

Electronic Supplementary Information for

Interfacial growth of metal organic framework (UiO-66) on the functionalization of graphene oxide (GO) as a suitable seawater adsorbent for extraction of uranium(VI)

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SI.1 Characterization of GO, GO-COOH, UiO-66 and GO-COOH/UiO-66 composites

Table S1. The table compares the atomic percentage of the element consisting in GO, GO-COOH, UiO-66 and

GO-COOH/UiO-66

Element	GO	GO-COOH	UiO-66	GO-COOH/UiO-66
	Atom %	Atom %	Atom %	Atom %
C	62.7	60.2	47.8	49.1
O	37.3	39.8	38.7	39.1
Zr			13.5	11.8
Total	100	100	100	100

SI.2 Effect of contact time and kinetics study on the adsorption of U(VI) on UiO-66 and GO-COOH/UiO-66 composites

As the sorption kinetics govern the residence time of the sorption reaction and determine the solute uptake rate or the efficiency of the reaction, the following pseudo-first-order, pseudo-second-order and Weber-Morris (W-M) models are employed to interpret the mechanism controlling the sorption process. The linear form of the two models can be expressed by the following Eqs. S1-S3:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{S1})$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (\text{S2})$$

$$q_e = K_{ip} \sqrt{t} + C \quad (\text{S3})$$

Where 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 ($\text{g mg}^{-1} \text{min}^{-1}$) are the respective rate constants.

Table S2 Kinetic parameter for adsorption of U(VI)

Kinetics model	T/ K	Materials	K	q_e^{exp}	q_e^{cal}	R^2
Pseudo-first order	298	UiO-66	0.01675	839	581	0.89156
		GO-COOH/UiO-66	3.3×10^{-5}	1002	910	0.98565
Pseudo-second order	298	UiO-66	0.01193	839	900	0.99357

In order to probe the maximum adsorption capacity and the progress of adsorption, the adsorption isotherms were studied. The adsorption of U(VI) on the UiO-66 and GO-COOH/UiO-66 composites increased with increasing temperature and the Langmuir and Freundlich models were applied to simulate experimental data.

$$C_e/q_e = 1/b \cdot q_m + C_e/q_m \quad (S4)$$

$$\ln q_e = \ln k + 1/n \ln C_e \quad (S5)$$

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 adsorbents capacity at equilibrium. K (L mg⁻¹) is a Langmuir constant related to the energy of the adsorbent and q_m (mg g⁻¹) is the saturation capacity at complete monolayer coverage.

Table S3 Isotherm parameter for adsorption of U(VI)

Materials	T (K)	Langmuir isotherm			Freundlich isotherm		
		q_0 (mg g ⁻¹)	b (L mg ⁻¹)	R^2	K (L mg ⁻¹)	n	R^2
UiO-66	298	1012	0.1823	0.99214	303.481	2.89	0.81628
	308	1096	0.2769	0.99919	373.310	3.29	0.87707
	318	1213	0.3635	0.99481	400.234	3.903	0.90166
GO-COOH/UiO-66	298	1097	0.2489	0.99932	269.04	2.9986	0.83439
	308	1290	0.3664	0.99972	288.885	3.05	0.87132
	318	1336	0.3678	0.99822	344.261	3.659	0.88349

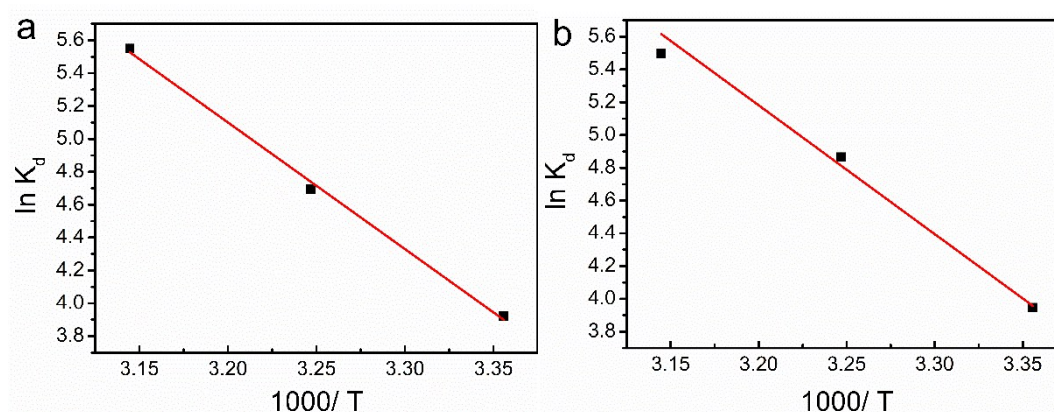


Fig. S1. The influence of temperature on the U(VI) sorption on the UiO-66 (a) and GO-COOH/UiO-66 (b) relationship curve between $\ln K_d$ and $1000/T$ (1000/K). pH= 8.0; T= 25 °C; amount of adsorbent 0.01 g; C_0 = 512.29 mg L⁻¹ and t = 230 min.

Table S4 The thermodynamic parameters of UiO-66 and GO-COOH/ UiO-66 for U(VI) adsorption

material	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
UiO-66	65.33	252.15	298.15K	308.15K	318.15K
			-75.11	-77.63	-80.16
GO-COOH/UiO-66	64.07	247.43	-73.7	-76.12	-78.66

SI.3 Effect of co-existing ions on UiO-66 and GO-COOH/UiO-66 adsorbents

The selectivity coefficient (S_U) for U(VI), is defined as a specific term to describe the potency and degree of selectivity of the adsorbents as follows:

$$S_U = \frac{K_d^U}{K_d^M} \quad (S6)$$

Where K_d^U and K_d^M are the distribution ratio of the U(VI) ion and other competing ions in sorbent and solution, respectively

Table S5 The selectivity coefficients ($S_{U/M}$) of U(VI) for different metal ions in water.

	Ca	Al	Ba	Na	Mg	Mn
UiO-66 $S_{U/M}$	1477	347	904	354	762	800
GO-COOH/UiO-66 $S_{U/M}$	2072	5378	1442	1366	1522	15843

	Sr	Ni	Pb	Zn	K	Cu	Fe
UiO-66 $S_{U/M}$	1127	1179	624	638	446	336	96
GO-COOH/UiO-66 $S_{U/M}$	2835	4276	734	1422	501	534	113

SI.4 adsorption-desorption experiments of GO-COOH/UiO-66 adsorbents

SI.4.1 U(VI) desorption experiments

In a typical experiment, 20 mg of sorbent with U(VI) ions was added into 50 mL eluent solution, which included in 0.1 M HCl, 0.1 M NaHCO₃, 0.1 M NaOH and H₂O, respectively. The flasks were stirred for specified time (t, min) at room temperature, and then the solid phase was separated from the solution by centrifuge. The results were analysed with WGJ-III Trace Uranium Analyser to obtain the concentrations of U(VI) ions. The elution rate of U(VI) ions was calculated.

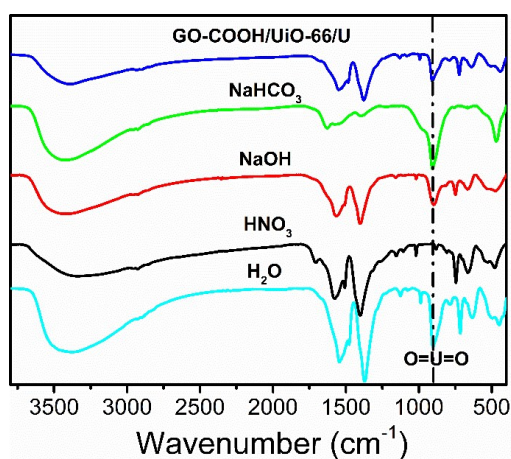


Fig. S2 FTIR spectroscopy of different eluent agent for GO-COOH/UiO-66 composites.

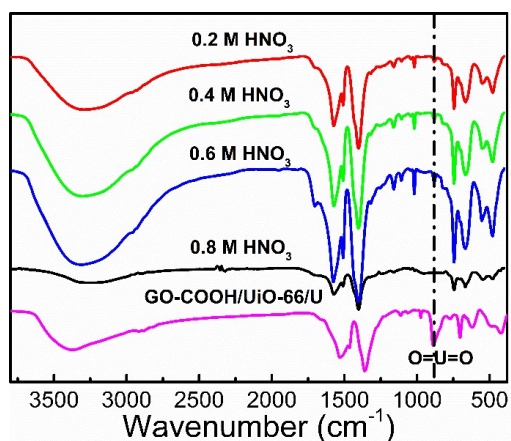


Fig. S3 FTIR spectroscopy of different concentration of HNO_3 .

SI.4.2 U(VI) absorption-desorption cycle experiments

In a typical experiment, 20 mg of sorbent was added into 50 mL of U(VI) solution and stirred for 6 h at room temperature. The solid phase was separated from the solution by centrifuge. Then, the sorbent in the vacuum drying oven for 24 h. The dried sorbent was placed in the 50 mL eluent solution (0.1 M HCl) for the 6 h. After elution, the GO-COOH/Uio-66 composites was washed with abundant deionized water to remove residual H^+ and UO_2^{2+} until cannot detect UO_2^{2+} in the aqueous solutions. The GO-COOH/Uio-66 composites were regenerated by drying at 80 °C for 24 h and then reused. Eventually the elution efficiency of U(VI) ions was calculated. Repeat this experiment operation for five times.

SI.5 The mechanism of absorption onto GO-COOH/Uio-66 composites

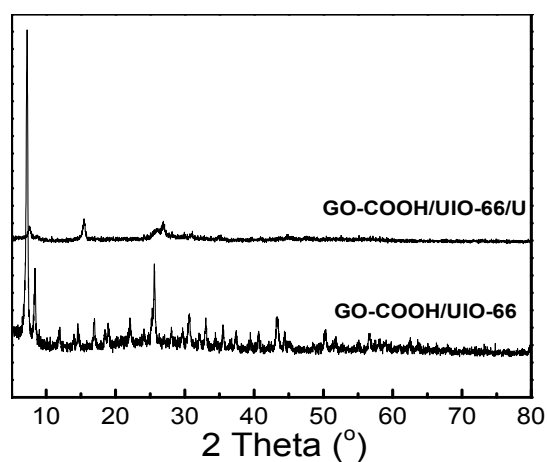


Fig. S4 XRD of after and before for U(VI) onto the GO-COOH/Uio-66 composites.