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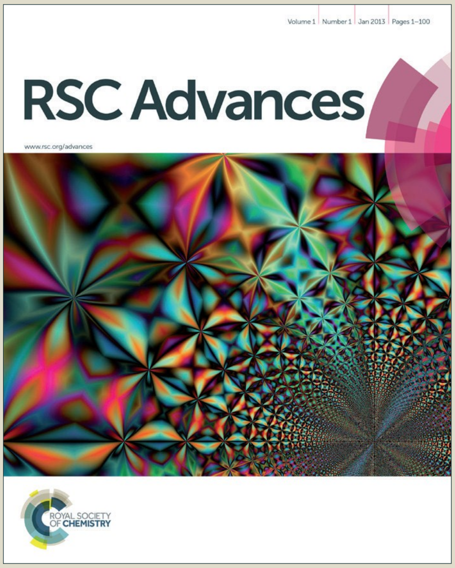
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Towards Understanding KOH Conditioning of Amidoxime-based Polymer Adsorbents for Sequestering Uranium from Seawater

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Abstract

Conditioning of polymer fiber adsorbents grafted with amidoxime and carboxylic acid groups is necessary to make the materials hydrophilic for sequestering uranium from seawater. Spectroscopic techniques were employed to study the effectiveness of the traditional KOH conditioning method (2.5% KOH at 80 °C) on recently developed high-surface-area amidoxime-based polymer fiber adsorbents developed at Oak Ridge National Laboratory. FTIR spectra reveal that the KOH conditioning process removes the proton from the carboxylic acids and also converts the amidoxime groups to carboxylate groups in the adsorbent. With prolonged KOH treatment (>1 hr) at 80 °C, physical damage to the adsorbent material occurs which can lead to a significant reduction in the adsorbent's uranium adsorption capability in real seawater during extended exposure times (>21 days). The physical damage to the adsorbent can be minimized by lowering KOH conditioning temperature. For the high-surface-area amidoxime-based adsorbents, 20 min of conditioning in 2.5% KOH at 80 °C or 1 hr of conditioning in 2.5% KOH

at 60 °C appears sufficient to achieve de-protonation of the carboxylic acid with minimal harmful effects to the adsorbent material. The use of NaOH instead of KOH can also reduce the cost of the base treatment process required for conditioning the amidoxime-based sorbents with minimal loss of adsorption capacity (≤ 7%).

Introduction

It has been estimated that land-based uranium sources will be depleted by the end of the century, necessitating that alternative sources of fuel be sought to maintain nuclear power production.[1, 2] Despite a low concentration in seawater (~3 ppb), the ocean contains a huge amount of uranium which could provide centuries of sustainable uranium supply.[3, 4] Developing effective and economic technology for sequestering uranium from seawater is a research area being actively pursued at the present time by scientists in the USA and other countries. Highly efficient, selective and stable uranium adsorbents are needed to economically mine uranium from the ocean.

A number of new adsorbents are currently being developed for sequestering uranium from seawater.[2, 5-7] The amidoxime-based polymer adsorbents, which have been pioneered by Japanese scientists in the past few decades, appear to be one of the most promising materials for sequestering uranium because of their good mechanical strength and high uranium loading capacities as demonstrated by marine tests.[1, 2, 8] The amidoxime-based fibers are traditionally prepared by radiation-induced grafting of acrylonitrile ($CH_2{=}CH{-}CN$) onto polyethylene fabrics, followed by chemical conversion of the –CN groups with hydroxylamine to amidoxime groups.[8] Carboxylic acid or other weak acid groups are also grafted onto the adsorbents during the synthesis process to make the polymer adsorbents hydrophilic.[9-13]

The radiation induced grafting procedure used by Oak Ridge National Laboratory (ORNL) and others for synthesizing amidoxime-based polymer adsorbents was described by Pan et al. (2014).[14] After grafting, the polymer adsorbent is treated with a KOH conditioning process, which typically involves heating the adsorbent in 2.5% KOH solution at 80 °C for 1–24 hours.[10, 15-18] The effects of the KOH conditioning process on chemical and physical properties of amidoxime-based polymer adsorbents has not been clearly articulated in the literature. KOH conditioning has been reported to convert carboxylic acid groups to carboxylates and also make the polymer adsorbent hydrophilic.[19] It has been suggested that KOH treatment of amidoxime-based polymer adsorbents at high temperatures could alter the polymer structures in such a way as to enlarge the spaces between crystallites, facilitating the adsorption of water.[10] It is known that single molecules containing amidoxime and cyclic imide dioxime groups, such as glutardiamidoxime and glutarimidedioxime, are not stable in highly alkaline solutions at high temperatures (e.g. 80 °C) and tend to convert to carboxylate groups.[19]

Understanding the physical and chemical effects of KOH conditioning on amidoxime-based polymeric adsorbents is important for optimizing uranium adsorption capacity, selectivity, and for adsorbent reuse. This paper describes the effects of the KOH conditioning process on the uranium adsorption capacity of the amidoxime-based polymer adsorbent with carboxylic acid groups on the surface synthesized by ORNL. This ORNL polymer adsorbent tested (the AF1 formulation) utilizes high-surface-area polyethylene fibers as the backbone material and has a high uranium adsorption capacity in real seawater experiments.[20] Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) was used to measure the conversion of amidoxime to carboxylate in the adsorbent during KOH conditioning. In addition, scanning electron microscopy (SEM) was used to monitor structural changes in the polymer adsorbent that resulted from the duration of the conditioning process. We believe this information will be of particular importance to researchers who are currently engaging in synthesis and characterization of new polymer adsorbents for sequestering uranium from seawater.

Experimental Section

KOH Conditioning of Adsorbent

The high-surface-area amidoxime-based polyethylene adsorbent fibers (ORNL-AF1L2R1) were prepared by a radiation-induced graft polymerization (RIGP) method described in our previous work.[14] The adsorbents (~50 mg) were immersed in a 2.5% KOH solution at 80 ^{o}C for various durations at a ratio of 1 mL KOH per mg of adsorbent. After the KOH conditioning step, the adsorbents were immediately washed with deionized water until the rinse water attained a pH of about 7. The adsorbents were kept submerged in deionized water prior to spectroscopic characterization and uranium adsorption experiments.

Seawater Uranium Adsorption Procedure

The performance of adsorbents in real seawater was assessed at the Marine Sciences Laboratory (MSL), a part of the Pacific Northwest National Laboratory (PNNL) located in Sequim, Washington. A detailed description of experimental setup of continuous flow seawater testing facility and analytical methods are given elsewhere.[20, 21] Adsorbent beds of flow-through experiments were prepared using 1 in. internal diameter by 6 in. long columns fabricated from plastic components, mostly PVC and polypropylene. The adsorbent after alkaline treatment was dispersed and packed in the column, where it was held in place by acid-cleaned glass wool and 5 mm glass beads that were used to fill up the empty space of the columns. Marine testing was performed using 0.45µm filtered Sequim Bay seawater at a temperature of 20±1°C and at a flow rate of 250–300 mL min^{-1} (~ 2 cm/sec linear velocity) by active pumping through a multi-channel flow system. Seawater exposure of adsorbents was conducted in replicates (n = 2 to 5) in multiple experiment batches to confirm the adsorption capacities of different adsorbent samples. The flow rate was determined using an in-line turbine-style flow sensor (Model DFS-2W, Digiflow Systems). Seawater salinity and pH were determined daily using a hand-held salinometer (YSI, Model 30), and pH meter calibrated with NIST buffers, respectively. Temperature was monitored every 10 min using a temperature logger equipped with a flexible hermetic sealed RTD sensor probe (OMEGA Engineering, Stamford, CT, USA). The seawater exposure duration in this test was 42 days.

After the seawater exposure was completed, the adsorbents were removed from columns, desalted by rinsing with DI water, dried in a heating block, and weighed. The adsorbents were digested in a 50% aqua regia solution at 75°C for 6 hours, and further diluted with DI water before analysis. Analysis of uranium and other trace elements was conducted using a Perkin-Elmer Optima 4300DV inductively coupled plasma optical emission spectrometer (ICP-OES), with quantification based on standard calibration curves. Uranium concentrations of the tested adsorbents were normalized to 35 psu (average ocean salinity) for consistency in data comparison.

FTIR Measurements

FTIR spectra were acquired using a Nicolet Magna 760 FTIR spectrometer equipped with a DTGS detector. FTIR measurements were made with a SplitPea attenuated total reflection accessory (Harrick Scientific Corporation) along with a silicon internal reflection element used as a reflection medium. FTIR spectra in the range of 4000−700 cm^{-1} were acquired using 500 co-added scans at 2 cm^{-1} resolution with Norton–Beer “medium” apodization function.

SEM Characterization

Microscopic morphologies of the high-surface-area amidoxime-based polymer fiber adsorbents were investigated by field emission gun scanning electron microscopy (SEM-FEG; Zeiss Supra 35 SEM). All samples were coated with a thin layer of carbon for the SEM observations.

Results and Discussion

FTIR Spectra of Amidoxime-based Adsorbents Before and After KOH Conditioning

The FTIR spectra of the ORNL AF1 adsorbent before and after conditioning with 2.5% KOH solution at 80 ^{o}C are shown in Figure 1. The KOH treatment time varied from 20 minutes to 5 hours. A broadband in the region of 3000−3600 cm^{-1} is attributed to the stretching vibrations of –OH (3100−3330 cm^{-1}) and –NH$_2$ (3400−3500 cm^{-1}) groups.[22-24] The two peaks observed at 2918 and 2849 cm^{-1} are characteristic asymmetrical stretching and symmetrical stretching vibrational bands for –CH$_2$–, respectively, which show no evidence of being affected by the KOH treatment. The region between 800−2000 cm^{-1} where absorptions of various vibrational modes of amidoxime and carboxylate groups occur is of interest to this study.

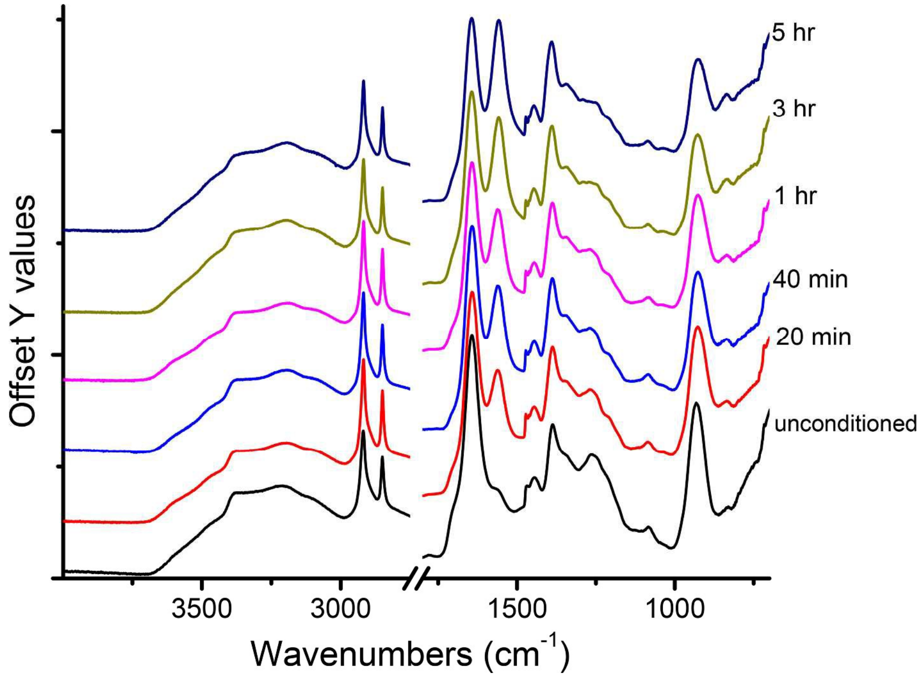

Figure 1. FTIR spectra of the ORNL AF1 adsorbent before (unconditioned) and after KOH conditioning at 80 °C for times between 20 minutes and 5 hours. (Note: There is no characteristic adsorption band between 2750 and 1800 cm^{-1}. The spectra are normalized to the –CH_2− asymmetrical stretching peak at 2918 cm^{-1}.)

Three prominent peaks of interest in this region are the 928 cm^{-1} band (N−O stretching), the 1559 cm^{-1} band ($-COO^-$ asymmetrical stretching), and the 1643 cm^{-1} band (C=N stretching). The explanation for the assignment of the 1559 cm^{-1} $-COO^-$ band is given in the Supplementary Information. The N-O and C=N stretching bands are associated with the amidoxime ligand, while the $-COO^-$ asymmetrical stretching is due to the carboxylic acid monomer co-grafted to the polymer to give it hydrophylic behavior. In the original unconditioned adsorbent, there is a small shoulder peak around 1570 cm^{-1} which is probably from amidoxime (N–H bending band) not from amide. The 1559 cm^{-1} band ($-COO^-$ asymmetrical stretching) is prominent in the first scan after 20 minutes of KOH treatment. This confirms that the KOH conditioning is converting the carboxylic acid groups (−COOH) present from the grafting process to carboxylate ($-COO^-$). Deprotonation of carboxylic acid −COOH is expected to be rapid in alkaline solutions.

The time series spectrum scans also show decreases in the N−O band (928 cm^{-1}) and the C=N band (1643 cm^{-1}) intensity with KOH conditioning time. Simultaneously, the $-COO^{-}$ band intensity is increasing with KOH conditioning time, suggesting that convertion of amidoxime groups to carboxylate anion occurs during the KOH conditioning process. Table 1 provides the itensity of the 928 cm^{-1} peak (N−O stretching) and the relative ratio of the 1643 cm^{-1}/1559 cm^{-1} peaks (C=N/$-COO^{-}$ stretching) as a function of increasing KOH conditioning durations. The peaks are normalized to the $-CH_2-$ asymmetrical stretching band at 2918 cm^{-1} which is not affected by the KOH treatment as described above. A contiuous decrease in the absorbance of the 928 cm^{-1} peak from the original material to those treated with KOH provides evidence for its conversion to other groups. The decrease in the ratio of the 1643 cm^{-1} /1559 cm^{-1} peaks with increased KOH treatment time also supports the continuous conversion of the amidoxime groups to the carboxylate groups during the KOH conditioning process.

Table 1. Peak intensity of N–O stretching (928 cm^{-1}) and ratio of C=N/$-COO^{-}$ stretching (I_{1643}/I_{1559}) of the amidoxime polymer adsorbent under different KOH (2.5%) conditioning durations at 80 °C. The peak intensities are normalized to $-CH_2-$ asymmetrical stretching peak at 2918 cm^{-1}. Uranium adsorption capacity (mg/g) after 42 days of exposure in filtered natural seawater was normalized to 35 psu.

KOH conditioning reaction time	IR peak ratio of I_{1643}/I_{1559}	IR peak intensity of I_{928}	Uranium Adsorption Capacity (mg/g)[a]
unconditioned	-------	0.634	0.00
20 min	1.371	0.565	3.36 ± 0.12
40 min	1.262	0.525	3.46 ± 0.07
1 hr	1.251	0.494	3.28 ± 0.12
3 hr	1.100	0.442	1.63 ± 0.49

5 hr	1.007	0.410	0.26 ± 0.09

[a] Average of 3-5 replicate seawater adsorption experiments.

Chemistry of KOH Conditioning and Uranium Adsorption Capacity

Kang et al. (2012)[19] reported that single amidoxime molecules can be converted to carboxylate molecules in highly alkaline solutions at 80°C as illustrated in Figure 2. Because KOH conditioning of the adsorbent is typically carried out under alkaline conditions (2.5% KOH has a pH > 13.5), conversion of amidoxime groups to carboxylate groups is expected to occur. The conversion would lower amidoxime group density in the adsorbent which may lead to a reduction in uranium sorption capacity.

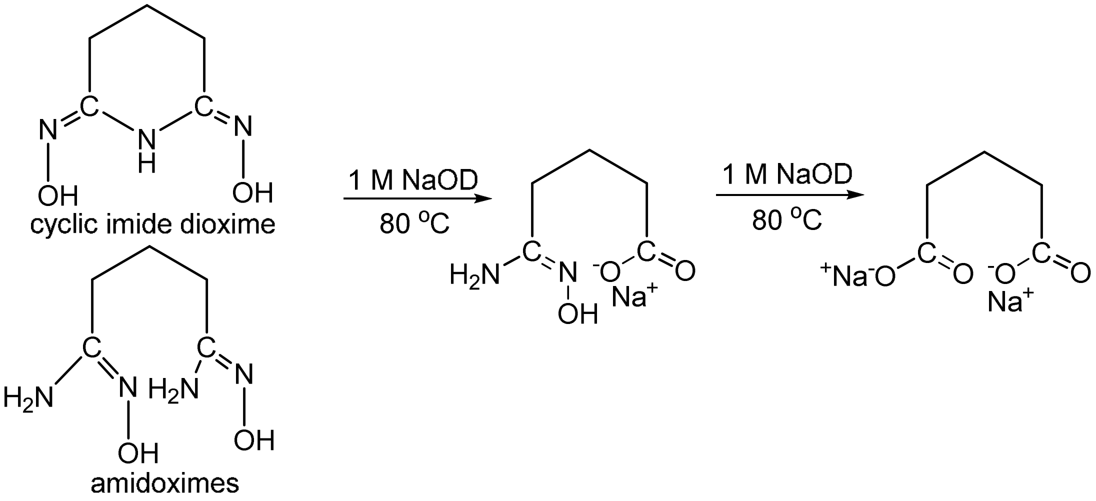

Figure 2. Conversion of amidoxime and cyclic imide dioxime groups to carboxylate groups in alkaline solution at 80 °C.

Figure 3 shows 42 day uranium adsorption capacity determinations of the ORNL AF1 amidoxime-based adsorbent in natural seawater at 20°C as a function of KOH conditioning time. The uranium adsorption capacity remains nearly constant (~3.36 mg U/g adsorbent) for 20, 40, and 60 minutes of KOH treatment at 80°C, but starts to decline with conditioning times longer than 1 hour. The uranium adsorption capacity decreased by more than 50% with 3 hours of KOH conditioning at 80°C and by an order of magnitude after 5 hours of KOH conditioning at 80°C.

The drop in adsorption capacity observed with KOH conditioning at 60°C was not as dramatic (Figure 3). After 3 hours of KOH conditioning at 60 ^{o}C, there was no significant decrease in uranium adsorption capacity. However, after 5 hours of KOH conditioning at 60 ^{o}C, the uranium adsorption capacity was reduced by about 9%. It appears that lowering the KOH conditioning temperature from 80 to 60 °C does not affect the achievable capacity of the adsorbent and can significantly reduce the loss of adsorption capacity associated with longer KOH conditioning times.

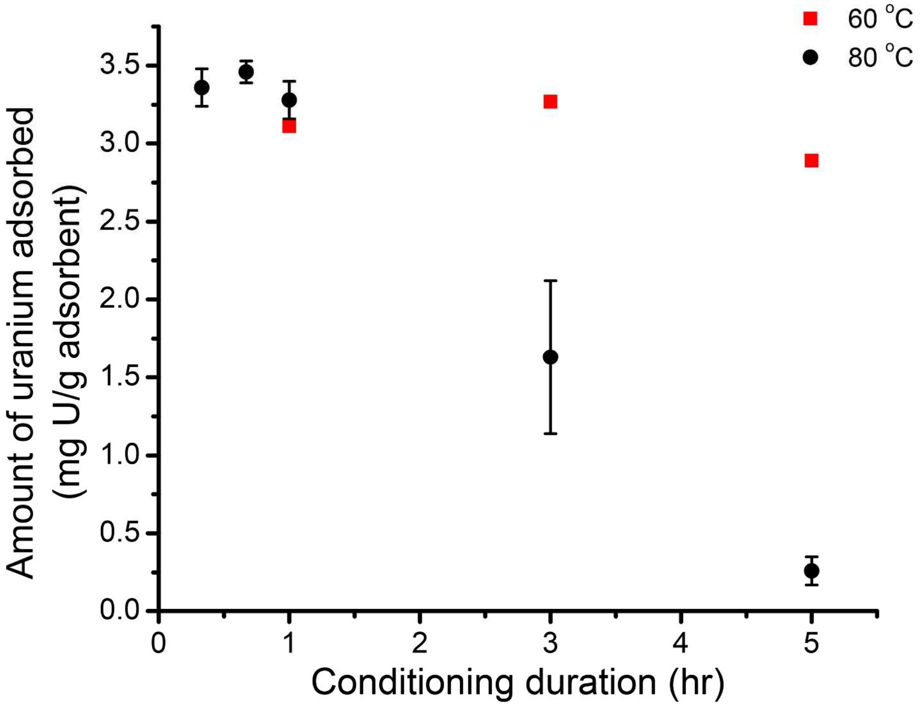

Figure 3. Uranium adsorption capacity (mg U/ g adsorbent) for the ORNL AF1 adsorbent at 20 ^{o}C after 42 days of exposure in natural filtered seawater as a function of KOH conditioning time (2.5% KOH at 60 ^{o}C or 80 ^{o}C). Data were normalized to a salinity of 35 psu.

According to the FTIR data shown in Table 1, the continuous decrease in absorbance of the N–O stretching (928 cm^{-1}) and in ratio of C=N/–COO^{-} stretching (I_{1643}/I_{1559}) within 1 hour of KOH treatment indicate continuous degradation of amidoxime molecules to carboxylate molecules. Interestingly, the degradation of amidoxime groups to carboxylate groups doesn't seem to affect the uranium adsorption capacity within the first hour of KOH treatment at 80°C. This observation implies that a 10-20% decrease in amidoxime groups (based on the decrease in the intensity of the –NO stretching peak, or I_{928}) does not cause appreciable reduction in uranium adsorption capacity of the adsorbent. Notice that the large drop in uranium adsorption capacity at 3 and 5 hours of KOH treatment at 80 °C do not correlate well with the FTIR data which show only a small (<10%) and continuous decrease in absorbance of the N–O stretching (928 cm^{-1}) and the ratio of C=N/–COO^{-} stretching (I_{1643}/I_{1559}) (see Table 1). Factors other than loss of amidoxime groups appear to be involved to result in such drastic reductions in the adsorbent's uranium adsorption capability after 1 hour of KOH treatment at 80°C.

It is generally accepted that uranyl ions are bound to amidoxime groups in a 1:2 mole ratio.[25, 26] Actually, how uranyl ions are coordinated with amidoxime groups in the adsorbent is unknown. Shi and co-workers recently reported that the complexing of uranyl ions with bifunctional amidoxime/carboxylate groups is thermodynamically more favorable than those with two amidoxime groups based on their density functional theory (DFT) calculations.[27] There is no experimental verification of this theoretical calculation yet, but our seawater experiments suggest that small changes in amidoxime/carboxylate ratio in the adsorbent is not critical for the uranium adsorption capacity.

Our experiments also indicate that without KOH conditioning, the amidoxime adsorbent shows little or no uranium adsorption capability after 42 days of contact with seawater. Thus, KOH conditioning is necessary for de-protonation of the carboxylic acid and to also make the adsorbent hydrophilic for sequestering uranium when in contact with seawater. According to the literature,[10, 15-18] amidoxime-based polymer adsorbents would typically require at least 1 hour of soaking in 2.5% KOH solution at 80 ^{o}C prior to uranium adsorption experiments. This condition is apparently too harsh for the amidoxime-based polymer adsorbents currently under development by ORNL. Based on the results obtained from this study, 20–40 minutes of KOH conditioning at 80 ^{o}C should be sufficient for de-protonation of the carboxylic acid groups grafted in the amidoxime-based adsorbents.

SEM Images Reveal Physical Damage to the Adsorbent During KOH Conditioning

The surface morphology of the adsorbent before and after the KOH conditioning process was examined by scanning electron microscopy (Zeiss Supra 35 SEM) to determine if any structural damage occurs from the conditioning process. Figure 4 shows SEM images of the grafted, but unconditioned adsorbent, and images after conditioning with 2.5% KOH for 20 minutes, 1 hour and 3 hours at 80°C, respectively. Figure 4a reveals the linear "multi-fin-like" or "gear-like" structure of the ORNL adsorbent fiber with no apparent physical surface damage. It is this unique "multi-fin-like" structure that provides the high surface area of the ORNL polymer adsorbent. After 20 minutes of KOH treatment (Figure 4b), the fin-like structure of the adsorbent fiber appears slightly bent. One possibility for this change in the polymer structures is due to swelling of the spaces between crystallites.[10] The adsorbent fiber begins to show surface damage after 1 hour of KOH conditioning (Figure 4c). The physical damage of the adsorbent becomes more prominent after 3 hours of KOH conditioning and some "fins" show signs of cracking (Figure 4d). It is not clear whether this physical damage has any relation to the drop in adsorption capacity associated with KOH conditioning time longer than 1 hour at 80 °C, but we speculate that this could be a factor.

If the adsorbent is partially damaged during harsh alkaline treatment condition (long treatment time), its physical strength will be weaken and thus it may lead to further physical damage during long-term (42 days) seawater exposure, especially under relatively strong flow rate (250 mL/min flow rate; linear velocity ~ 2 cm/s). The combination of the initial adsorbent damage associated with KOH conditioning times > 1 hour at 80°C, and long term exposure in seawater, may result in a loss of uranium adsorption capacity from chemical alterations in the binding ligands and structural damage. The high variability observed in the uranium adsorption capacity at 3 hours of KOH conditioning at 80 °C is consistent with the potential breakdown of polymer structures during extended seawater exposure. The SEM images shown in the Supplementary Information (Figure 2S) provide evidence of physical damages to the polymer structures after 42 days of exposure to seawater for the adsorbents conditioned with KOH at 80 ^{o}C for 1–3 hours. More physical breakdown of polymer structure is obvious for the 3 hour conditioned sample (Figure 2S (b)) than the 1 hour conditioned sample (Figure 2S (a)). Chemical degradation of amidoxime groups of the adsorbent during extended seawater exposure also occurs, but the degree of degradation does not seem to correlate to the KOH conditioning time as illustrated by the FTIR spectra given in the Supplement Information (Figure 3S). Chemical degradation of amidoxme-based polymer adsorbents in seawater appears to be a complicated problem which deserves further investigation in the future.

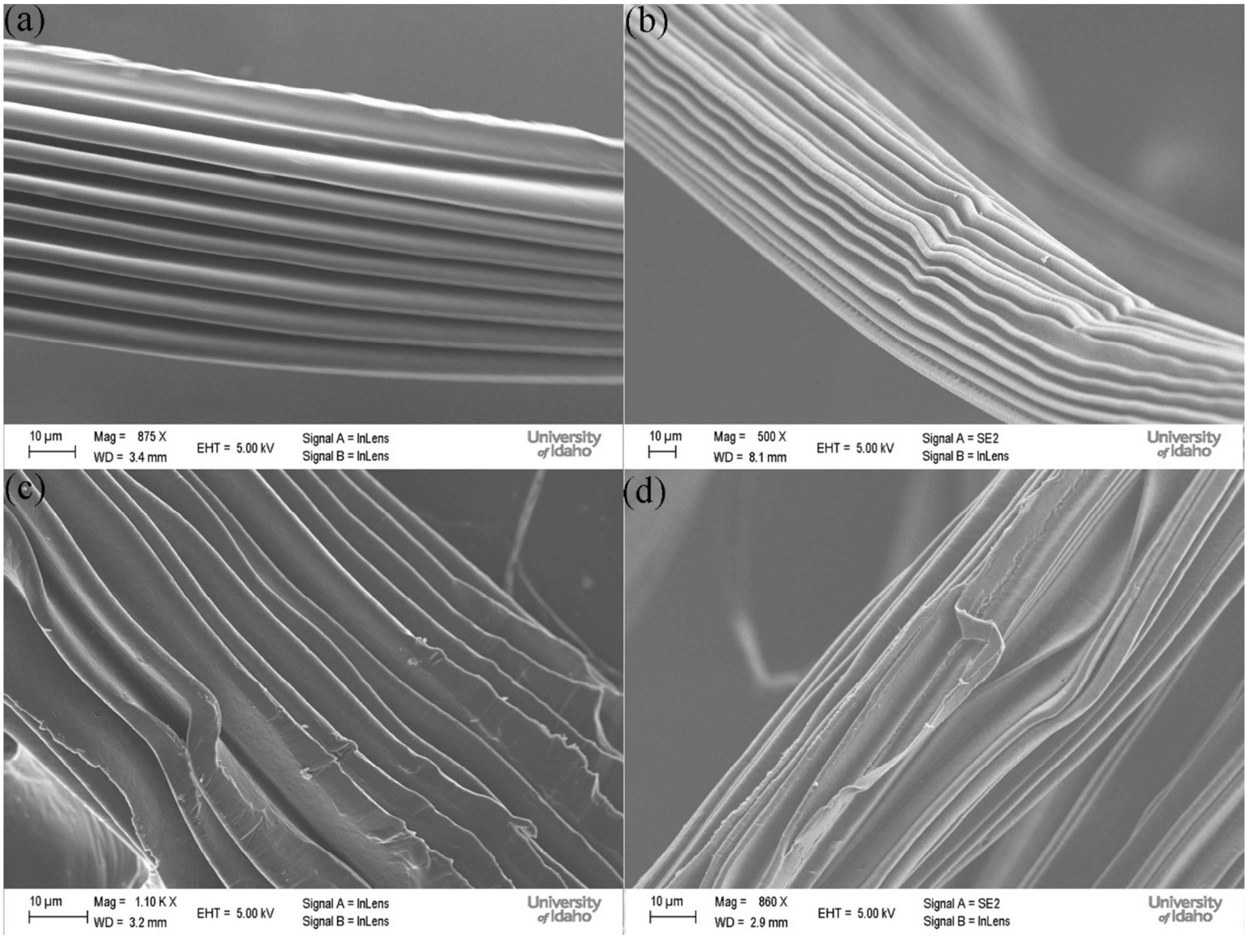

Figure 4. SEM images of the ORNL high surface area polyethylene fiber conditioned with 2.5% KOH at 80° C for different times: (a) original fiber, no KOH treatment, (b) 20 min, (c) 1 hr, and (d) 3 hr.

SEM images of the ORNL AF1 adsorbent treated with 2.5% KOH at 60 ^{o}C for 5 hours shows less physical damage compared to conditioning at 80°C (Figure 5). Some folding and waving of the surface fin-like structures are observed at the lower conditioning temperature, but it is less severe than that observed in the adsorbent treated with 2.5% KOH at 80 ^{o}C for 1 hour (see Figure 4c). Lowering the conditioning temperature from 80° to 60 ^{o}C results in significantly reduced physical damage to the adsorbent and at the same time does not significantly impact the uranium adsorption capacity as shown previously in Figure 3.

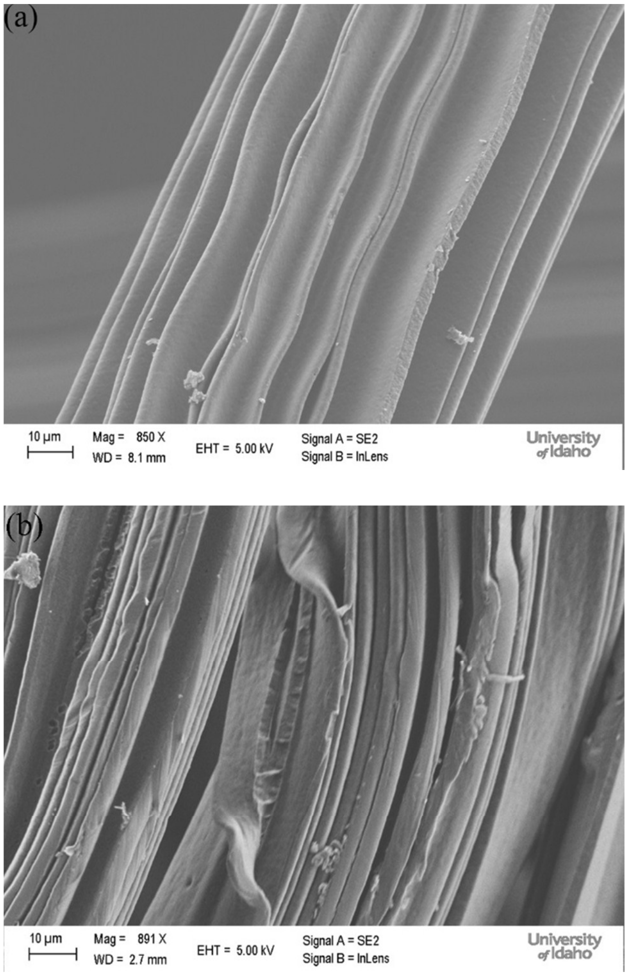

Figure 5. SEM images of the ORNL AF1 high-surface-area polyethylene fibers after 5 hours of KOH conditioning at (a) 60 ^{o}C and (b) 80 ^{o}C.

Base Conditioning with NaOH

The performance of the adsorbent was evaluated using NaOH for the conditioning instead of KOH at the same molarity and temperature. The NaOH solution used in this test is 1.76% by weight or 0.45 M NaOH which is equivalent to that of 2.5% KOH solution in molarity. Table 2 shows the uranium adsorption capacities of the NaOH conditioned adsorbent obtained from the same seawater flow-through column system as those of the KOH conditioned adsorbent experiments described in Figure 3. The amounts of uranium adsorbed by the NaOH conditioned adsorbent are slightly less than that retained by the KOH conditioned adsorbents. The drop in adsorption capacity for the 20 minute, 40 minute, and 1 hour conditioning using NaOH compared to KOH was 4.2%, 6.9%, and 7.3%, respectively. The seawater uranium adsorption results given in Table 2 suggest that alkalinity of the base plays a major role and the cation size of the base (K^+ or Na^+) is immaterial in the conditioning process. A detailed statistical analysis using a generalized linear model (GLM) shows that uranium adsorption capacities of the adsorbents conditioned by KOH and by NaOH are not statistically different (p=0.81) when there is no significant drop in uranium adsorption capacity (i.e. for conditioning durations 1 h or less). Some differences are observed between KOH and NaOH conditioning after prolonged conditioning durations (3 and 5 h) where reduction in uranium adsorption capacity occurs. Detailed information of the statistical analysis is given in the Supplementary Information. From an economic standpoint, NaOH is more desirable than KOH because the former is cheaper and readily available.

Table 2. Uranium adsorption capacity of the ORNL AF1 amidoxime-based polymer adsorbent after 42 days of exposure in natural seawater with different alkaline solution and conditioning durations at 80 °C. Uranium adsorption capacity (mg/g) was normalized to a salinity of 35 psu.

Reaction Time alkaline conditioning	Uranium Capacity (mg/g) 0.45 M KOH conditioning	Uranium Capacity (mg/g) 0.45 M NaOH conditioning
20 min	3.36 ± 0.12	3.22 ± 0.05
40 min	3.46 ± 0.07	3.22 ± 0.05
1 hr	3.28 ± 0.12	3.04 ± 0.05
3 hr	1.63 ± 0.49	1.13 ± 0.11
5 hr	0.26 ± 0.09	0.14 ± 0.01

0.45 M KOH = 2.5% KOH by weight; 0.45 M NaOH = 1.76% NaOH by weight.

Conclusion

High-surface-area polyethylene fibers grafted with amidoxime and carboxylic acid groups by ORNL exhibit high adsorption capabilities for sequestering uranium from seawater. A KOH conditioning process is necessary to make the adsorbent hydrophilic by de-protonation of the carboxylic acid. However, the conditions often reported in the literature for KOH treatment of the adsorbent (at least 1 hour in 2.5% KOH at 80 ^{o}C) appears too harsh for the ORNL AF1 high surface area amidoxime-based polymer adsorbent fibers. FTIR spectra indicate that conversion of amidoxime groups to carboxylate groups occurs during the KOH conditioning process. In addition, physical damage to the polymer structure during the conditioning process was observed from SEM images. Consequently, with longer than 1 hour of KOH treatment at 80 ^{o}C, the adsorbent would result in a significant reduction of uranium sorption capacity in extended exposures with real seawater. Using a shorter conditioning time (e.g. 20–40 min) and/or a lower temperature (e.g. 60 ^{o}C) can achieve the necessary de-protonation and reduce significantly the harmful effects to the adsorbent material The use of NaOH instead of KOH can also reduce the cost of the base treatment process required for conditioning the amidoxime-based sorbents with minimal loss of adsorption capacity ($\leq$ 7%).

Acknowledgement

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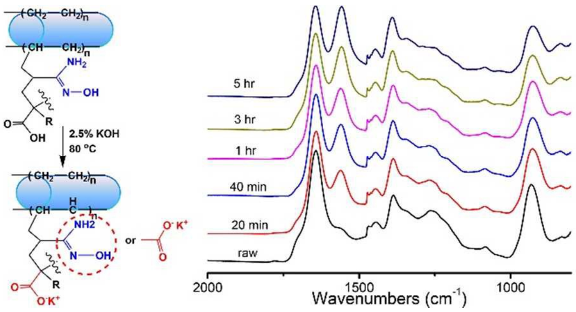

Utilizing spectroscopic and microscopic techniques to understand the KOH conditioning process required for preparing high-surface-area amidoxime-based polymer fiber adsorbents for sequestering uranium from real seawater.