Supplementary Information

Dual Crosslinked Polyamidoxime/Alginate Sponge for Robust and Efficient Uranium Adsorption from Aqueous Solution

Caina Han,[a, b ‡] Yaru Yue,[a, b, ‡] Xin Xu,[b] Dong Cai,[b] Zhongjie Liu,[b] Shuaifeng Chen,[b] Lijie Luo,[b] Juanxiu Xiao,[* b] and Dong Wang[* a, b]

a. School of Biomedical Engineering, Hainan University, Haikou, 570228, China

b. State Key Laboratory of Marine Resource Utilization in South China Sea, School of Materials Science and Engineering, Hainan University, Haikou, 570228, China

* Corresponding authors.

Email: xiaojuanxiu@hainanu.edu.cn; wangdong@hainanu.edu.cn

‡ These two authors contributed equally to this work.

S1. Experimental

S1.1 Preparation of PAO aqueous solution

PAO was obtained by amidoximation of polyacrylonitrile (PAN) with hydroxylamine in dimethyl formamide (DMF) solvent, which was reported in our previous study (*Advanced Energy Materials 8.33 (2018): 1802607*). After reaction, the PAO/DMF solution was slowly poured into 1 L of deionized (DI) water with intense stirring. PAO was flocculated and collected by filtration and freeze-drying. Then, PAO powder was added to 0.2 M NaOH solution and dissolved completely with magnetic stirring at 80 ℃ for 30 min to obtain 50 mg·mL^{-1} PAO alkali solution.

S1.2 Preparation of PAO/Alg sponge

0.5 g sodium alginate was added to 39.5 mL of DI water and stirred for 6 h to dissolve completely. 10 mL of 50 mg·mL^{-1} PAO alkali solution was mixed with 40 mL of Alg solution (12.5 mg·mL^{-1}) by magnetic stirring for 1 h to obtain homogeneous PAO/Alg (1:1) mixture solution. The mixed solution was degassed in vacuum for 10 min, and frozen in -20 ℃ refrigerator for at least 12 h, then dried in lyophilizer to obtain PAO/Alg sponge.

S1.3 Dual crosslinking of PAO/Alg sponge

Ionic crosslinking: The freeze-dried PAO/Alg sponge was soaked in 5wt% calcium chloride solution for in-situ crosslinking of alginate with Ca^{2+}. After 30 min, the sponge was taken out and washed with DI water. Covalent crosslinking: The sponge was immersed in 2wt% 1-ethyl-3-(-3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) solution. After 3 h, the sponge was taken out and immersed in a

mixed solution of 2% N-hydroxysuccinimide (NHS) and 1% adipic acid dihydrazide (AAD) for covalent crosslinking of carboxyl in alginate with AAD and at the same time with part of amino in amidoxime of PAO molecule. The dual crosslinked PAO/Alg sponge can be used directly for uranium adsorption after rinsing with deionized water for several times.

S1.4 Uranium adsorption tests

The natural seawater was collected from coastal water near the Boundary Island of South China Sea (18° 34' 44.30" North, 110° 11' 40.45" East), and filtered with 0.22-μm microfiltration membrane systems to remove sands and other impurities. A batch of circulation flow systems were developed and used for adsorption test (*Advanced Energy Materials 8.33 (2018): 1802607*). For each sample, 15 mg crosslinked PAO/Alg sponge was fixed and contacted with 5 L of uranium (8 ppm) spiked seawater (8 ppm for adsorption kinetics study; 4, 8, 16, 32, 64 and 128 ppm for adsorption isotherm study). The uranium concentration at certain time points was determined by spectroscopic method with arsenazo-III as a chromogenic reagent (*Journal of Materials Chemistry A 6.48 (2018): 24676-24685*).

S1.5 Preparation of 100× coexisting ions spiked seawater and the competitive adsorption test.

The 100× coexisting ions spiked seawater used for competitive adsorption study was prepared by the addition of proper amount of corresponding inorganic salt into natural seawater. The concentration of common co-existing ions such as U, V, Fe, Co, Ni, Cu, Zn, Pb, Ca and Mg in natural seawater were cited from *(Xie, et al., J. Mater.*

Chem. A, 2015, 3, 2552–2558) and listed in the Table S3. In order to create the coexisting ions spiked seawater with 100 times of concentrations of these interference ions in real seawater, firstly, various stock solution of these metal ion solution with 1000 ppm (1 mg/mL) concentration of metal element were prepared, respectively, by dissolving accurate amount of $UO_2((NO_3)_2 \cdot 6H_2O$, NH_4VO_3, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$ in deionized water completely. Then 3.3 mL of UO_2^{2+} stock solution, 2.0 mL of VO_3^- stock solution, 1.5 mL of Fe^{3+} stock solution, 50 μL of Co^{2+} stock solution, 1.0 mL of Ni^{2+} stock solution, 0.6 mL of Cu^{2+} stock solution, 4.0 mL of Zn^{2+} stock solution and 30 μL of Pb^{2+} stock solution was added to natural seawater, respectively, to get 10 L of 100× coexisting ions spiked seawater. It should be noted that since the concentration of Na^+, Mg^{2+}, Ca^{2+} ions in natural seawater is very high already (~10^6 ppb level), these three elements were not added additionally any more but only kept their natural concentration in seawater. The prepared 100×coexisting ions spiked seawater was further tested by ICP-MS/OES to get the accurate concentration before being used for competitive adsorption study, the results were listed in Table S3.

Competitive adsorption: 15 mg of PAO/Alg sponge was contacted with 10 L of 100× coexisting ions spiked seawater which was circulated by a submersible pump, the flow rate was adjusted to around 2.5 L/min. After adsorption for 24 h, the PAO/Alg sponge was taken out, rinsed with DI water several times with gentle shaking, then dried in vacuum oven for 24 h. The content of adsorbed metal elements in PAO/Alg sponge was analyzed by ICP-MS after microwave digestion.

S2. Equations

The **pseudo-second-order kinetic model** is given as Equation S1.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e}$$

(Eq. S1)

Where t (min) is the contact time, qt (mg·g-1) is the adsorption quantity at the time point of t, qe (mg·g-1) is the adsorption quantity at the equilibrium, and k2 is the adsorption rate constant (g·mg-1·min-1).

The **pseudo-first-order kinetic model** is given as Equation S2.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t$$

(Eq. S2)

where q_t (mg/g) and q_e (mg/g) are the amounts of adsorbed uranium at the contact and equilibrium times, respectively, t is the contact time (min), k_1 is the rate constant (min^{-1}).

The **Langmuir isotherm model** is shown in Equation S3.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_1 q_m}$$

(Eq. S3)

Where q_e is the quantity of adsorbed uranium at equilibrium (mg·g-1), C_e is the uranium concentration at equilibrium (mg·L-1), q_m is the maximum or saturated uranium adsorption capacity (mg·g-1) and k_1 is the equilibrium constant related to the binding strength $(L·mg^{-1})$.

The **Freundlich isotherm model** is shown in Equation S4.

$$lg q_e = lg k + \frac{1}{n} lg C_e$$

(Eq. S4)

where q_e is the amount of adsorbed uranium at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), the constant k is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process.

Table S1. Adsorption kinetic fitting parameters of PAO/Alg sponge in 5 L of uranium spiked seawater.

Initial Con. of U	pseudo-second order model			pseudo-first order model		
	R^2	q_e, cal (mg/g)	k_2 (mg/g/min)	R^2	q_e, cal (mg/g)	k_1 (mg/g/min)
8ppm	0.995	713.83	4.94×10^{-4}	0.935	595.7	3.19×10^{-1}

Table S2. Parameters of Langmuir and Freundlich isotherm model fitting.

Isotherm model	Langmuir model			Freundlich model		
	R^2	b (L/mg)	q_m (mg/g)	R^2	n	k (mg/g)
Value	0.993	0.015	718.38	0.604	6.488	369.49

Table S3. Coexisting metal ions concentration in natural seawater and the 100×Seawater used for selectivity test in this study.

Element	Con. in natural SW/ppb	Con. in 100×SW (calculated)/ppb	Con. in 100×SW (tested by ICP-MS/OES)/ppb	Ions
U	3.3-3.9	330	326.5	$UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$ etc.
V	1.5-2.5	200	194.6	VO_3^-, $VO_2(OH)_3^{2-}$, etc.
Fe	1.0-2.0	150	158.0	Fe^{3+}
Co	0.05	5.0	4.95	Co^{2+}
Ni	1	100	103.5	Ni^{2+}
Cu	0.6	60	61.5	Cu^{2+}

Zn	4.0	400	409.0	Zn^{2+}
Pb	0.03	3.0	5.5	Pb^{2+}
Mg	1.3×10^6	1.3×10^6	1.36×10^6	Mg^{2+}
Ca	0.4×10^6	0.4×10^6	0.43×10^6	Ca^{2+}
Na	10.8×10^6	10.8×10^6	10.78×10^6	Na^+
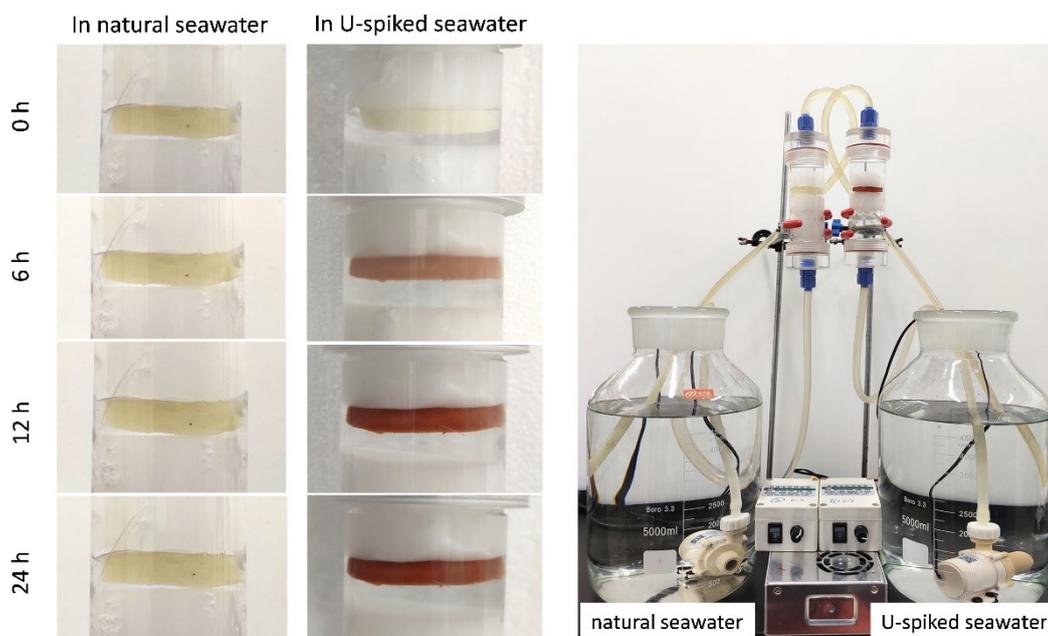
Fig. S1. The color change of PAO/Alg sponge in natural seawater and uranium (8 ppm)-spiked seawater within 24 h (Left), and the whole set of water circulation adsorption test platform (Right).
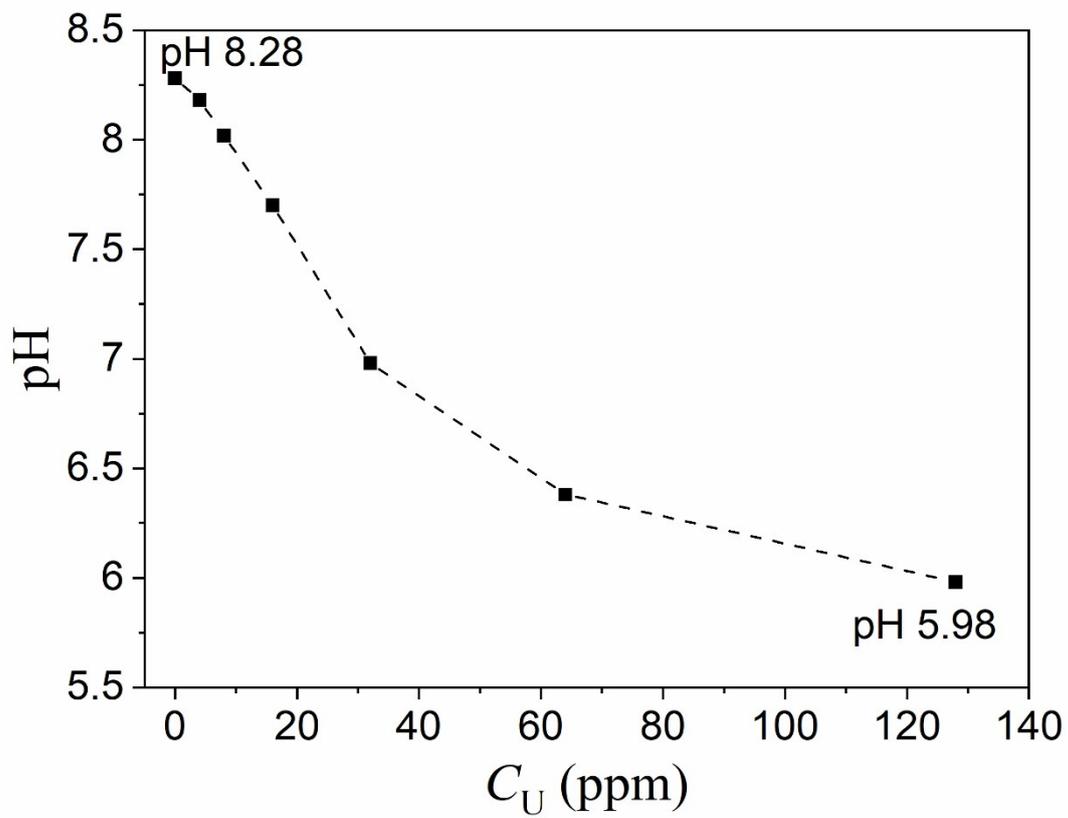
Fig. S2. The pH value of uranium-spiked seawater with different concentration of

uranium from 4 ppm to 128 ppm for the adsorption isotherms studies.
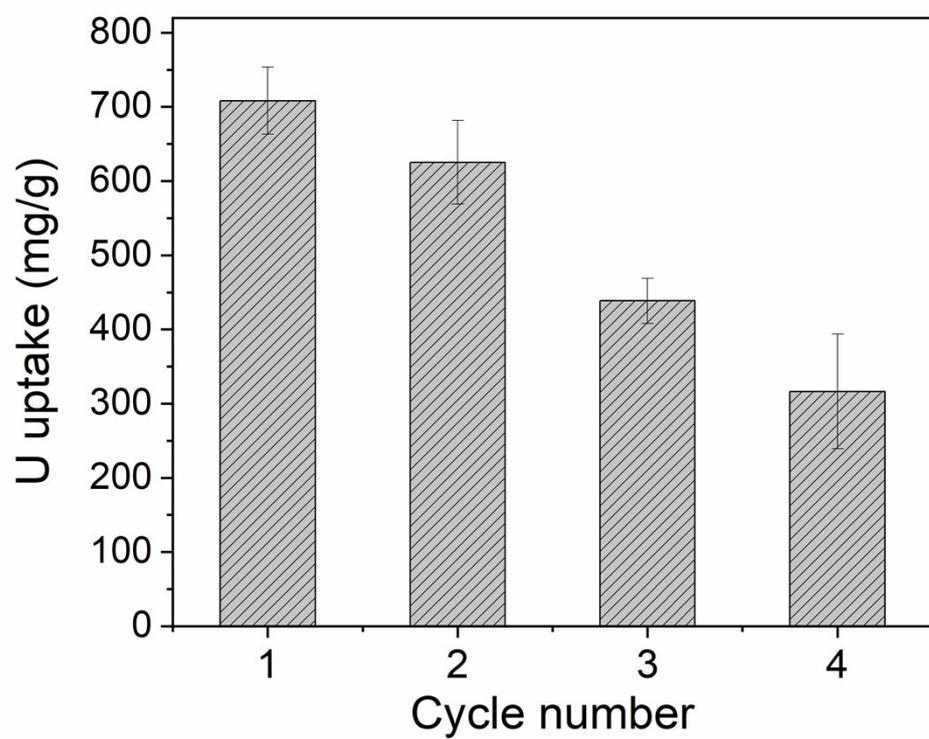
Fig. S3. Uranium adsorption performance in four successive adsorption–desorption

cycles.