Supplementary Information

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

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Explanation for the assignment of the 1559 cm^{-1} –COO^{-} band (How to distinguish –COO^{-} asymmetrical stretching band (1559 cm^{-1}) and amide II band (N–H bending 1570–1515 cm^{-1}) from FTIR spectra)

According to the Figure 1S, our assigned 1559 cm^{-1} –COO^{-} band of the KOH conditioned sorbent after HCl (0.5 M) elution is reduced to the size of the original sorbent (without KOH conditioning) and a shoulder peak at 1706 cm^{-1} (assumed to be from the carboxylic acid) reappears. This reversible conversion of 1559 cm^{-1} and 1706 cm^{-1} peak (under basic and acidic conditions) is consistent with the assignment of the former as a carboxylate anion (–COO^{-}). Amide is not expected to behave like this. In the original unconditioned sorbent, there is a small shoulder peak around 1570 cm^{-1} which is probably from amidoxime (N–H bending band) not from amide.

Note: The amide II band resulting from N–H bending (around 1570 cm^{-1}) has an intensity of 1/2 to 1/3 of the C=O adsorption band (amide I band around 1706 cm^{-1}).
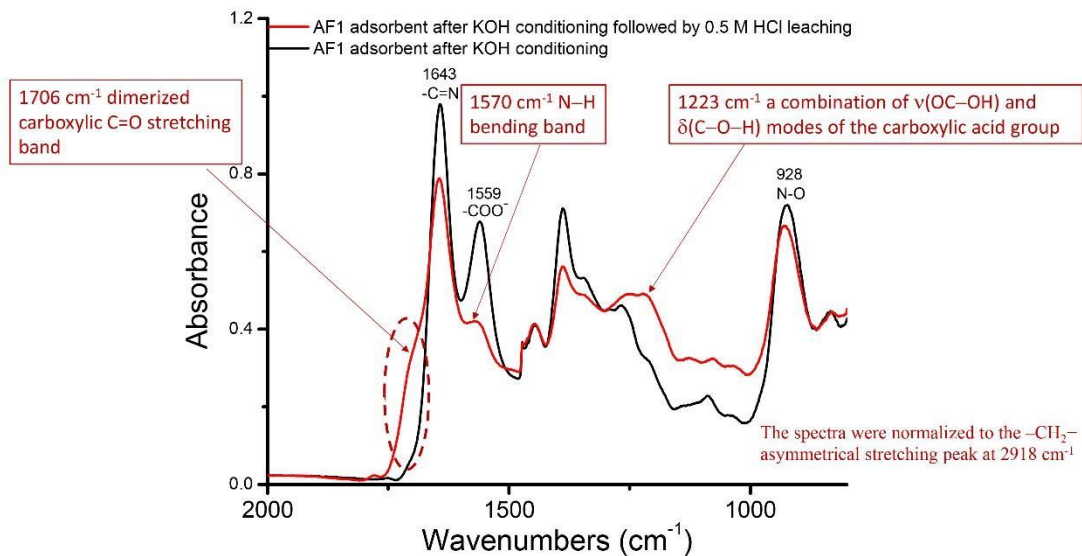
Figure 1S. FTIR spectra of the ORNL AF1 adsorbent after KOH conditioning and after KOH conditioning followed by 0.5 M HCl leaching.
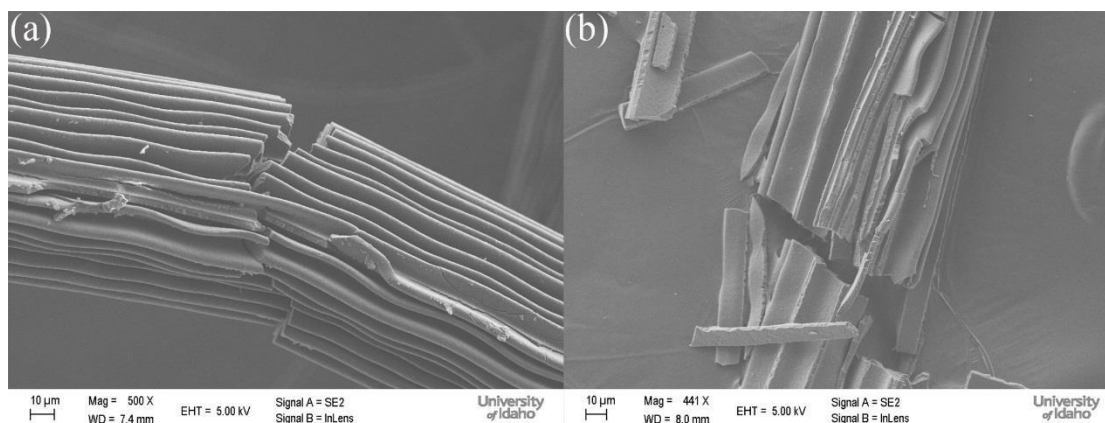

Figure 2S. SEM images of the ORNL high surface area polyethylene fiber conditioned with 2.5% KOH at 80° C for different times and subsequent exposure to seawater for 42 days: (a) 1 hr; (b) 3 hr.
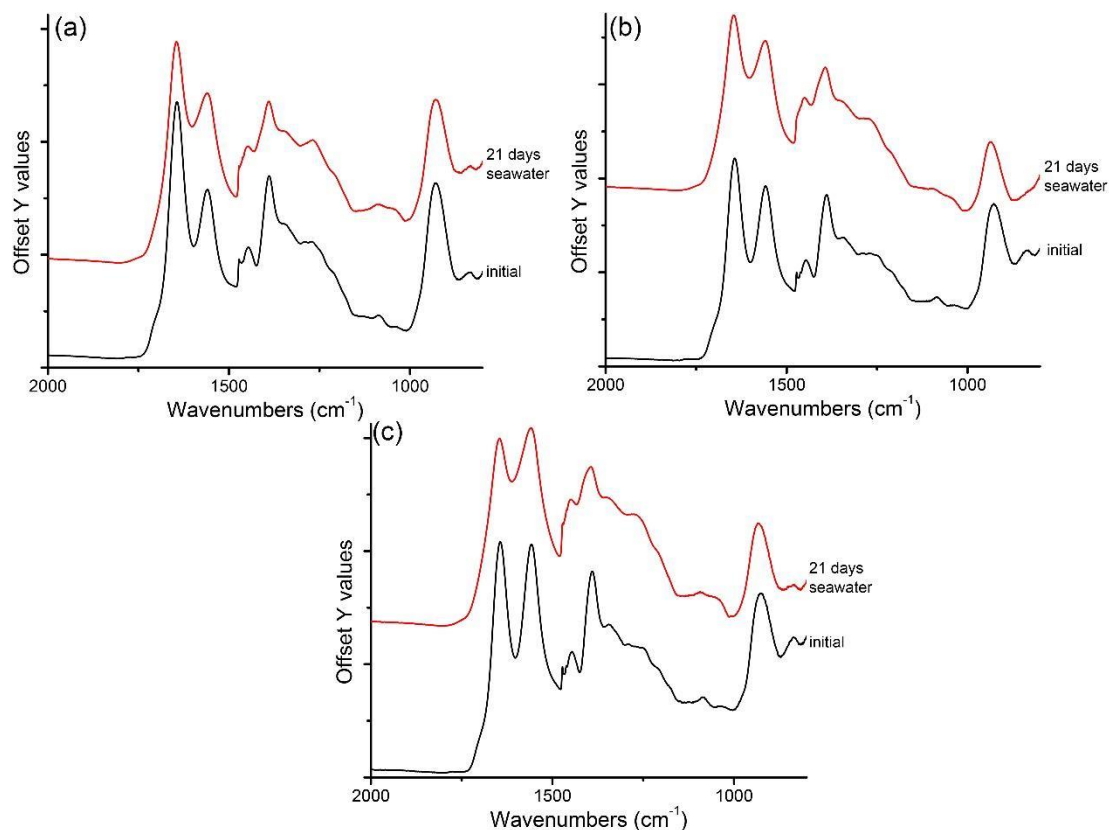
Figure 3S. FTIR spectra of the ORNL AF1 adsorbent after KOH conditioning at 80℃ for times between 1 hour and 5 hours and subsequent exposure to seawater for 21 days: (a) 1 hr; (b) 3 hr; (c) 5 hr.   The decrease in N-O band intensity is 14% for 1 hr, 37% for 3 hr, and 21% for 5 hr.   (Note: The spectra are normalized to the $-CH_2-$ asymmetrical stretching peak at 2918 cm^{-1}.)

Statistical Analysis Methodology

The data for n = 30 independent analytical runs of the Uranium Sorption study, summarized in Table 1S, was analyzed with a generalized linear model (GLM) with main effects of reaction time, alkaline conditioning, and their interaction. The data was transformed to the natural log of the U capacity (mg/g) to reduce the within class heterogeneity.   A series of regression models based on a segmented model for the transformed U capacity and each alkaline conditioning (y_i) was fit against reaction time (x).   The full model had a shared intercept (a) and separate linear slopes (b_{1i} and b_{2i}) and join points (c_i) for i = 1 to 2 for KOH and NaOH conditioning respectively:

$$y_i = \begin{cases} a + b_{1i}\,x \text{ for } x < c_i \\ a + b\,c_i + b_{2i}\,(x - c_i) \text{ for } x \geq c_i \end{cases}.$$

For each alkaline condition the null hypothesis that the first slope was shared and equal to 0 ($b_{1i} = 0$) was tested with an F-test.   A model (Model 1) with the first slope b_{1i} set

equal to 0, shared join point ($c_1 = c_2$), and separate second slopes (b_{2i}) was compared to a second model (Model 2) with the first slope b_{1i} set equal to 0, separate join points (c_{1i}), and shared second slope ($b_{21} = b_{22}$) using the Akaike's Information Criteria (AICc) to determine the model most likely to have generated the response observed over reaction time.

Table 1S.   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 ºC.   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 (n=4)	3.22 ± 0.05 (n=2)
40 min	3.46 ± 0.07 (n=2)	3.22 ± 0.05 (n=2)
1 hr	3.28 ± 0.12 (n=5)	3.04 ± 0.05 (n=2)
3 hr	1.63 ± 0.49 (n=5)	1.13 ± 0.11 (n=2)
5 hr	0.26 ± 0.09 (n=4)	0.14 ± 0.01 (n=2)

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

Statistical Results

The interaction term from the GLM on the Ln(U mg/g) was not significant (Table 2S; $F = 1.67$ with d.f. = 4, 20; $p = 0.196$). The main effects of reaction time (min) and alkaline condition were significant (F = 177 and 7.05 with d.f. = 4, 20 and 1, 20 respectively; $p < 0.02$). Since the interaction term was not significant, a series of nested segmented linear models with a common intercept were fit to the transformed U capacity for each alkaline condition (KOH and NaOH) against reaction time. The first slope was not found to be significantly different from 0 for either alkaline conditioning (F=0.21; d.f.=2,23; $p = 0.81$). This model (common intercept and slope 1 set to 0, unconstrained join points and second slopes) had an R^2 value of 0.97 and the error mean square (EMS) of 0.1934. A nonparametric runs test of the goodness-of-fit conducted separately for each alkaline conditioning was not significant ($p > 0.2$).

Model 1 (Figure 4S (A)) with a shared intercept (a), slope 1 set to zero ($b_{1i} = 0$), a shared join point ($c_1 = c_2$), and separate slope 2 values (b_{2i}) was not significantly different from a model with separate join points (F = 0.70; d.f. = 1, 25; $p = 0.412$) and had an R^2 value of 0.97 and EMS value of 0.1923. The runs test of goodness-of-fit for each alkaline conditioning separately was not significant ($p > 0.3$). Model 2 (Figure 4S (B)) with a shared intercept (a), slope 1 set to zero ($b_{1i} = 0$), separate join points (c_i), and common slope 2 values ($b_{21} = b_{22}$) was significantly different from a model with separate slope 2 values (F = 1.42; d.f. = 1, 25; $p = 0.245$) and had an R^2 value of 0.97 and EMS value of 0.1949. The runs test of goodness-of-fit for each alkaline conditioning separately was not significant ($p > 0.2$).

The two models, Model 1 = common join point separate slope 2 values and Model 2 = separate join points and common slope 2 values were compared using the Akaike's Information Criteria. The probability that Model 1 generated the data was 52% for KOH and 87% for NaOH and Model 2 was 48% for KOH and 13% for NaOH. Thus, the preferred model was Model 1 with an estimated slope and 95% confidence interval for KOH b_{21} = -0.015 (-0.017 to -0.013) and for NaOH b_{22} = -0.018 (-0.019 to -0.018). The decline in U sorption after 127 minutes (slope 2) for NaOH was significantly greater than for KOH (F = 17.9; d.f. = 1, 28; $p < 0.001$).

$$y = \begin{cases} 1.189 \text{ for } x < 127 \\ 1.189 + b_{2i}(x - 127) \text{ for } x \geq 127 \end{cases}$$

Table 2S. General linear model ANOVA

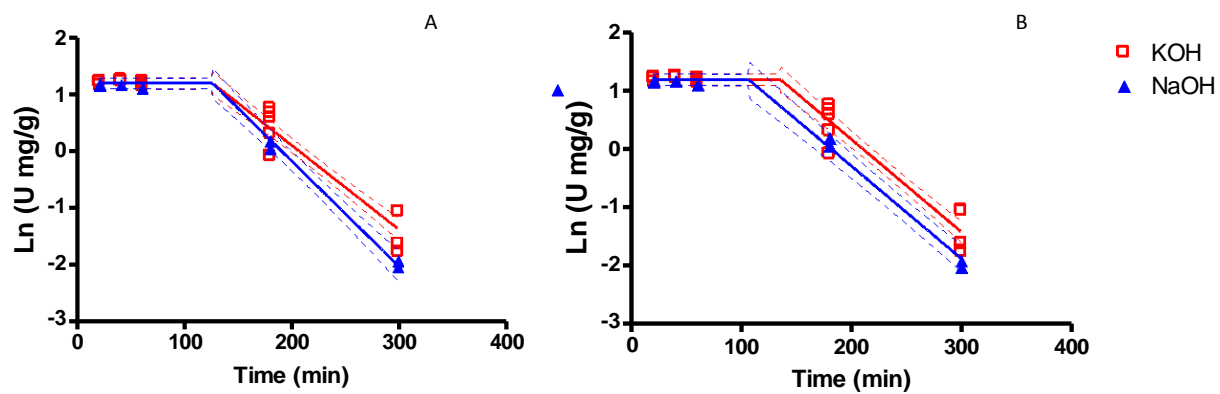| Source	DF	Adj SS	Adj MS	F-Value	P-Value
Time (min)	4	32.5065	8.12662	177.81	< 0.001
Alkaline Condition	1	0.3221	0.32211	7.05	0.015
Time (min)*Alkaline Condition	4	0.3056	0.07641	1.67	0.196
Error	20	0.9141	0.0457		
Total	29	35.7986			

Figure 4S. Model 1 (A) and Model 2 (B) fit to natural log of U capacity against reaction time