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Elution of Uranium and Transition Metals from Amidoxime-Based Polymer Adsorbents for Sequestering Uranium from Seawater

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Abstract

High-surface-area amidoxime and carboxylic acid grafted polymer adsorbents developed at Oak Ridge National Laboratory were tested for sequestering uranium in a flowing seawater flume system at the PNNL-Marine Sciences Laboratory. FTIR spectra indicate that a KOH conditioning process is necessary to remove the proton from the carboxylic acid and make the sorbent effective for sequestering uranium from seawater. The alkaline conditioning process also converts the amidoxime groups to carboxylate groups in the adsorbent. Both Na_2CO_3–H_2O_2 and hydrochloric acid elution methods can remove ~95% of the uranium sequestered by the adsorbent after 42 days of exposure in real seawater. The Na_2CO_3–H_2O_2 elution method is more selective for uranium than conventional acid elution. Iron and vanadium are the two major transition metals competing with uranium for adsorption to the amidoxime-based adsorbents in real seawater. Tiron (4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt, 1 M) can remove iron from the

adsorbent very effectively at pH around 7. The coordination between vanadium (V) and amidoxime is also discussed based on our ^{51}V NMR data.

Introduction

Amidoxime-based polymer adsorbents have been extensively studied in the past decades for sequestering uranium from seawater because of their high uranium adsorption capacities.[1-3] Recently, a class of high-surface-area polymer fiber adsorbents containing amidoxime and carboxylate groups has been developed by Oak Ridge National Laboratory (ORNL) which show uranium adsorption capacities in marine water experiments exceeding 3 g uranium per kg of adsorbent.[4, 5] This adsorption capacity is equivalent to a distribution coefficient of 10^6 favoring the adsorbent over the uranium in natural seawater (about 3 ppb or 3 μg U/kg seawater). The high-surface-area amidoxime-based polymer adsorbent has the highest uranium adsorption capacity known in the literature for real seawater tests.[4] The adsorbents are synthesized by radiation induced grafting of acrylonitrile and carboxylic acid (e.g. methacrylic acid) to high-surface-area polyethylene fibers followed by converting the –CN groups with hydroxylamine to amidoxime groups.[6] The adsorbent synthesis procedure is described in a previous paper.[6] The amidoxime-based polymer adsorbents require a conditioning step to make them hydrophilic and effective for sequestering uranium from seawater. The reported conditioning processes involve immersing the adsorbents in a 2.5% KOH solution at 80 ºC from 1 to 24 hours.[7-11] The uranium adsorption and elution characteristics of the high-surface-area polymer adsorbents in real seawater systems have not been extensively studied. It is known that transition metals especially vanadium and iron are also adsorbed to the amidoxime-based adsorbents in seawater experiments.[4, 12] We have recently studied the adsorption and elution characteristics of uranium, iron and vanadium using the ORNL high-surface-area amidoxime-based polymer adsorbents in a flowing seawater system. This paper

summarizes the results of the study with respect to (1) conditioning and spectroscopic characterization of the adsorbents, (2) adsorption characteristics of uranium, iron, and vanadium in a flowing seawater system, and (3) elution of uranium and transition metals from the adsorbent using different eluents.

Experimental Section

KOH Conditioning of Adsorbent

The high-surface-area amidoxime-based polyethylene braided adsorbents (ORNL-AF1) were prepared by a radiation-induced graft polymerization (RIGP) method described in our previous work.[6] The braided adsorbents (~ 7 g) were immersed in a 2.5% KOH solution at 80 ^{o}C for 1 hour at a ratio of 1 mL KOH per mg of adsorbent. After the KOH conditioning step, the braided adsorbents were immediately washed with deionized water until the rinse water attained a pH of about 7. The braided adsorbents were kept submerged in deionized water prior to spectroscopic characterization and uranium adsorption experiments.

Seawater Uranium Adsorption Procedure

The performance of the amidoxime-based polymeric braid adsorbents in real seawater was assessed at the Marine Sciences Laboratory (MSL), a part of 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.[4, 13, 14] Amidoxime-based polymeric braid adsorbents were deployed in a flume system exposed to filtered seawater at 20±1.5 ℃ for 42 days. Adsorption kinetics was assessed by analyzing small amounts (about 50 mg) of sorbent fibers taken at different time intervals of the adsorption process. The saturation uranium adsorption capacity was evaluated by extrapolating the time-dependent data to equilibrium utilizing a one-site ligand saturation model.

Na_2CO_3–H_2O_2 elution

Elution of uranium was performed with about 50 mg of dry sorbent fibers immersed in 20 mL of a solution consisting of 1 M hydrogen peroxide and 1 M sodium carbonate at room temperature (21 °C) with stirring for two hours. After the elution, the adsorbent were digested in 50 % aqua regia at 85 °C for 3 hours to remove uranium and other trace elements remaining in the sorbent. Elemental analysis of the acid solution was performed 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 adsorbents were normalized to 35 psu (average ocean salinity) for consistency in data comparison. Other elution methods were performed with a similar procedure given above using different eluents or chelating agents.

FTIR Measurements

FTIR spectra were acquired on dry sorbent samples using a Nicolet Magna 760 FTIR spectrometer equipped with a deuterated triglycine sulfate (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. High resolution FTIR spectra in the range of 4000 to 700 cm^{-1} were acquired using 500 co-added scans at 2 cm^{-1} resolution with Norton-Beer "medium" apodization function. The spectra were normalized to the 2918 cm^{-1} peak, the C–H asymmetrical stretching band of the polyethylene, to facilitate comparison.

Results and Discussion

1. *KOH Conditioning and FTIR Characterization of the Adsorbents*

Without conditioning the amidoxime-carboxylate grafted polymer adsorbents are not capable of adsorbing uranium from seawater. The polyethylene fibers are hydrophobic. The

purpose of introducing carboxylic acid or other acid groups to the polymer fibers is to make the material hydrophilic. However, the original adsorbent after synthesis is in the acid form and deprotonation is required to convert the carboxylic acid –COOH to carboxylate $–COO^-$ so the material becomes hydrophilic. FTIR is a convenient tool for characterizing functional groups present in the adsorbents. Figure 1 shows the FTIR spectra of the original high-surface-area amidoxime-carboxylic acid-based polymer fiber adsorbent ORNL AF1 before and after KOH conditioning.

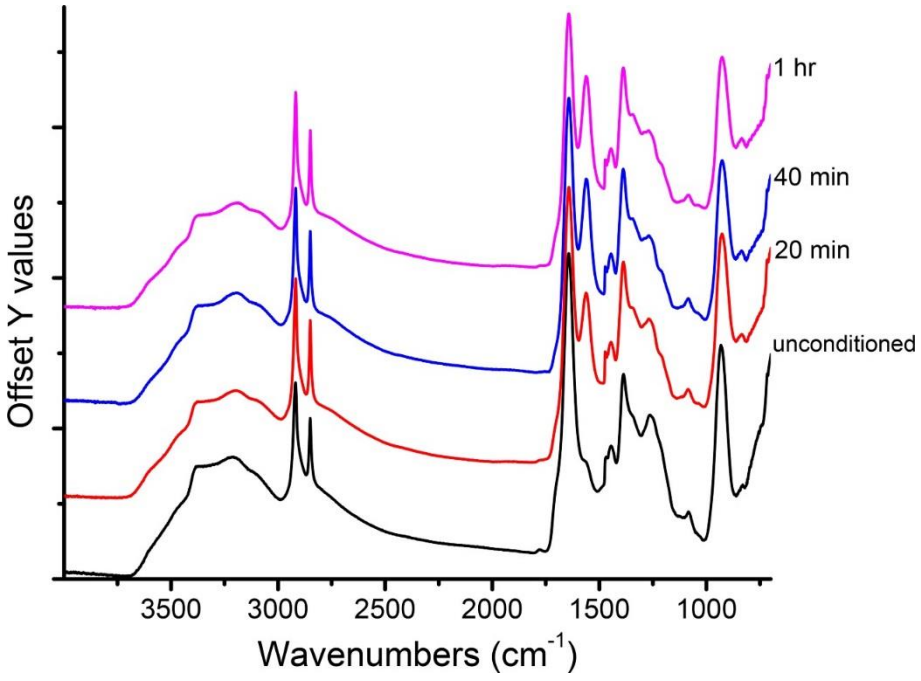

Figure 1. FTIR spectra of ORNL AF1 adsorbent before and after conditioning at 80 ºC with 2.5% KOH. (Note: The spectra were normalized to the $–CH_2–$ asymmetrical stretching peak at 2918 cm^{-1})

A broadband in the region of 3000−3600 cm^{-1} is attributed to the stretching vibrations of –OH (3100 to 3330 cm^{-1}) and $–NH_2$ (3400 to 3500 cm^{-1}) groups. The two peaks observed at 2918 and 2849 cm^{-1} are characteristic asymmetrical stretching and symmetrical stretching bands for $–CH_2–$,

respectively. The other peaks in each sample are normalized to the $–CH_2–$ asymmetrical stretching band at 2918 cm^{-1} which is not affected by the KOH conditioning and different elution methods. The region between 800−2000 cm^{-1} where absorption of various vibrational modes of amidoxime and carboxylate groups occur is of interest to this study. According to the spectrometric identification textbook,[15, 16] the assessment of functional groups in ORNL AF1 adsorbent form characteristic absorption bands in the FTIR spectra (Figure 1) is given in Table 1.

Table 1. Summary of FTIR characteristic absorption bands of ORNL AF1 adsorbent shown in Figure 1.

Characteristic absorption bands (cm^{-1})	Functional group and vibration mode
3600–3000	stretching vibrations of $–NH_2$ ($3400–3500\ cm^{-1}$) and –OH ($3100–3330\ cm^{-1}$)
2918	ν_{as} $–CH_2–$ symmetrical stretching
2849	ν_{s} $–CH_2–$ symmetrical stretching
1643	C=N stretching
1559	COO^- stretching
1472	$–CH_3$ bending, or $–CH_2–$ scissoring
1389	C–N stretching
928	N–O stretching

The conditioning was done by immersing the polymer adsorbent in a 2.5% KOH solution at 80 ºC from 20 min to1 hr. Deprotonation of the carboxylic acid groups in the ORNL AF1 sample occurs in the conditioning process as illustrated by the appearance of the $–COO^-$ peak at 1559 cm^{-1}. The assignment of the peak at 1559 cm^{-1} to a carboxylate anion ($–COO^-$) is based on the fact that peak disappears in contact with 0.5 M HCl and re-appears in contact with KOH. The reversible behavior of the 1559 cm^{-1} peak and the weak shoulder peak at 1706 cm^{-1}(C=O stretching), which we attributed to -COOH peak, is consistent with the protonation and deprotonation of carboxylic acid

under acidic and basic conditions. Figure 2 illustrates the reversible behavior of the 1559 cm^{-1} peak and the 1706 cm^{-1} peak in basic and in acidic conditions. We also considered the possible presence of amide in the sorbent after KOH conditioning which has an N−H bending band around 1570 cm^{-1}. However, amide would not show this reversible behavior under acid/base conditions illustrated in Figure 2. The presence of a small band around 1570 cm^{-1} (N−H bending) in the original adsorbent may suggest the presence of amide in the original sample.

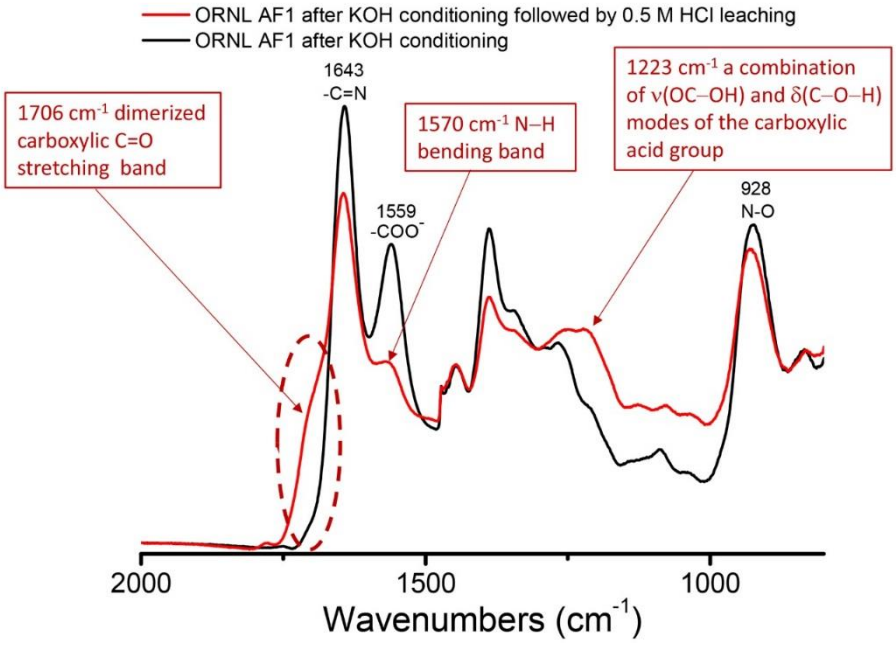

Figure 2. FTIR spectra of ORNL AF1 adsorbent in acid and in alkali solutions. Acid solution: 0.5 M HCl; alkaline solution: 2.5% (0.45 M) KOH. (Note: The spectra were normalized to the –CH_2− asymmetrical stretching peak at 2918 cm^{-1})

The KOH conditioning process also converts amidoxime to carboxylate as revealed by the increase in the 1559 cm^{-1} peak relative to the 1643 cm^{-1} C=N or the 928 cm^{-1} N−O stretching band in the ORNL AF1 adsorbent with increasing conditioning time. The 1643 cm^{-1} and the 928 cm^{-1}

peaks are related to the amidoxime groups in the adsorbent. Figure 1 also shows that the 1559 cm^{-1} peak is well developed after 20 min of KOH conditioning of the ORNL AF1adsorbent at 80 °C. The ratio of the COO^- to C=N or to N–O increases by about 20% from 20 min to 1 hr of the KOH conditioning suggesting conversion of amidoxime to carboxylate groups occurs with increasing conditioning time. A more clear evidence of this amidoxime-carboxylate conversion during KOH conditioning can be seen from the FTIR spectra of another type of ORNL adsorbent, AI8 (amidoxime and phosphonic acid based adsorbents), where no carboxylic acid is present in the original sample. After KOH conditioning, the 1559 cm^{-1} carboxylate band is clearly present in the FTIR spectrum as shown in Figure 3.

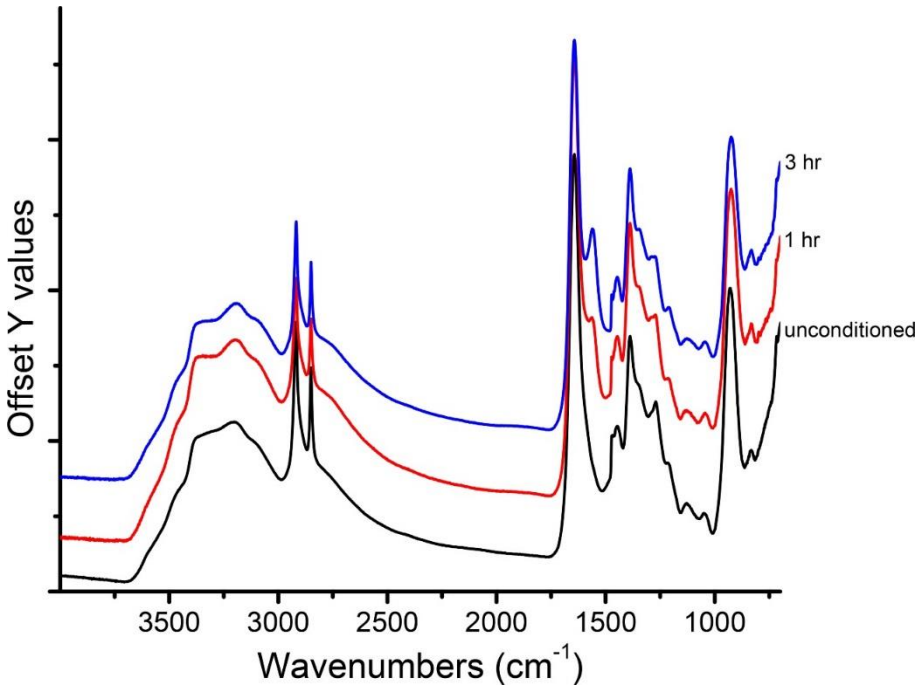

Figure 3. FTIR spectra of ORNL AI8, an amidoxime and phosphonic acid-based adsorbent before and after conditioning at 80 °C with 2.5% KOH. (Note: The spectra were normalized to the $–CH_2–$ asymmetrical stretching peak at 2918 cm^{-1})

2. *Adsorption Behavior of Uranium from Seawater*

The high-surface-area amidoxime-based polymer adsorbent ORNL AF1 was conditioned using 2.5% KOH at 80 °C for 1 hr followed by rinsing with sufficient deionized water before the seawater adsorption experiments. The ambient seawater was pumped from Sequim Bay, WA and filtered before flowing into a flume testing system.[14] Braided polymer adsorbent samples were immersed in the flowing seawater in the flume for the adsorption test. Small aliquots (~100 mg for duplicate analysis) of the polymer samples were taken at different time intervals to measure the rate of adsorption of uranium and other metals to the adsorbents. Figure 4 shows the amounts of uranium adsorption to the ORNL AF1 adsorbent with respect to time in a typical seawater adsorption experiment. The adsorbed uranium continues to increase after 42 days of exposure to seawater suggesting equilibrium has not been reached even after 6 weeks of exposure to the seawater.

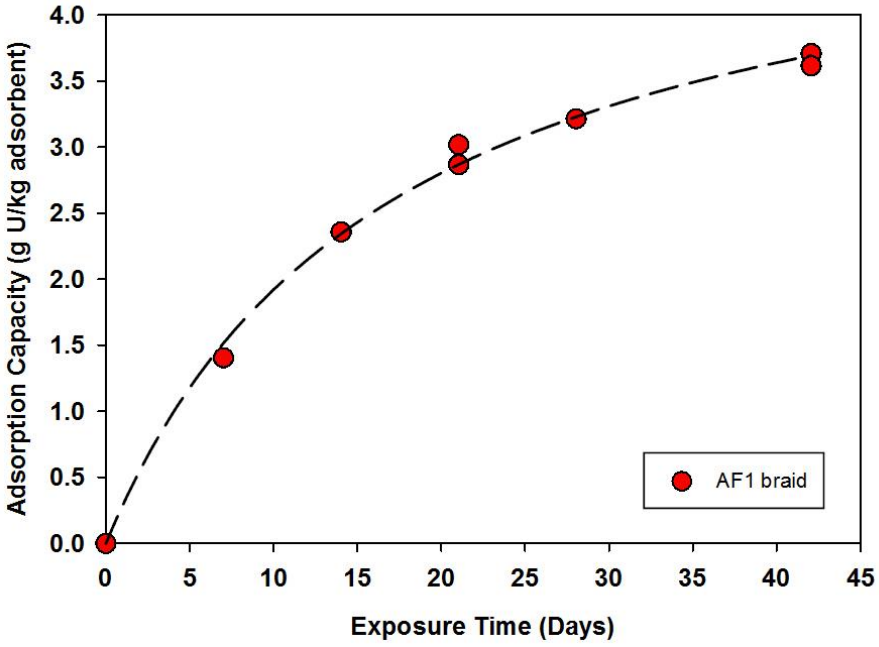

Figure 4. Rate of uranium adsorption by ORNL AF1 at 20 °C from the Sequim Bay marine water

The experimental data were fed into a SigmaPlot software to estimate the saturation (or equilibrium) uranium adsorption capacity using a one-site ligand saturation model. The best-fit line representing the time series adsorption of uranium is given as follows.

$$U = \frac{\beta_{max}\ t}{K_d + t} \qquad (1)$$

Where U is uranium capacity (g U/kg adsorbent), t is exposure time (days), β_{max} is the adsorption capacity at saturation (g U/kg adsorbent), and K_d is the half-saturation time (days). The saturation uranium adsorption capacity is about 5.20 ± 0.20 g U per kg of the adsorbent for this particular sample shown in Figure 4. In addition to uranium, iron and vanadium are also adsorbed by the adsorbent with amounts comparable to that of uranium on weight basis. On molar basis, the amounts of iron and vanadium present in the adsorbent are actually higher than that of uranium indicating that the amidoxime-based adsorbent is not specific for uranium. The effect of relatively long-term seawater exposure on the chemical properties of amidoxime-based polymeric adsorbents was also investigated by FTIR analysis. FTIR measurements given in the Supporting Information (Figure S1) show that conversion of amidoxime groups to carboxylate groups also occured to ORNL AF1 braided adsorbents during 42 days of seawater exposure. This is based on the decrease in absorbance of the N–O stretching (928 cm^{-1}) and in the ratio of C=N/–COO^- stretching (I_{1643}/I_{1559}) shown in the Supporting Information (Table S1). There is about a 20% decrease in the amidoxime groups (based on the decrease in the intensity of the –NO stretching peak I_{928}) for the adsorbents after 42 days of exposure in seawater. It is unclear if this conversion is due to a biotic or abiotic process.

3. *Elution of Uranium from the ORNL Adsorbent*

Several elution methods, including acid (HCl), carbonate–H_2O_2, and chelating agents were tested for removing uranium and transition metals from the high-surface-area amidoxime-based polymer adsorbents after the seawater adsorption experiments. The elution methods and the results are described as follows.

Acid elution — Hydrochloric acid is typically used to remove uranium from amidoxime-based adsorbents. The elution of uranium and transition metals from a typical high-surface-area amidoxime-based polymer adsorbent with different concentrations of hydrochloric acid solutions is shown in Figure 5. About 95% of the adsorbed uranium can be eluted from the adsorbent using 0.5 M hydrochloric acid. The elution is fast, taking about 90 min but not specific for uranium. Transition metals with the exception of iron and vanadium are all eluted with uranium using 0.5 M HCl. About 70% of iron could be eluted under this condition. Vanadium (V) can only be partially stripped from the adsorbent with elevated HCl concentration (>3 M) and temperature (e.g. 60℃). However, under such harsh acid treatment, the adsorbent is severely damaged.

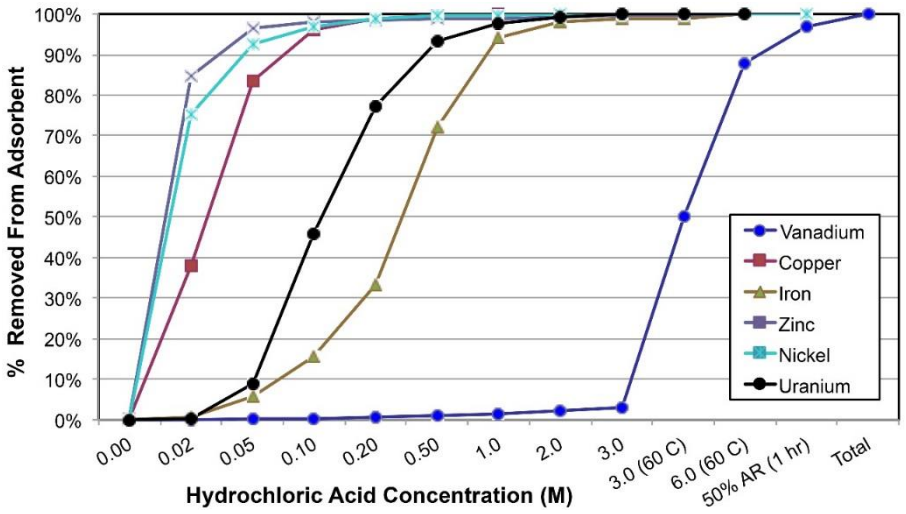

Figure 5. Elution of uranium and transition metals from the AF1 adsorbent after seawater exposure using HCl with different concentrations at room temperature (21℃) for 90 minutes.

Carbonate–H_2O_2 Elution ― Carbonate solutions at high concentrations are able to elute uranium from amidoxime-based adsorbents by formation of the stable uranyl tris-carbonato complex (equation 2)[17]

$$UO_2A_2^{2-} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-} + 2A^{2-} \qquad (2)$$

where A represents the amidoxime group. A recent report shows that with a mixture of sodium carbonate and hydrogen peroxide, uranium elution from the ORNL AF1 adsorbent is significantly improved compared with just sodium carbonate alone.[6] The reason of this improvement in elution efficiency is due to the formation of an extremely stable uranyl peroxo-carbonato complex according to equation (3).

$$UO_2A_2^{2-} + 3CO_3^{2-} + H_2O_2 \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + 2A^{2-} + HCO_3^- + H^+ \qquad (3)$$

The thermodynamic stability of the uranyl peroxo-carbonato complex is 4 orders of magnitude greater than that of the uranyl tris-carbonato complex as illustrated by equation (4).[18]

$$[UO_2(CO_3)_3]^{4-} + HO_2^- \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + HCO_3^- \qquad (4)$$

$K = 5\times10^4$ (24.4 ºC)

Elution of uranium from the adsorbent using Na_2CO_3–H_2O_2 is quite selective for uranium and the elution efficiency depends on the concentrations of the eluents. In simulated seawater, near quantitative elution of uranium from the adsorbent can be achieved in 1 hr of elution at room temperature (21 ºC) using a solution of 1 M Na_2CO_3 and 0.1 M H_2O_2.[6] A higher concentration of H_2O_2 (>0.1 M) would speed up the uranium elution rate but may cause damage to the sorbet material because H_2O_2 is an oxidizing agent.

In real seawater experiments, elution of uranium from the amidoxime-based adsorbent is much slower relative to the simulated seawater experiments. The uranium elution rate using 1 M Na_2CO_3 and 0.1 M H_2O_2 is very slow. About 85% of uranium can be stripped from real-seawater exposed adsorbent using 1 M Na_2CO_3 and 0.1 M H_2O_2 after 4 hours at room temperature. The results given in Figure 6 is obtained from an elution experiment using 1 M Na_2CO_3 and 1 M H_2O_2 for 2 hours at room temperature. About 95% leaching of uranium from the adsorbent can be achieved as compared to digestion of the adsorbent using aqua regia. Small amounts of iron (~25%) and vanadium (~38%) are co-eluted with uranium in the Na_2CO_3–H_2O_2 elution process. Nickel, copper, manganese, and cobalt cannot be eluted by the Na_2CO_3–H_2O_2 elution method.

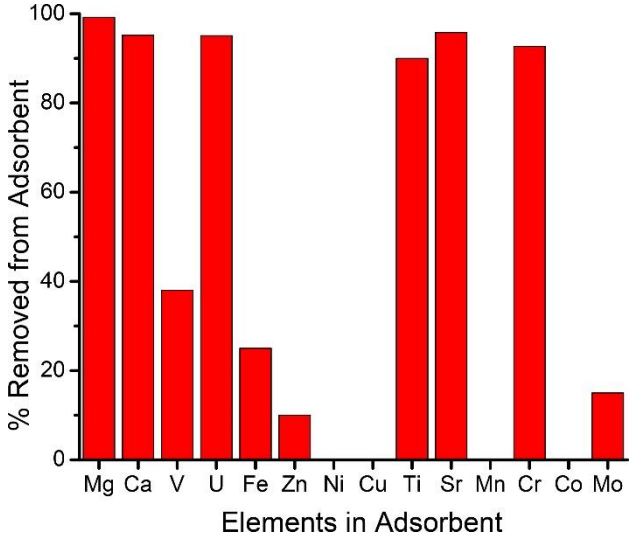

Figure 6. Elemental distribution of ORNL AF1 adsorbent eluted by using 1 M Na_2CO_3 and 1 M H_2O_2 for 2 hours at room temperature.

4. *Elution of Iron and Vanadium from the ORNL Adsorbent*

Iron and vanadium are the two major transition metals which are known to compete with uranium for adsorption to the amidoxime-based adsorbents in real seawater experiments.[4, 19] A

large number of chelating agents were tested in this study for elution of iron and vanadium from the ORNL adsorbent. Several common complexing agents such as ethylenediaminetetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA) are not capable of eluting iron from the adsorbent. The results of iron elution results obtained from ORNL AF1 adsorbent after 42 days of seawater exposure using 3 different chelating agents are given in Table 2.

Table 2. Elution of transition metals (Fe and V) from amidoxime-based adsorbents by different metal chelating ligands.[a]

Ligand[b]	pH	% iron removed from adsorbent	% vanadium removed from adsorbent
0.5 M Tiron	12.59	83.4	6.1
0.5 M Tiron	7.17	94.0	7.0
0.5 M Tiron	3.36	36.6	0.3
1M TSCIT	7.98	29.6	0.0
1M TSCIT[c]	6.42	84.9	4.28
1M TRIS	4.41	61.2	1.5
1M TRIS[c]	4.50	69.0	1.0

[a] Leaching condition: at 40 ^{o}C for 24 hr.
[b] Tiron = 4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt; TSCIT = Trisodium citrate dehydrate; TRIS = Nitrilotris(methylene)triphosphonic acid.
[c] Adding 0.1 M Tiron.

Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) was found most effective for removing iron from the adsorbent. With 0.5 M Tiron at pH 7.2, over 94% of the iron adsorbed by the adsorbent can be removed in 24 hr at 40 ^{o}C. The FTIR spectra (Figure 7) indicate that after the Tiron elution, both 1643 and 928 cm^{-1} band intensities remain unchanged, suggesting that the Tiron treatment would not alter the amidoxime groups present in the adsorbent. A slight decrease in the carboxylate intensity (1559 cm^{-1}) most likely results from the protonation of some carboxylate anions at the elution pH of approximately 7. Other two chelating agents are not effective for removing iron from the amidoxime-based adsorbents.

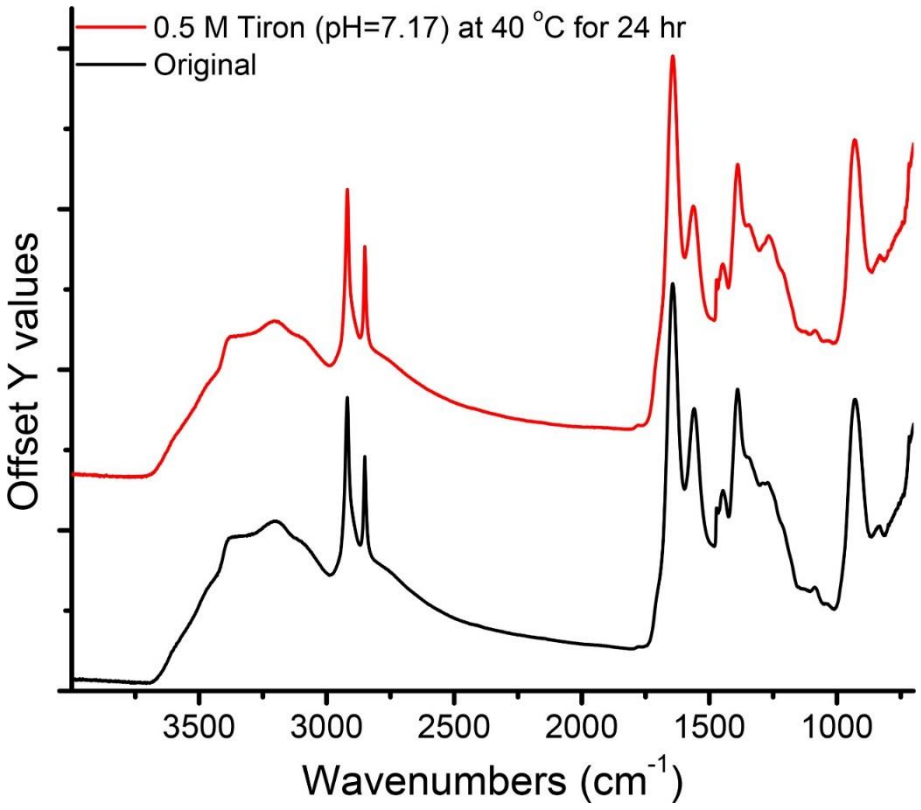

Figure 7. FTIR of ORNL AF1 adsorbent before and after 0.5 M Tiron elution at 40 ºC. (Note: The spectra were normalized to the –CH_2– asymmetrical stretching peak at 2918 cm^{-1})

Elution of vanadium from the amidoxime-based adsorbents is difficult because vanadium bound strongly to the amidoxime groups. Our preliminary ^{51}V NMR results (Figure 8) indicate that only the cyclic glutarimidedioxime reacts with V(V) prepared from Na_3VO_4 in simulated seawater and the branch-chained glutardiamidoxime does not react with V(V) using synthesized single amidoxime molecule systems.

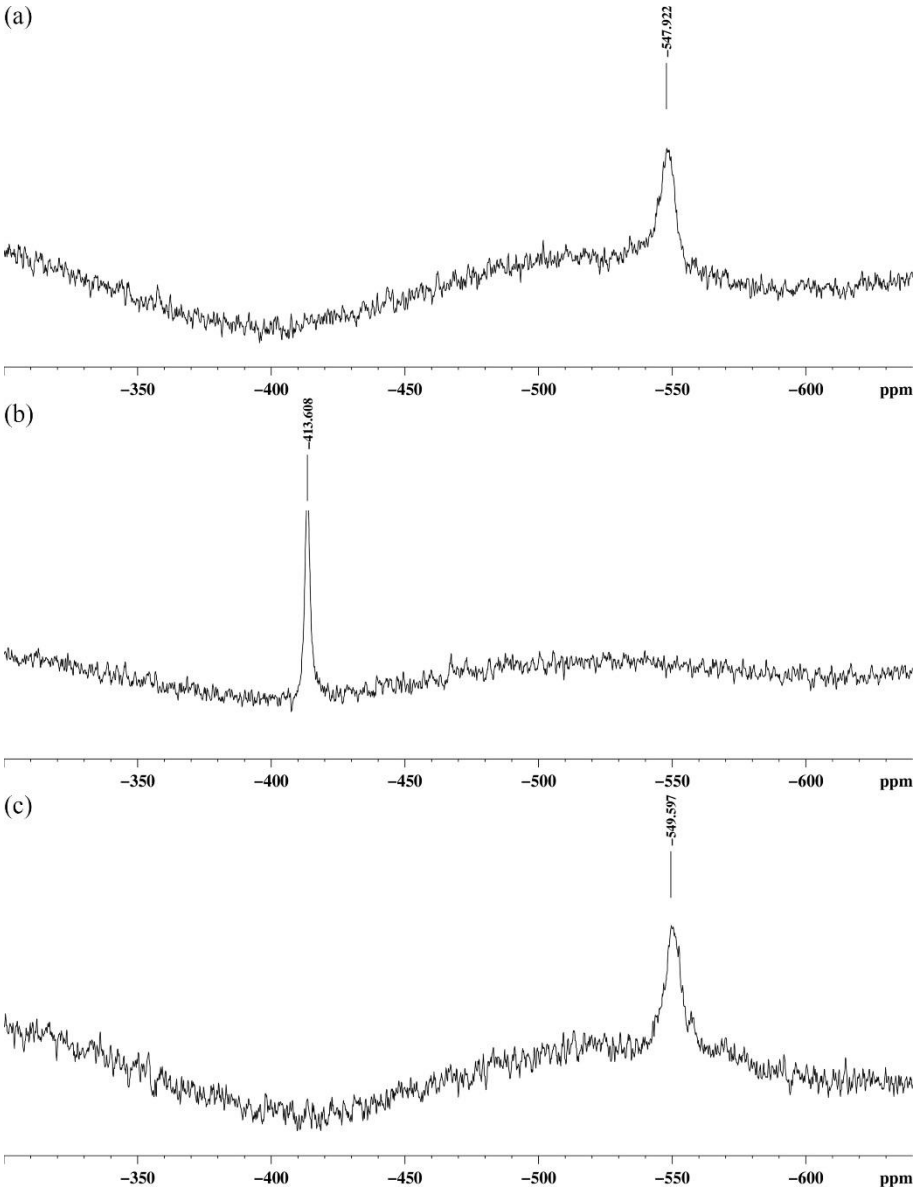

Figure 8. ^{51}V NMR spectra of 0.2 mM Na_3VO_4 in simulated seawater: (a) without any ligand, (b) with 0.2 mM of the cyclic glutardiamidoxime and (c) with 0.2 mM of the branch-chained glutardiamidoxime.

The stoichiometric ratio of the coordination between vanadium and cyclic ligand (glutardiamidoxime) is determined by ^{51}V NMR shown in Figure 9.

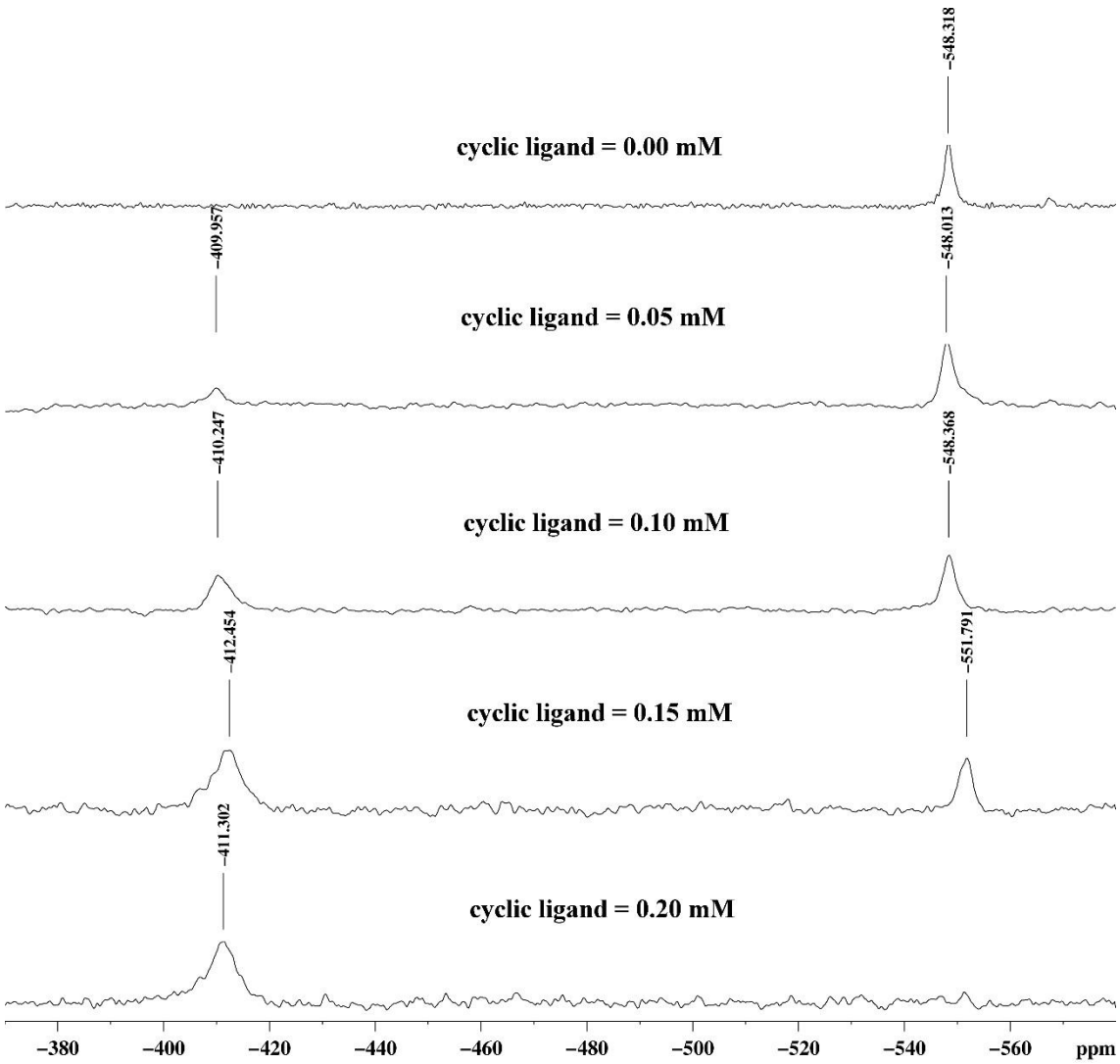

Figure 9. ^{51}V NMR spectra of 0.2 mM Na_3VO_4 in 0.5 M NaCl aqueous solution (pH = 8.3) followed by addition of different concentration of cyclic ligand (glutarimidedioxime).

Without adding the cyclic amidoxime ligand, a ^{51}V NMR peak was observed at -548 ppm from free vanadates ($H_2VO_4^-$ and HVO_4^{2-}) at pH = 8.3 which is consistent with previous literatures.[20-22] Addition of the cyclic ligand (<0.2 M) produced a new ^{51}V NMR peak at -411 ppm in addition to the free V(V) peak at -548 ppm. The -411 ppm peak is assumed to be a vanadium(V) amidoxime complex. When the cyclic ligand reached 0.2 mM, the -548 ppm peak disappeared and only the -411 ppm peak was observed. The ^{51}V NMR results suggest that the complex is probably

composed of 1 vanadium(V) and 1 glutarimidedioxime under our experimental conditions. However, it is well known that vanadium in its higher oxidation states (+5) tends to form polynuclear, anionic metal-oxygen clusters (polyoxovanadate ions).[22-25] Depending on the pH, the concentration, and the ionic strength, aqueous vanadate solutions prepared by dissolving orthovanadate (e.g., Na_3VO_4) can contain a variety of vanadate species in different protonation and condensation states.[22-24] Therefore, in higher concentrations of vanadate and the cyclic ligand, stoichiometric ratio of the vanadium and the ligand (glutardiamidoxime) may not be 1:1. Of many reagents tested in this study, oxalic acid and 1M H_2O_2 appear to show some ability of removing vanadium from the amidoxime complex. Elution of vanadium and understanding vanadium coordination with amidoxime groups in the polymer adsorbents are currently under investigation.

Conclusion

A high-surface-area amidoxime-carboxylic acid-based polymer adsorbent (ORNL AF1) was tested for sequestering uranium in a flowing seawater flume system for 42 days at the PNNL-Marine Sciences Laboratory. The saturation uranium adsorption capacity is estimated to be 5.20 ± 0.20 mg U/g of the adsorbent. Conditioning the adsorbent with KOH is important for determining the adsorbent's uranium uptake capability from seawater. FTIR spectra reveal that the KOH conditioning process not only removes the proton from the carboxylic acid but also converts the amidoxime groups to carboxylate groups in the adsorbent. About 95% of the adsorbed uranium can be eluted from the ORNL adsorbent using conventional acid elution (0.5 M HCl) within 90 min. A sodium carbonate-hydrogen peroxide (1 M each) solution can also elude 95% of uranium from the adsorbent. The carbonate–H_2O_2 elution method is more selective than the acid elution. Tiron (1 M) is most effective for elution of iron from the adsorbent. After the Tiron

elution, the vibrational features of the adsorbent are similar to the original adsorbent suggesting that the functional groups of the adsorbent are unaltered. The coordination between vanadium (V) and amidoxime was investigated using ^{51}V NMR. According to our preliminary ^{51}V NMR results, only the cyclic glutarimidedioxime reacts with vanadium (V) and probably forms a 1:1 vanadium (V)–glutarimidedioxime complex.

Acknowledgement

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

FTIR spectra of the ORNL AF1 braided adsorbents after 42 days of seawater exposure (Figure S1). A table of peak intensity of N–O stretching (928 cm^{-1}) and ratio of C=N/–COO^- stretching (I_{1643}/I_{1559}) of the ORNL AF1 braided adsorbents after 42 days of seawater exposure (Table S1). (PDF)

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