

**Elution by Le Chatelier Principle for Maximum Recyclability of
Adsorbents: Applied to Polyacrylamidoxime Adsorbents for
Extraction of Uranium from Seawater**

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Experimental:

Acetamidoxime synthesis. The synthesis of acetamidoxime was carried out, following a similar procedure reported by Zulfiqar,²² in a dry 1000 mL round bottom flask equipped with a magnetic stirrer. The reaction flask was charged with acetonitrile (86 mL, 1.6 mol), followed by the addition of 800 mL of ethanol, then the corresponding amount of hydroxylamine solution (50 wt. % in H₂O) (100 g 1.5 mol) was added and the mixture was stirred overnight at 70 °C. The progress of the reaction was monitored by TLC and confirmed by NMR, as shown in Figure S1. The transparent and colorless reaction mixture was slowly concentrated under rotavap with warm water. Once most of the solvent was removed, colorless needle-like crystals began to grow. The crystals and the residue were washed with n-hexane and this mixture was kept in a refrigerator to increase the yield of the crystalline product. The crystals obtained were finally dried under vacuum. ¹H NMR (500 MHz; DMSO-d₆): δ 8.68 (s, 1H), 5.34 (s, 2H), 1.62 (s, 3H). ¹³C NMR (100 MHz; DMSO-d₆): δ 149.8, 16.0. ESI-MS: [MS+H]⁺ 75.07 (+ve). The proton NMR also shows water in the crystals peak near 5.2.

Elution of PE adsorbents with acetamidoxime or hydroxylamine. The amount of amidoxime or hydroxylamine used for the elution was determined based on the approximated degree of grafting of the adsorbent, obtained by evaluating elemental analysis. We determined the estimated density of the amidoxime groups with a degree of grafting of approximately 380%. According to the changes in the elemental analysis we determined that about a 35% of these groups are converted to amidoxime

groups. Additionally, we determined a ratio of nitriles groups to carboxylic acid groups of 2.6 to 1. Therefore, 15 mg of adsorbent correspond to 3.12 mg of the polyethylene trunk with 11.89 mg of grafted copolymer. From this copolymer, 62% is composed of nitriles (7.30 mg) and from those nitriles 35% are amidoxime (2.6 mg). The 2.6 mg of amidoxime per 15 mg of adsorbent is the upper approximation of the ratio. The 2.6 mg correspond to 0.035 mmols of amidoxime.

The uranium was eluted from the fiber using a 10 mL solution containing 50% acetamidoxime or hydroxylamine and water and shaking the mixture at 500 rpms for 1 h at 20 °C or 65 °C. A sequence (1 h of shaking the adsorbent in the elution solution) of three elution aliquots was performed on one adsorbent sample and after each elution sequence the fiber was transferred to a new 10 mL hydroxylamine solution without any further manipulation or washing. To determine the residual amount of uranium left on the adsorbent, the fibers were filtered from the solution and digested following the procedure for the seawater samples (described below).

Digestion of fibers to determine metal residue after different elution methods.

Seawater exposed adsorbent fibers were collected from adsorbent beads, rinsed with 0.1 M HCl to remove salts, and dried under vacuum. This step was done exclusively as part of the study to split the sample and obtain individual weights of the adsorbent; under realistic scenarios the adsorbent weight is already known and therefore, no reconditioning is necessary for reuse. The dried fibers were then digested with freshly prepared high-purity (Optima, Fisher Scientific) aqua-regia (3:1; HCl:HNO₃) by first adding nitric acid followed by hydrochloric acid. The mixture was shaken

and place in an oven at 60-65 °C for 1 hour and mixed by intermittent shaking. The acid solution was diluted to 50% with high-purity DI water (Optima, Fisher Scientific), and place in an oven for another 3 h at 60-65 °C. An additional 60-mL of 0.1 M HCl solution was added and the sample was shaken for 3 h (500 rpms) at room temperature to complete the digestion process. The uranium concentration of the final solution was measured using a Perkin Elmer Optima 2100 DVICP-OES. Several emission wavelengths (U367.007 nm, U385.958 nm and U409.014 nm) were measured to ensure accuracy by avoiding matrix effects (no impurity peaks overlap with measured peaks). The reported results are based on the measurements obtained from the emission wavelength at U385.958 nm because it provided the highest intensity and was able to verify its maximum sensitivity with different matrices and signal/noise ratios.

Characterization:

NMR Spectroscopy. The ^1H and ^{13}C NMR spectras of Acetamidoxime were recorded on a Varian VNMRS 500 MHz NMR Spectrometer in deuterated DMSO or water (DMSO-d_6 , D_2O). Compounds were characterized by a hybrid quadrupole time of flight mass spectrometer fitted with electrospray ionization mass spectrometer, AB Sciex QSTAR® Elite Hybrid LC/MS/MS System.

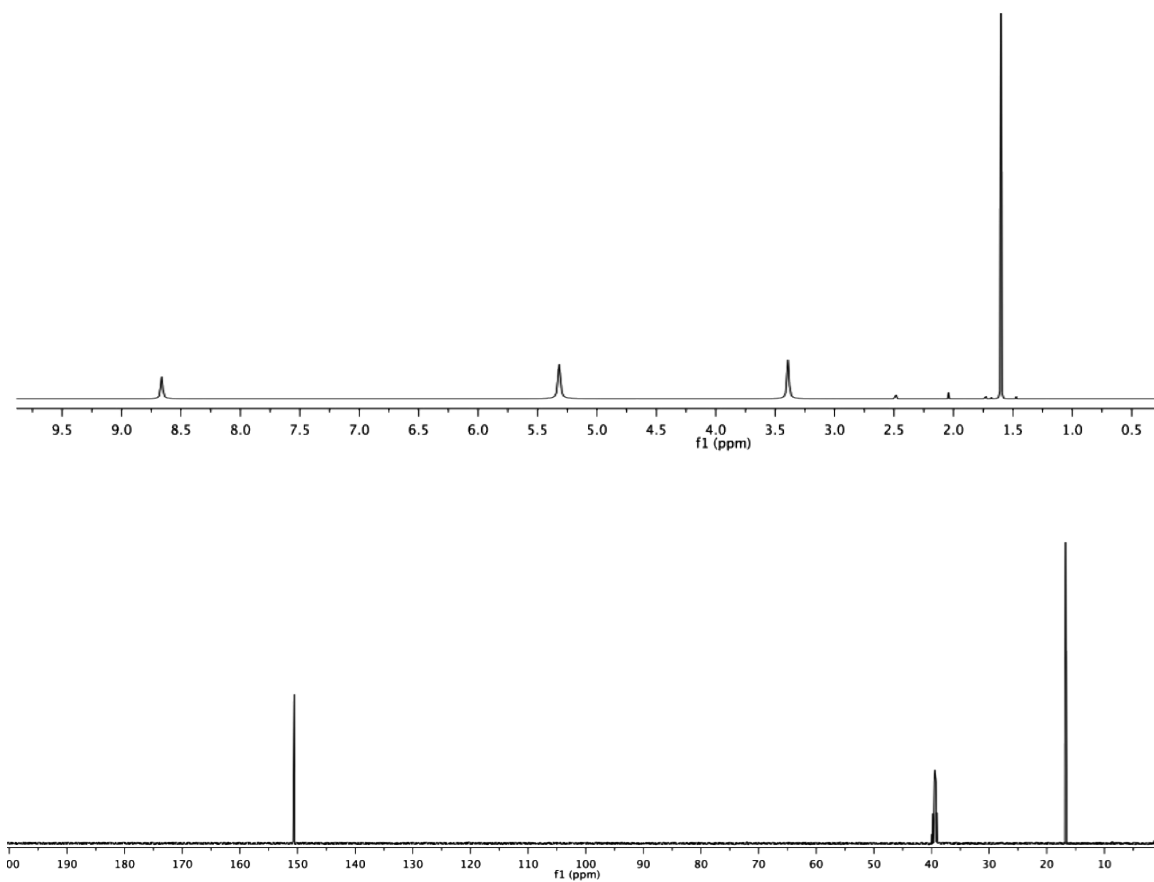


Figure S1. ^1H NMR (top) and ^{13}C NMR (bottom) of acetamidoxime in deuterated DMSO.

Table S1. Successive elution of uranium from adsorbent using 10 mL aliquots of acetamidoxime solution at room temperature.

Elution sequence	Uranium quantity (%)
Elution 1	58.0
Elution 2	24.4
Elution 3	16.8
Residual amount	0.8

Table S2. Representative results of the elution of uranium from polymer fiber adsorbents with 50% hydroxylamine in H₂O monitored over three consecutive elutions.

Elution	Uranium amount (%)	Uranium Concentration (g _U /Kg _{Ads.})
Elution 1	90.0	115.3
Elution 2	8.6	11.0
Elution 3	1.2	1.5
Residue	0.2	0.3
Total U		128.1

Elution with carbonate or carbonate-H₂O₂ solution

Elution of uranium was performed with uranium-loaded fibers (~15 mg, dry sorbent weight) immersed in 10 mL of a 2.0 M sodium carbonate (20 mmol) solution or a freshly prepared solution of 1.0 M sodium carbonate (10 mmol) and 0.1 M H₂O₂ (3%) while stirring for 120 minutes at ~21 °C. Aliquots of ~0.5 mL of the leaching solution were collected at specific time intervals and diluted with 2.5 mL of 0.1 M HCl. The concentration of the solution was analyzed by ICP-OES.

In order to study the recyclability²¹ of the adsorbent material after undergoing this elution process, several adsorption/elution cycles were conducted. The adsorbent fibers were separated from by filtration after each cycle, rinsed with DI water and without further manipulation or drying, and placed in a simulated seawater solution for uranium reloading. It is important to note that the polymer fiber should stay moist to prevent the collapse of the grafted polymer chains, which can only be rehydrated with a KOH solution.

The results of our sodium carbonate and hydrogen peroxide elution of uranium from the amidoxime-based adsorbent are given in Table S3. Using 2 M sodium carbonate, elution of uranium from the adsorbent at room temperature (21 °C) reaches a near constant value after one hour. When a small amount of hydrogen peroxide is added to 1 M sodium carbonate solution, there is a significant increase in the efficiency of uranium elution. Even with 0.01 M of H₂O₂ in 1 M sodium carbonate, the uranium elution efficiency increased over each cycle.

Table S3. Change in elution capacity (g_U/Kg_{Ads.}) of uranium from polymer adsorbent fibers over multiple cycles after being exposed to simulated seawater solutions.

Elution Method	Sample Quantity	Elution Stage	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6
Elution with 1M Na ₂ CO ₃ and 0.1 M H ₂ O ₂	Sample 1 17.69 mg	Initial U loading	144.2	119.9	120.5	92.9	76.2	74
		Total eluted after 120 min	162.2	161.0	138.4	123.1	100.5	
		Performance Comparison (%)	100	99.3	86.0	88.9	81.6	73.7
		Decrease in Performance (%)	0	0.7	14.0	11.1	18.4	
	Sample 2 20.15 mg	Initial U loading	141.7	119.1	113.7	91.4	79.8	71.7
		Total eluted after 120 min	169.8	165.9	147.2	125.4	101.8	
		Performance Comparison (%)	100.0	97.7	88.7	85.2	81.2	70.4
		Decrease in Performance (%)	0.0	2.3	11.3	14.8	18.8	
Elution with 2M Na ₂ CO ₃	Sample 1 18.54 mg	Initial U loading	132.9	116.8	106.7	77.6	74.6	61.7
		Total eluted after 120 min	119.2	116.1	109.6	93.9	88.8	
		Performance Comparison (%)	100	97.4	94.4	85.6	94.6	69.5
		Decrease in Performance (%)	0	2.6	5.6	14.4	5.4	

Table S4. The concentration (ppm) of eluted uranium over time at different pH values using 0.5 mL aliquots of acetamidoxime as the elution agent at temperatures

of 20 °C or 65 °C.

Time (min)	pH 5	pH 7	pH 9	T 65
10	5.8	22.4	87.0	63.2
25	7.2	56.4	95.2	81.3
60	8.7	80.8	95.4	83.0
120	9.1	92.8	120.0	110.7
Residual Amount	107.6	67.2	65.7	68.5
Total amount of U in sample	116.7	160.0	185.7	179.1

Table S5. Representative results of the elution of uranium from fiber adsorbents with 50% hydroxylamine in H₂O monitored over time at room temperature.

Aliquot Time (min)	Uranium Eluted (%)	Uranium Concentration (gU/Kg_{Ads.})
15	76.3	101.4
30	90.2	119.9
45	90.4	120.2
60	90.7	120.5
120	93.0	123.6
Residue	7.0	9.3
Total U		132.9

Seawater Exposed Samples

Amidoxime-based polyethylene fiber were conditioned with KOH for 3 hours, then loaded in columns with beads as reported in previous studies with the same adsorbents. The columns were exposed to six weeks in real seawater in the Pacific Northwest National Laboratory in Sequim as in previous reports.^{10,18}

The metals on weighed samples of adsorbent exposed to seawater for six weeks were eluted with 3.5 M acetamidoxime solution, 1.0 M sodium carbonate with 0.1 M peroxide solution, or 50% hydroxylamine solution. Each sample was first rinsed

with 0.1 M HCl (~50-60 mL) then eluted twice with 20 mL of the corresponding solutions and then the metal content left on the adsorbent was determined after digestion, representative samples with different metal concentration at all stages are listed in Table 6. The polymer adsorbent was dried and rinsed with 0.1 M HCl to determine the weight, therefore; there is no way to determine if this has an effect on the efficiency of the elution. When the fibers are dried the grafted polymer chains collapse and the fiber diameter contracts, to determine the effect, a pre-weighted dry sample of the adsorbent exposed to six weeks of seawater was swelled again with DMSO. The polymer adsorbent fibers that were exposed to seawater were immersed in different elution solutions two times to extract Cu, Fe, V and U as shown in Table S6. In the case of washing the adsorbent fiber with DMSO, the following procedure was followed. The adsorbent was heated in an oven with 10 mL DMSO at 60 °C for 1 h. Then the fibers were filtered and added to 10 mL of 3.5 M acetamidoxime and were shaken at 500 rpms for 1 h. The solution was then diluted to 13 mL with 0.1 M HCl. Then 5 mL of the solution was further diluted to 15 mL with 0.1 M HCl and 0.5 mL of concentrated HCl before being analyzed by ICP-OES.

Table S6. The elution of metals from polymer adsorbents fibers exposed to seawater for six weeks with different elution solutions.

Eluent	sample quantity (mg)	elution stage	Cu 327.393 nm (g _{Cu} /Kg _{ads.})	Fe 238.204 nm (g _{Fe} /Kg _{ads.})	V 292.464 nm (g _V /Kg _{ads.})	U 385.958 nm (g _U /Kg _{ads.})
Acetamidoxime 3.5 M	37.38	0.1M HCl rinse	0.36	0.14	0.00	0.66
		elution 1	0.04	0.03	1.55	0.93
		elution 2	0.03	0.06	0.52	0.69
		Residual	0.04	1.02	1.02	0.97
		total on sample	0.47	1.26	3.10	3.26
Acetamidoxime 3.5 M after DMSO wash	28.28	0.1 HCl rinse	0.76	0.57	0.02	0.30
		elution 1	0.03	0.04	1.89	2.42
		elution 2	0.09	0.41	1.51	1.01
		Residual	0.02	2.36	2.09	0.32
		total on sample	0.91	3.37	5.51	4.05
0.1 M H ₂ O ₂ in 1 M Na ₂ CO ₃	48.43	0.1M HCl rinse	0.78	0.52	0.40	0.86
		elution 1	0.06	1.01	2.59	1.02
		elution 2	0.07	0.00	0.23	0.76
		Residual	0.06	0.97	1.83	0.01
		total on sample	0.96	2.51	5.06	2.65
50 % Hydroxylamine	31.22	0.1M HCl rinse	0.32	0.19	0.02	0.59
		elution 1	0.17	0.44	5.62	2.49
		elution 2	0.09	0.29	1.03	0.16
		Residual	0.00	-0.15	-0.14	-0.04

total on sample	0.58	0.92	6.67	3.24
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List of Equipment:

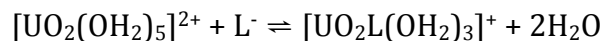
1. Metal free Nalgene bottles
2. Seawater

Seawater exposed adsorbent fibers were collected from adsorbent beds, washed with deionized (DI) water to remove salts, and dried under vacuum filtration using a nylon membrane filter with a pore size of 200 nm (Pall Life Sciences, Port Washington, NY, USA).

Details of Calculations

Calculations were performed using the Gaussian 09 B.01 program. Method employed was the B3LYP density functional theory. Basis set used for uranium was Stuttgart small-core (SSC) 1997 where 60 core electrons were replaced with relativistic effective core potential (ECP) while the valence electrons were treated with 6-31+G(d). Other atoms were treated with full 6-31+G(d) basis set. Frequency calculations were performed to verify that geometries were minima (no negative frequencies), to compute zero point energies and thermal corrections for 298 K. Energies of solvation in water were calculated with integral equation formalism polarized continuum model (IEF-PCM).

Energies reported are energies for the complexation reaction of uranyl ion in aqueous solution:



where $[\text{UO}_2(\text{OH}_2)_5]^{2+}$ is the predominant species of solvated uranyl ion in aqueous solution, L⁻ the anionic ligands acetamidoxime and hydroxylamine, $[\text{UO}_2\text{L}(\text{OH}_2)_3]^+$ the complex, and 2H₂O displaced water molecules.

Full reference for Gaussian09:

Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.