Electronic Supplementary Information for

Ion cross-linking assisted synthesis ZIF-8/chitosan/melamine sponge with anti-biofouling activity for enhanced uranium recovery

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SI Experimental section

SI.1 Materials

Zinc nitrate hexahydrate, glutaraldehyde and methanol were obtained from Tianjin Guangfu Fine Chemical Co., Ltd., China. Chitosan and 2-methylimidazole (HMeIM) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. The marine algae (*Nitzschia*) were obtained from the Center for Collections of Marine Algae (CCMA).

SI.2 Synthesis of ZIF-8 nanoparticles

The 24 mL of methanol solution containing $Zn(NO_3)_2 \cdot 6H_2O$ (2.5 mmol) was added into 40 mL of 2-methylimidazole (20 mmol) methanol solution, followed by stirring at 25 °C for 4 h. Then, the white precipitate was obtained by high-speed centrifugal separation and washed with methanol three times, and dried at 60 °C for 24 h. The obtained product was ZIF-8 (Z8) nanoparticles as the control sample.

SI.3 Instrumentation

The morphology and structure of the sponges and pure ZIF-8 nanoparticles were characterized by a field emission scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscope (TEM, JEOL, JEM-2010), respectively. The X-ray diffraction (XRD) patterns were taken in a Rigaku D/max-IIIB diffractometer (Tokyo) using nickel-filtered Cu K_α radiation at 40 kV, 150 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5700 ESCA spectrometer with Al KR radiation (h_v= 1486.6 eV). Fourier-transform infrared (FTIR) spectra were recorded to analyze the surface characteristics of the materials by an Avater 370 FTIR spectrophotometer in the 500-4000 cm^{-1} region. Nitrogen adsorption isotherm was measured at 77 K using Quantachrome NOVAtouchTM. Degassing of the sample was performed at 393.15K for 4 h before adsorption measurements. The algae cell concentration was observed via an optical microscope (Leica DML 300B,

Germany) and fluorescence microscope (Nikon Ci-L 710375). The Zeta potential test was using Zetasizer NanoPlus. The concentration of U(VI) at mg/L or μg/L level was determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy ((ICP-AES, Optima-7000 DV) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Bruker 820-MS).

SI.4 Anti-biofouling assays

The common diatoms, *Nitzschia*, were selected as the fouling bio-template to confirm the antifouling properties of Z8, MS, CMZn and CMZ8 sponges. The *Nitzschia* cells were obtained from the Center for Collections of Marine Algae of Xiamen University, (Pearl River Estuary, China) and cultured in artificial seawater-based culture media with a 12:12 h light: dark (L/D) cycle of fluorescent illumination (2000 lux), followed by stirring twice daily at 21±2°C. The products were sterilized for 2 h by ultraviolet irradiation. When the number of cells is 10^5 cells/mL, 10 mg of products and 50 mL of cell suspension were co-cultured for defined time periods in a biochemical incubator. The *Nitzschia* cell concentration was counted on a cell count chamber hemocytometer. All of the experiments were performed in triplicate.

SI.5 Batch adsorption experiments

The actual adsorption properties of Z8, MS, CMZn and CMZ8 sponges were determined by a series of batch experiments. The stock solution of uranium was prepared with different pHs by adjusting (0.1 M HNO_3 and Na_2CO_3). 10 mg of the obtained samples were put into 50 mL of $UO_2(NO_3)_2 \cdot 6H_2O$ solution ($C_{U\text{-}initial}$= 50 mg/L) with different pH and vibrated at 25°C for 12 h. The adsorbents were separated and the residual U(VI) concentration in solutions were tested via ICP-AES. The adsorption amount (q_e) and removal rate (R) of U (VI) can be expressed by the following:

$$q_e = (C_0 - C_e)V/m \quad \text{（S1）}$$

$$R=[(C_0-C_e)/C_0]\times 100\% \quad \text{（S2）}$$

Where q_e（mg/g）is the saturated adsorption capacity of the samples; C_0（mg/L）is the initial concentration of U (VI) in the solution; C_e（mg/L）is the concentration of U (VI) in the supernatant after adsorption equilibrium.

SI.6 Effect of contact time and kinetics study on the U (VI) adsorption of Z8 and CMZ8 sponge

The following pseudo-first-order, pseudo-second-order and Weber-Morris (W-M) models are employed to interpret the mechanism controlling the sorption process (m=10 mg; V=50 mL; pH=8.0; T=298 K; $C_{U\text{-}initial}$= 50 mg/L). The linear form of the three models can be expressed by the following:

$$q_e(mg\ g^{-1}) = (C_o - C_e) \cdot \frac{V}{m} \quad \text{(S3)}$$

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad \text{(S4)}$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad \text{(S5)}$$

$$q_e = K_{ip}\sqrt{t} + C \quad \text{(S6)}$$

Where C_o and C_e (mg L^{-1}) are the initial and equilibrium concentrations of U (VI) ions, V (L) is the volume of the solution and m is the weight of sorbent (g), q_t and q_e (mg g^{-1}) are the capacity of U (VI) at time t (min) and at equilibrium, K_{ip} is internal diffusion constant, respectively, and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the respective rate constants.

SI.7 The adsorption isotherms study on the U (VI) adsorption of Z8 and CMZ8 sponge

The adsorption isotherms were also tested with different initial concentration of U (VI) (m=10 mg; V=50 mL; pH=8.0; T=298 K; t= 3 h; $C_{U\text{-}initial}$=5-200 mg/L). Then, the Langmuir, Freundlich and Dubinin-Radushkevich models were applied to simulate experimental data. The linear form of the three models can be expressed by the following:

$$C_e/q_e = 1/b \cdot q_m + C_e/q_m \quad \text{(S7)}$$

$$\ln q_e = \ln k + 1/n \ln C_e \quad \text{(S8)}$$

$$\ln q_e = ln\, q_m - \beta\varepsilon^2 \quad \text{(S9)}$$

$$\varepsilon = RTln\,(1 + {}^1/C_e) \quad \text{(S10)}$$

Where C_e (mg L^{-1}) is the equilibrated U (VI) concentration; q_e (mg g^{-1}) is the amount of U (VI) adsorbed on the capacity of the adsorbent at equilibrium; b (L mg^{-1}) is a Langmuir constant and K is a Freundlich constant; q_m (mg g^{-1}) is the saturation capacity at complete monolayer coverage; β is the activity coefficient and ε is the Polanyi potential.

SI.8 Adsorption cycle experiments of CMZ8 sponge

Typically, 10 mg of CMZ8 sponge were added into 50 mL of $UO_2(NO_3)_2 \cdot 6H_2O$ solution ($C_{U\text{-}initial}$= 50 mg/L, pH=8.0) and vibrated at 25°C for 3 h. The CMZ8-U were separated and washed with deionized water for three times; moreover, we collected the supernatant to test by ICP-AES to obtain the concentrations of U (VI). Then, CMZ8-U was added into different desorbents (20 mL, 0.25 mol/L), followed by shaking at 25°C for 6 h. The supernatants were further analysed to obtain the concentrations of U (VI). Afterwards, CMZ8-U was added into 20 mL of EDTA with different concentration, followed by shaking at 25°C for 6 h. The adsorbent is separated from the liquid and the supernatants were analysed to obtain the concentrations of U (VI). The eluent efficiency is calculated by the following formula:

$$C_{ad} = C_0 - C_e \quad \text{（S11）}$$

$$D = C_{de}/C_{ad} \times 100\% \quad \text{（S12）}$$

Where D is the eluent efficiency, C_{ad} and C_{de} are the U (VI) concentration (mg/L) in the solution after adsorption and desorption, respectively.

Next, the best concentration was selected to carry out the cyclic adsorption-desorption experiment. The adsorbent was washed by deionized water three

times before the next cycle adsorption experiment. The adsorbent was named as CMZ8-Dx (x is the cycles). Repeat this experiment operation for five times.

SI.9 Adsorption tests in natural seawater

We conducted a series of batch experiments in the seawater (Bohai Sea, China) to further evaluated the practical adsorption ability of CMZ8 sponge (m = 0.01 g, V = 50 mL, T = 298.15 K, t = 12 h). The content of adsorbed metal elements was analyzed to determine the competitive adsorption behavior by ICP-MS. Moreover, extra uranium (10-200 μg/L) was added into natural seawater as radioactive contaminated seawater.

SII. Characterization of CMZ8 sponge

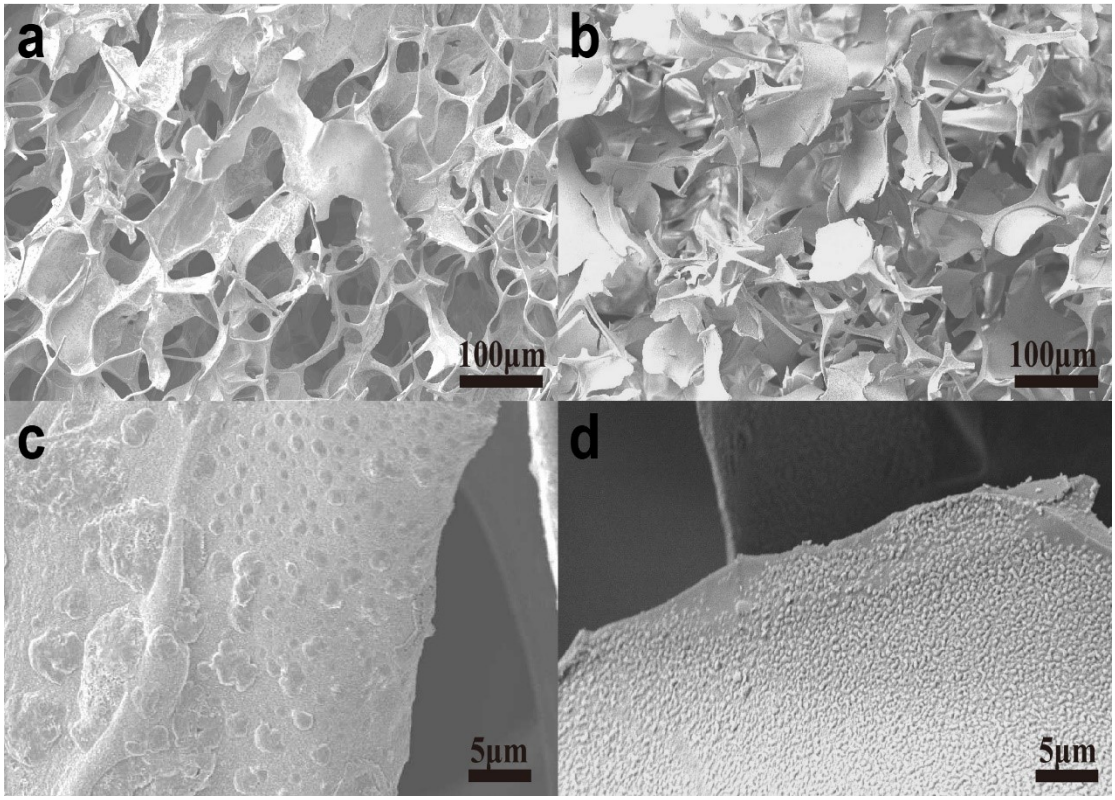

Figure S1 The SEM images of CMZ8-2 (a, c) and CMZ8-6 sponges (b, d)

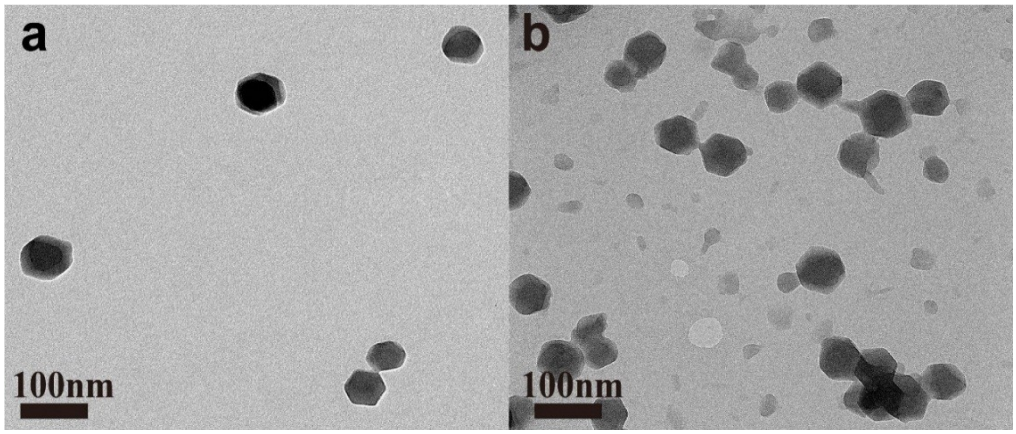

Figure S2 The TEM images of Z8 (a) and CMZ8 sponge (b)

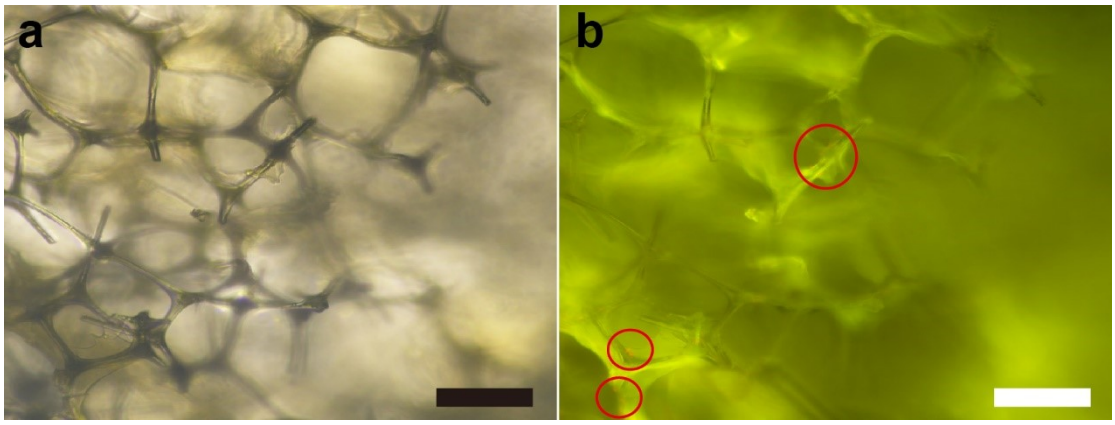

Figure S3 The natural light (a) and fluorescence (b) images of CMZ8 sponge after 7 days

(all scale bars are 100 μm)

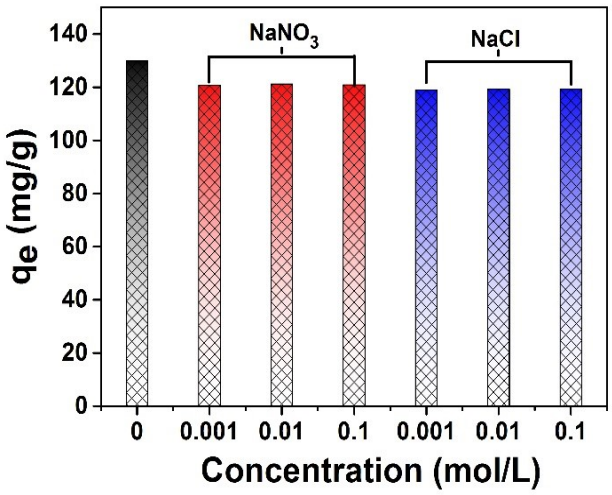

Figure S4 The adsorption amounts of CMZ8 sponges in uranium-containing aqueous solution with different ionic strength (T = 298 K, m = 0.01 g, V = 50 mL, C_0 = 50 mg/L, pH = 8.0)

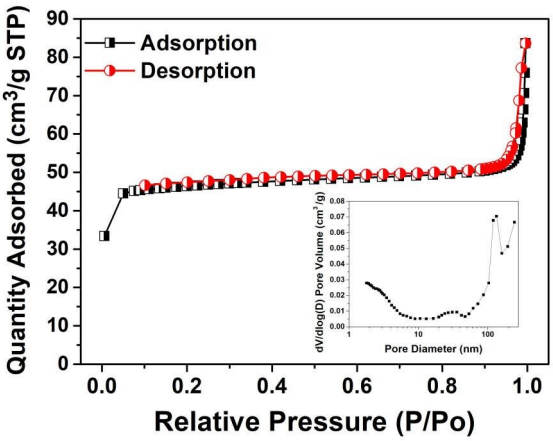

Figure S5 N_2 adsorption-desorption isotherms curve of CMZ8 sponge (insert is pore size distribution curve)

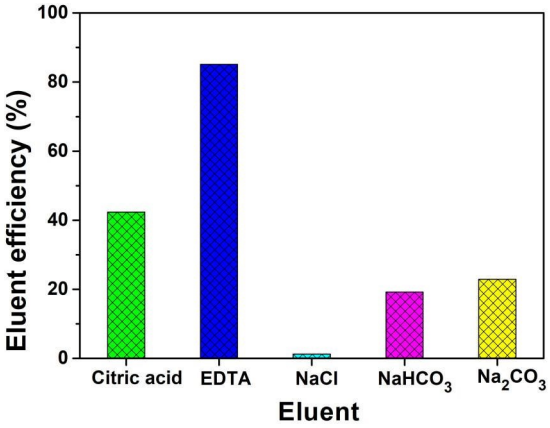

Figure S6 The eluent efficiency of CMZ8 sponge with different desorbents

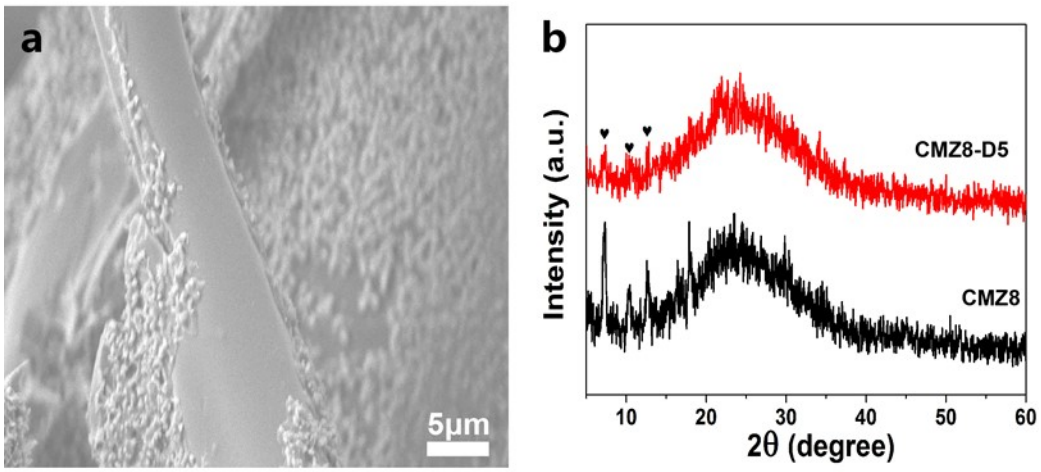

Figure S7 The SEM image of CMZ8-D5 (a); the XRD patterns of CMZ8 and CMZ8-D5 (b)

Table S1 Kinetic parameter for U (VI) adsorption

Materials	q_e（mg/g）（exp）	Pseudo-first-order			Pseudo-second-order		
		q_e（mg/g）（cal）	k_1（min^{-1}）	R^2	q_e（mg/g）（cal）	k_2（min^{-1}）	R^2
Z8	95.35	36.49	0.01172	0.809	97.28	0.00081	0.999
CMZ8	130.27	62.21	0.01706	0.921	136.24	0.00054	0.999

Table S2 Isotherm parameter for adsorption of U (VI)

Materials	Freundlich			Langmuir			D-R
	n	K ($L\ g^{-1}$)	R^2	q_m ($mg\ g^{-1}$)	b ($L\ mg^{-1}$)	R^2	R^2
Z8	1.74	12.55	0.979	180.51	0.04	0.997	0.634
CMZ8	1.77	19.59	0.991	299.40	0.04	0.977	0.579

Table S3 Comparison on the U(VI)-uptake capacity of the CMZ8 with other materials

Adsorbents	Adsorption Capacity mg-U/g-adsorbent	Conditions	Ref.
Cross-linked chitosan	72.46	pH=3.0	1
Activated carbon	28.3	pH=3.0	2
Fe_3O_4@ZIF-8	523.5	pH=3.0	3
in situ ZIF-8/PAN	530.3	pH=3.0	4
PPy@ZIF-8	534	pH=3.5	5
MIL-101(Cr)	27.99	pH=4.0	6
Fe_3O_4@AMCA-MIL53(Al)	227.3	pH=6.0	7
guanidine-modified polyamidoxime-functionalized fabric	112.0	pH=8.0	8
Wool-AO@TiO_2	113.12	pH=8.0	9
CMZ8 sponge	299.4	pH=8.0	**This paper**

References

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