Supplemental Information

Surface Functionalized Nanostructured Ceramic Sorbents for the Effective Collection and Recovery of Uranium from Seawater

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1. Evaluation of sorbents for collection of uranium from seawater

Material parameters of selected sorbent materials, such as particle size, pore size, and ligand density of the materials, as well as percent sorption of uranium from seawater are provided in Table SI 1.

Table SI 1. Physical properties for sorbents and uranium collection from seawater

Sorbent Material	Particle Size (μm)	Mean Pore Diameter (Å)	Ligand Density (L/nm^2)	% Sorption[a]
Custom Sorbents				
Diphos- PC Silica	250-500	73.6	0.42	99
Diphos-NF Silica	0.2-0.3	N.A.	0.38	99
3,4HOPO-NP Silica	Variable	362	1.22	100
PropPhos- NP Silica	Variable	57.8	1.34	99
AcPhos- NP Silica	Variable	68.7	1.03	99
IDAA-NF Silica	0.2-0.3	N.A.	0.90	97
IDAA- NP Silica	Variable	57.2	0.83	92
Commercial Sorbents				
Ln Resin	25-50	38.2	-	95
Diphonix Resin	150-250	13.5	-	78
Activated Carbon	150	42.1	-	72
SAX Resin	75-150	19.1	-	59
SCX Resin	~45	70.9	-	56
Chelex 100 Resin	75-150	93.5	-	47
Purolite®S910	3.2	100	-	13
Support Sorbents				
PC Silica	250-500	153	-	36
NF Silica	0.2-0.3	225	-	92
NP Silica	1-5	56.5	-	98

a) The initial concentration of uranium of 59 ppb at equilibrium pH of 6, L/S of 50000 mL/g sorbent Average of triplicate data and std. Dev. < 5%.

2. Evaluation of stripping solutions

The stability of the selected sorbent materials in the eluent solutions was also evaluated as data shown in Table SI 2, to determine whether the stripping solution was causing sorbent degradation that would negatively impact cyclic use of the collection materials. Sorbent core materials that were exposed to the eluents were observed to leach silica. The moderate leachate affects the recycling and generation of sorbent material, and the sorbents lose the ability to collect uranium for the next process cycle.

Table SI 2. Silica leachate from the selected support materials in eluents

Materials	Si leachate (mg/g material)[a]			
	0.01 M HNO_3	0.01 M HCl	4.0 M NaCl/ 0.01 M HNO_3	1.0 M Na_2 CO3
Diphos-NF Silica	2.6	2.9	4.3	0
Diphos-PC Silica	2.4	2.5	4.0	0
3,4 HOPO- NP Silica	3.1	3.7	11.4	180
PropPhos-NP Silica	5.7	3.5	7.7	18.8
AcPhos-NP Silica	13.9	11.3	10.7	0
IDAA-NF Silica	1.1	1.5	2.8	0
IDAA- NP Silica	16.6	11.5	21.5	483
NF Silica	8.4	10.7	41.4	302
NP Silica	6.1	7.4	32.0	403

L/S =50000 mL/g sorbent.

[a] Average of triplicate data and S.D. is in between ±0.4 to ±21.02 mg/g

3. Sorption capacity

The Langmuir model was used to fit the experiment data and explain the sorption capacities of materials. The estimated parameters of Langmuir isotherm and calculated capacity at the 3.3 ppb concentration of uranium in sweater for selected sorbents are given in Table 4, and where calculated using the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

where C_e is the equilibrium concentration of uranium in the solution, q_e is the amount of uranium adsorbed on the unit mass of sorbent, q_{max} is the uranium adsorbed at saturation and represents the maximum capacity of sorbent for uranium sorption, and b is the Langmuir constant, defined as the sorption affinity of the sorbent for uranium. The regression coefficient, R^2, indicates the sorption isotherm of sorbents fits the Langmuir adsorption model.

Table SI3. Estimated parameters for the Langmuir isotherm model for uranium sorption on functionalized and commercial sorbents.

Materials	Estimated Capacity in Actual Seawater [a] (mg/g sorbent)	Estimated Langmuir Parameters[b]		
		q_{max} (mg/g sorbent)	b (L/mg)	R^2
Diphos-NF Silica	1.17	128	1.9	0.998
3,4 HOPO-NP Silica	3.15	69	8.5	0.997
PropPhos-NP Silica	1.08	68	4.9	0.997
NF Silica	1.37	30	14.3	0.998
SAX Resin	0.26	38	2.1	0.993
SCX Resin	0.07	14	1.5	0.983
Activated Carbon	0.25	1.4	70.2	0.981

[a] The estimated capacity was calculated using linear Langmuir equation and based on, due to large volume of seawater, equilibrium concentration of uranium in actual seawater is insignificantly changed from 3.3 ppb

[b] Sorption isotherm of uranium on functionalized sorbents in seawater (final pH~ 6.6-7.0), L/S of 10000 mL/g

4. Applications of nanostructured sorbents to uranium collection in seawater

The small uniform particle sizes of the NF silica are ideal for the dispersion of polymeric that can be used to create composite thin films. Typical particle size images and thin film morphology are provided in Figure SI 1.

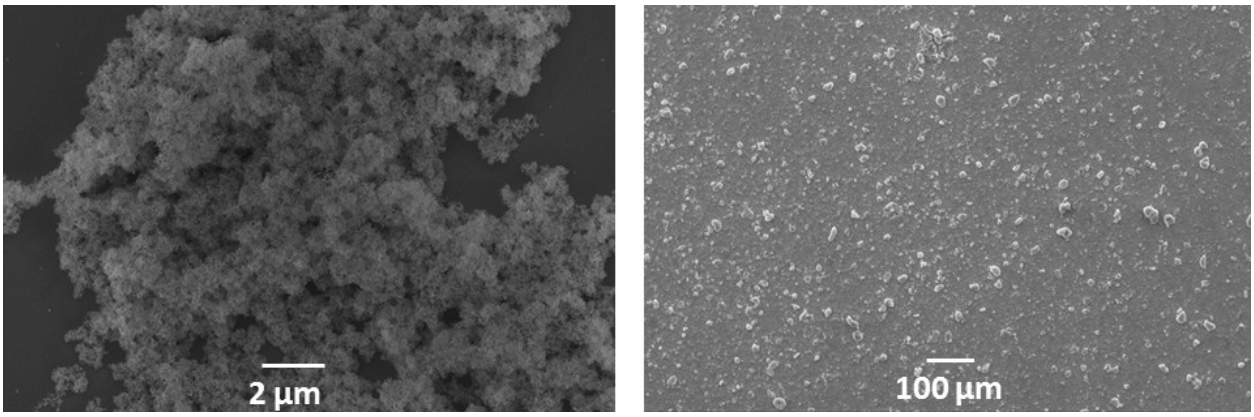

Figure SI 1 Particle size image of Cabosil® EH 5, NF silica (Left) and thin film surface and morphology of NF silica Nafion composite thin film (right). NF silica was loaded at 54%(wt/wt) in the thin films.

5. Thin film capture of uranium from seawater as a function of time

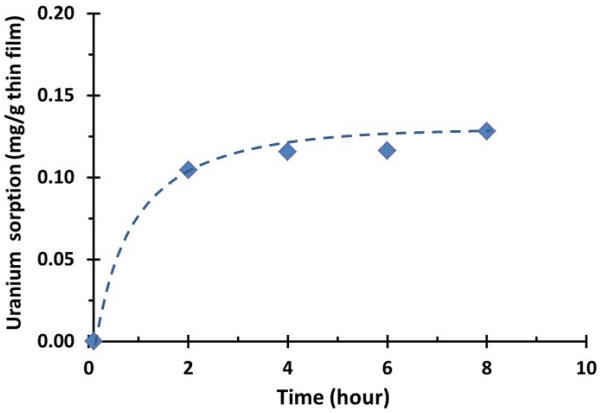

Figure S2 The performance of a 25 µm thick thin film (54% (wt) Diphos-NF silica with Nafion polymer binder) in contact with 200 mL gentle stirred seawater as function of time.