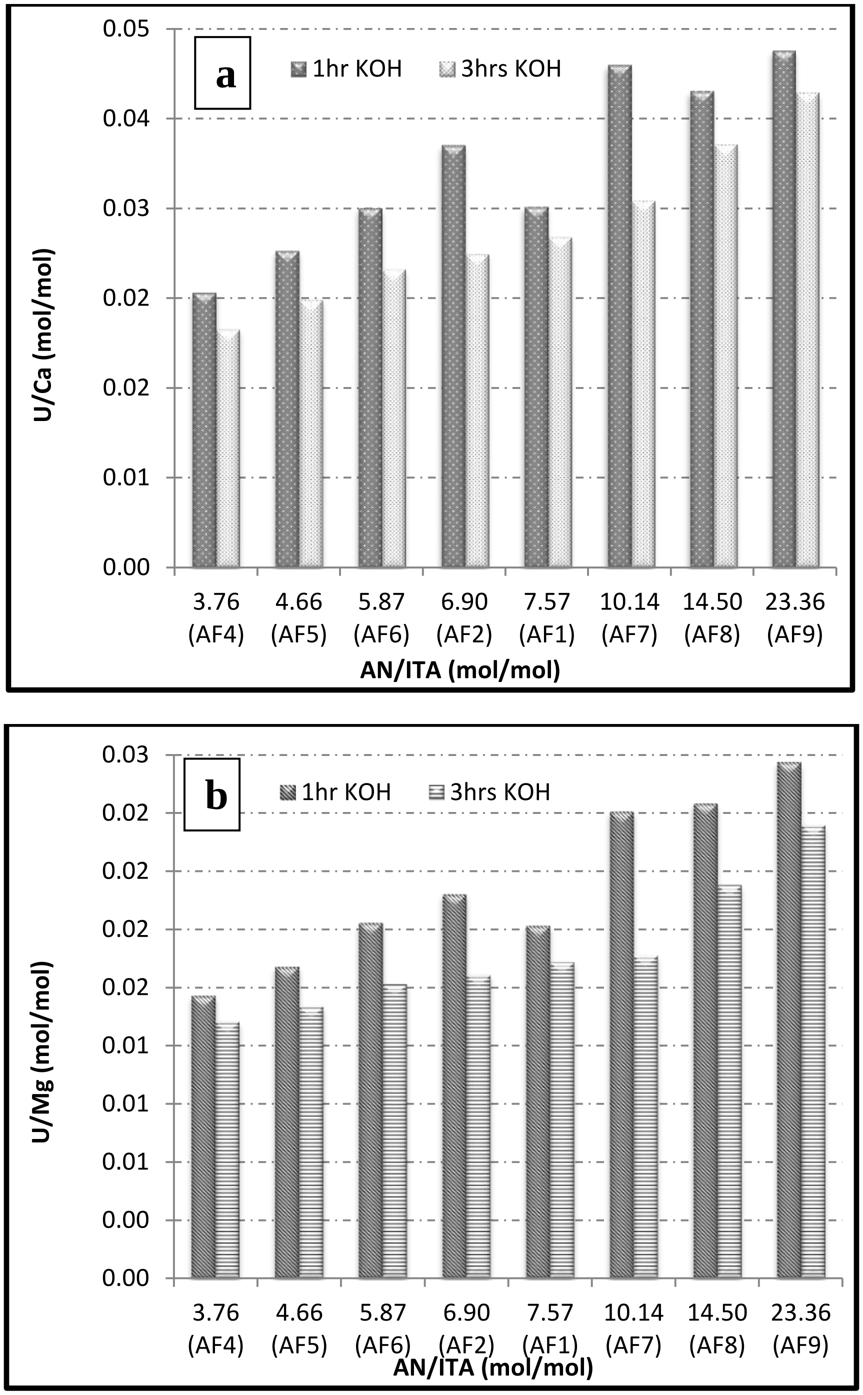

Figure 6. Adsorption of uranium over calcium (a) and magnesium (b) as a function of AN and ITA molar ratio in the AF series adsorbents after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

KOH conditioning. Uranium adsorption over calcium and magnesium gradually increased with increasing AO content in the adsorbents, irrespective of the time of KOH conditioning.

Kinetics of metal ions adsorption

The AF1 adsorbent was used to study the adsorption kinetics of uranium, vanadium, iron, calcium and magnesium from seawater, after conditioning with 0.44M KOH at 80 ºC for one hour and three hours. About 50 mg of KOH treated AF1 samples were packed in columns

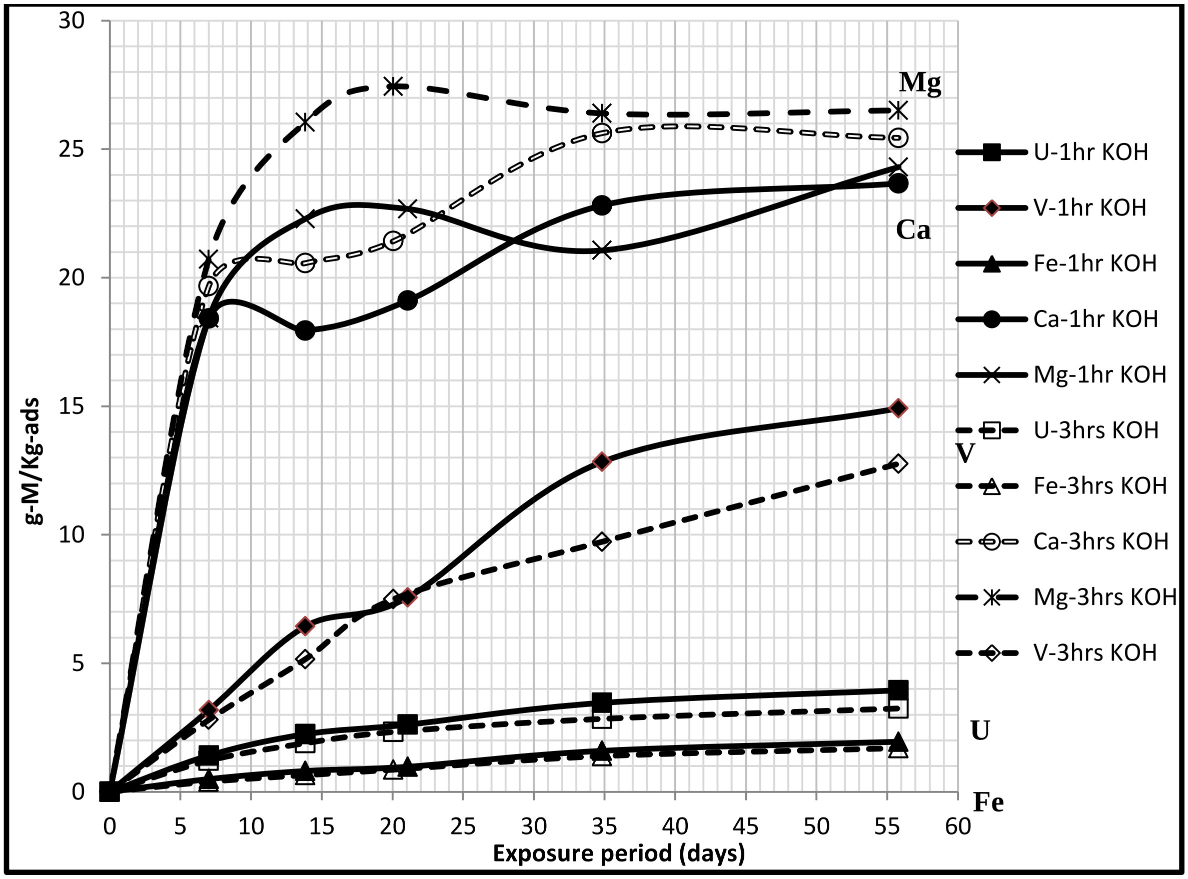

Figure 7. Adsorption kinetics of uranium, vanadium, iron, calcium and magnesium by the AF1 adsorbents after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 80 ºC for one hour and three hours.

through which filtered seawater from Sequim Bay was passed at a flow rate of 250-300 mL/min, at 20 ºC, over the fixed durations (i.e., 7, 14, 21, 35 and 56 days). The adsorption kinetics of uranium, vanadium, iron, calcium and magnesium from seawater is illustrated in Figure 7. The adsorption kinetics of the metals follows the trend in increasing order as: Fe < U < V < Ca < Mg, irrespective of the KOH conditioning time. The adsorption kinetics of iron, uranium and vanadium was faster in AF1 conditioned with KOH for one hour. On the other hand, the adsorption kinetics of calcium and magnesium was faster when the AF1 adsorbent was conditioned with KOH for three hours.

Conclusions

The AF series adsorbents with different mol ratios of AN and ITA were successfully prepared by electron beam induced graft polymerization onto polyethylene fibers with a high degree of grafting. The elemental analysis and FTIR studies confirmed the conversion of acrylonitrile into amidoxime upon reaction with hydroxylamine. Some parts of the amidoxime were converted to carboxylates after conditioning with KOH. The SEM images indicated that the fibers retain their hollow gear definition throughout the whole process of adsorbent preparation. The uranium adsorption studies of the AF series samples were performed by two methods: 1) by contacting with simulated seawater spiked with 8 ppm uranium for 24 hours at ORNL and 2) in natural seawater at PNNL-MSL with filtered water from Sequim Bay for 56 days in flow-through columns. The uranium adsorption from natural seawater gradually increases with increasing AN/ITA molar ratio in the adsorbents. Both the adsorption studies performed at ORNL and PNNL showed that 10.14 and 7.57 was the optimum AN/ITA molar ratio in the case of one hour and three hours KOH conditioning, respectively for the highest uranium adsorption capacity. A combined effect of chemical composition and KOH conditioning time seemed to play an important role not only for uranium adsorption but also for selectivity over other metals. Uranium adsorption over vanadium and iron was gradually increased with the AO content in the adsorbent after three hours of KOH conditioning. On the other hand, the AF7 adsorbent (i.e., AN:ITA=10.14 mol/mol) favored more uranium adsorption over vanadium and iron after conditioned with KOH for one hour. The adsorption kinetics of heavy metals e.g., uranium, vanadium and iron was faster after one hour KOH conditioning of the adsorbent.

Acknowledgement

This work was sponsored by the US department of Energy, Office of Nuclear Energy.

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