Electronic Supporting Information

Highly selective adsorption for uranium in strong HNO_3 media achieved on phosphonic acid functionalized nanoporous polymer

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Synthesis of carboxyl functionalized nanoporous polymer adsorbent P1

Nanoporous polymer adsorbent P1 was prepared according to the following steps. In a typical synthesis, 1.5 g ethyleneglycol dimethacrylate (EGDMA) and 1.5 g acrylic acid (AA) were dissolved in 5 mL ethyl acetate, and then 0.05 azobisisobutyronitrile (AIBN) was added. After stirring for 4 h at room temperature, the solution was put in an autoclave with 25 mL of Teflon liner and then treated at 100 ℃ for 24 h. The system was cooled to room temperature and a solid monolith P1 was obtained after the slow evaporation of ethyl acetate.

Synthesis of amide functionalized nanoporous polymer adsorbent P2

Nanoporous polymer adsorbent P2 was prepared according to the following steps. In a typical synthesis, 1.5 g ethyleneglycol dimethacrylate (EGDMA) and 1.5 g acrylamide (AM) were dissolved in 5 mL ethyl acetate, and then 0.05 azobisisobutyronitrile (AIBN) was added. After stirring for 4 h at room temperature, the solution was put in an autoclave with 25 mL of Teflon liner and then treated at 100 ℃ for 24 h. The system was cooled to room temperature and a solid monolith P2 was obtained after the slow evaporation of ethyl acetate.

Synthesis of hydroxyl functionalized nanoporous polymer adsorbent P3

Nanoporous polymer adsorbent P3 was prepared according to the following steps. In a typical synthesis, 1.5 g ethyleneglycol dimethacrylate (EGDMA) and 1.5 g Hydroxyethyl methacrylate (HEMA) were dissolved in 5 mL ethyl acetate, and then 0.05 azobisisobutyronitrile (AIBN) was added. After stirring for 4 h at room temperature, the solution was put in an autoclave with

25 mL of Teflon liner and then treated at 100 ℃ for 24 h. The system was cooled to room temperature and a solid monolith P3 was obtained after the slow evaporation of ethyl acetate.

Synthesis of phosphonic acid functionalized nanoporous polymer adsorbent P4

Nanoporous polymer adsorbent P4 was prepared according to the following steps. In a typical synthesis, 2.0 g ethyleneglycol dimethacrylate (EGDMA) and 1.0 g vinylphosphate (VPA) were dissolved in 5 mL ethyl acetate, and then 0.05 azobisisobutyronitrile (AIBN) was added. After stirring for 4 h at room temperature, the solution was put in an autoclave with 25 mL of Teflon liner and then treated at 100 ℃ for 24 h. The system was cooled to room temperature and a solid monolith P2 was obtained after the slow evaporation of ethyl acetate.

Synthesis of phosphonic acid functionalized nanoporous polymer adsorbent P5

Nanoporous polymer adsorbent P5 was prepared according to the following steps. In a typical synthesis, 1.0 g ethyleneglycol dimethacrylate (EGDMA) and 2.0 g vinylphosphate (VPA) were dissolved in 5 mL ethyl acetate, and then 0.05 azobisisobutyronitrile (AIBN) was added. After stirring for 4 h at room temperature, the solution was put in an autoclave with 25 mL of Teflon liner and then treated at 100 ℃ for 24 h. The system was cooled to room temperature and a solid monolith P4 was obtained after the slow evaporation of ethyl acetate.

Selectivity experiments for P1, P2, P3, P4 and P5

When studying selective adsorption of polymer adsorbent P1, P2, P3, P4 and P5, the concentrations of U(VI) and other metal ions in supernatants were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

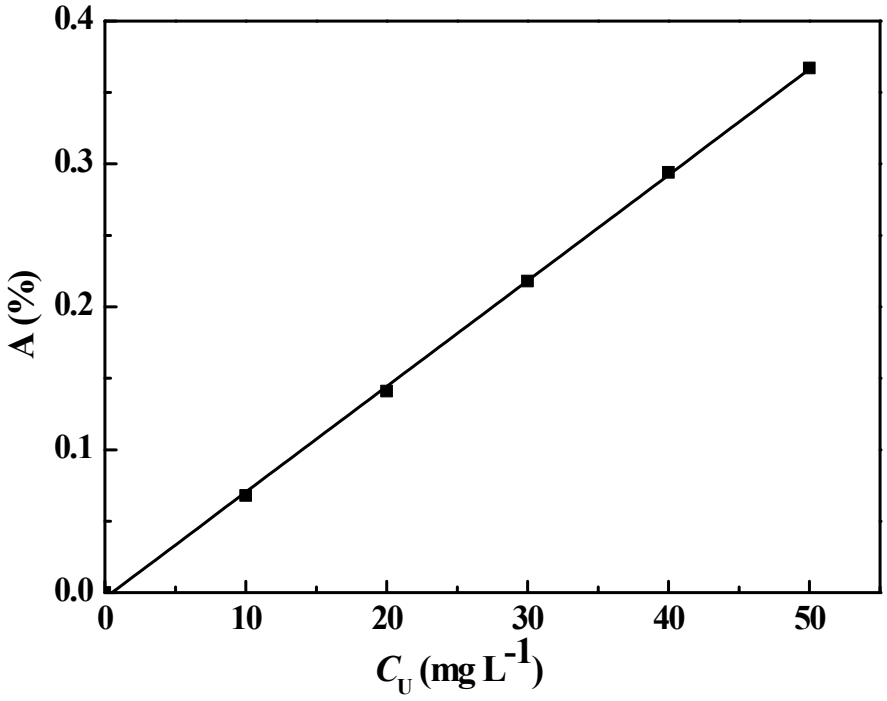

Fig. S1 The calibration curve

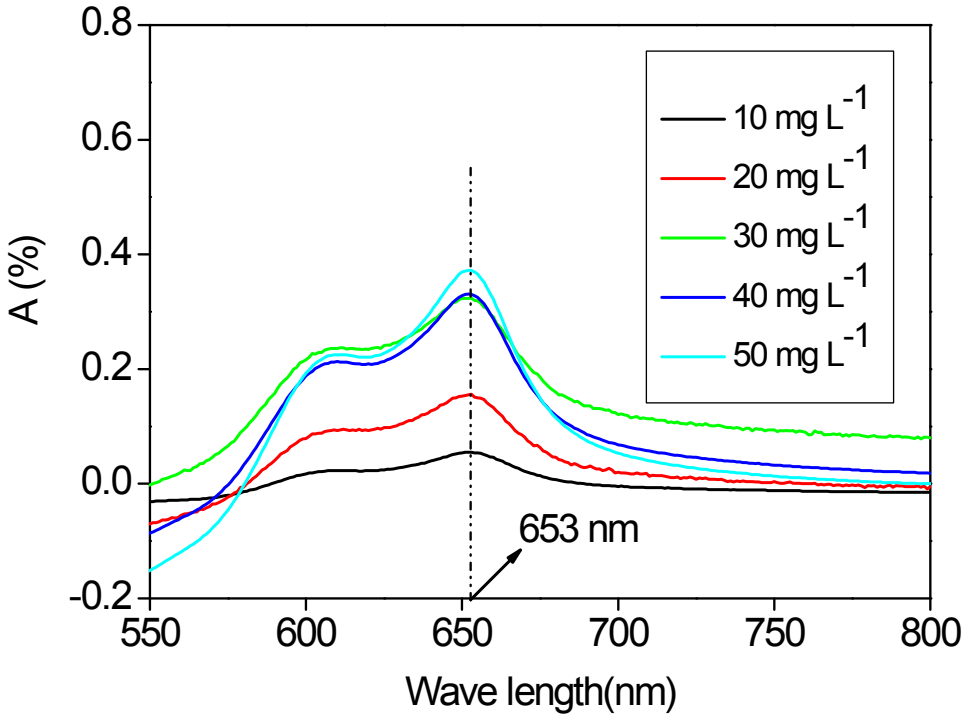

Fig. S2 UV-Vis spectra for standard solutions

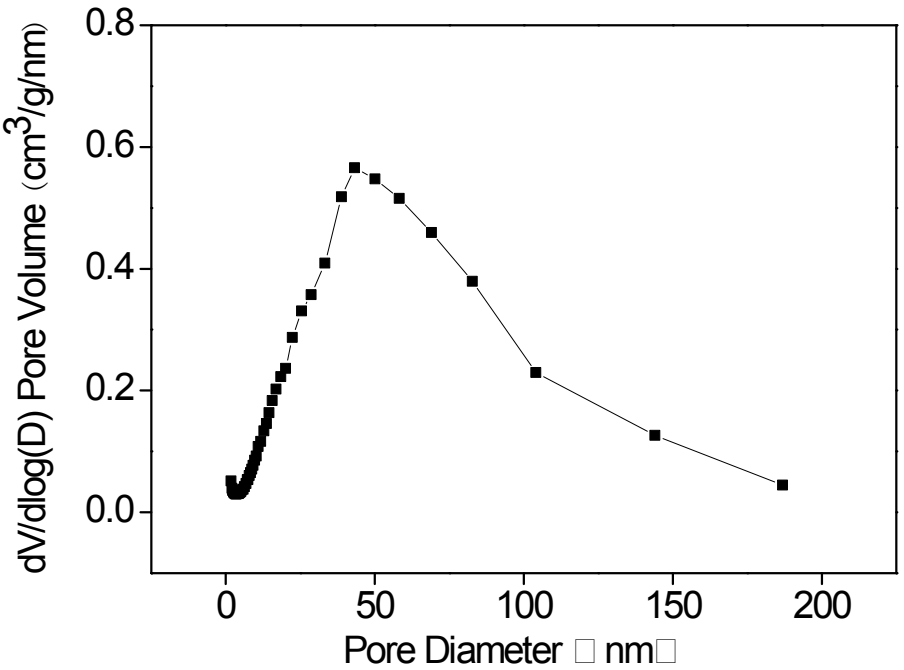

Fig. S3 Pore size distribution of POP-EDVP

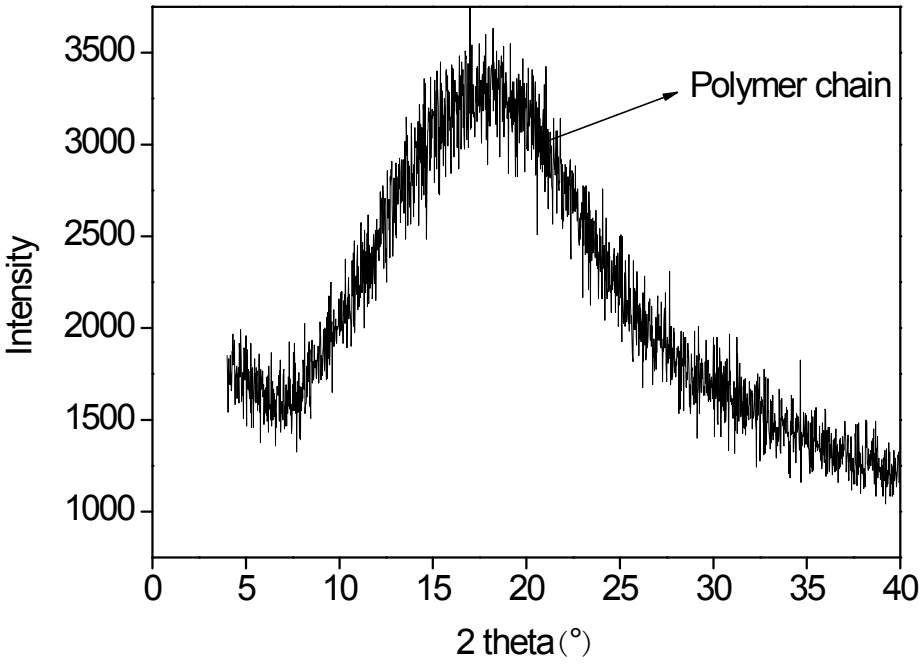

Fig. S4 XRD pattern of POP-EDVP

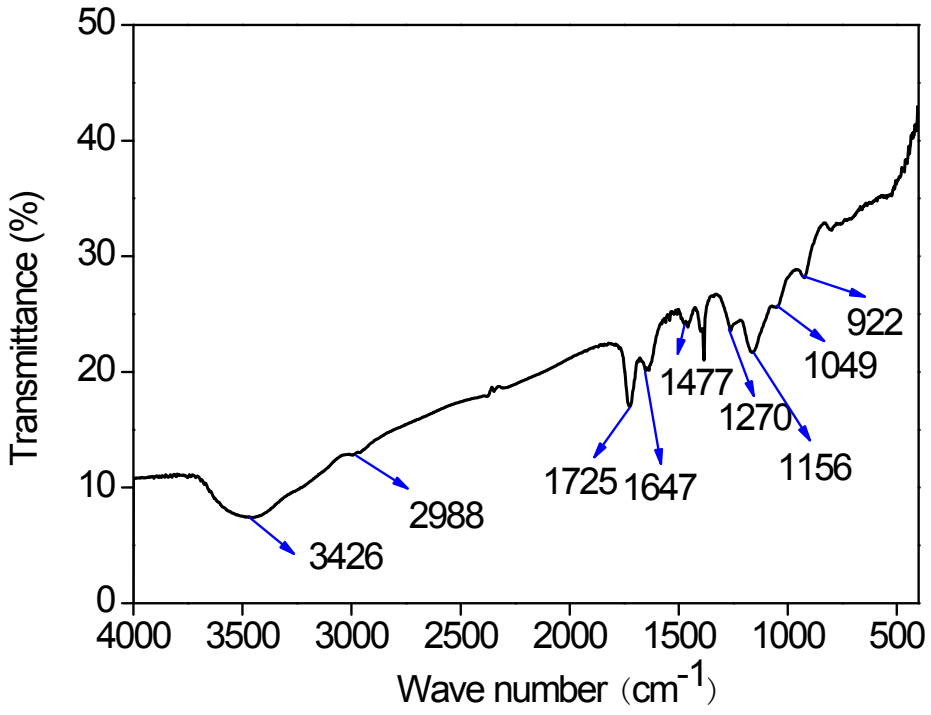

Fig. S5 FTIR spectra of POP-EDVP

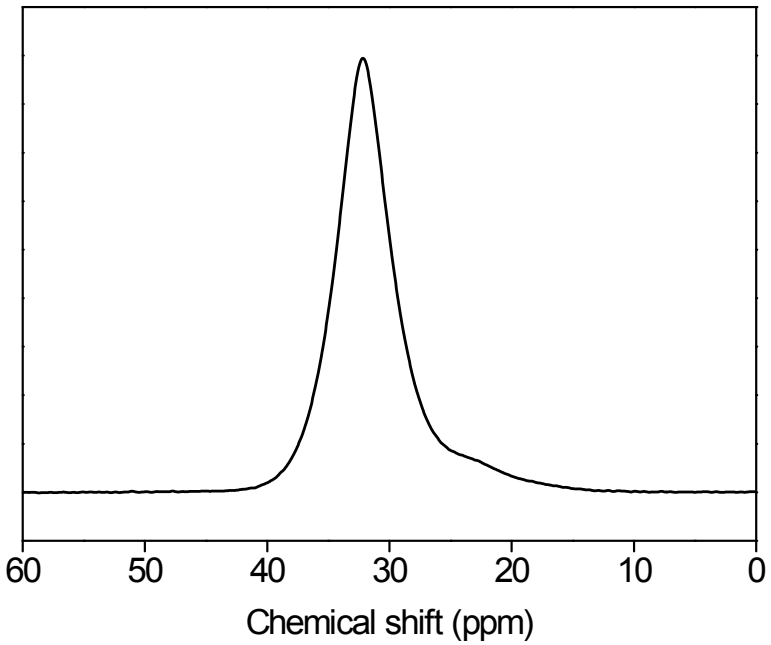

Fig. S6 ^{31}P MAS NMR spectra of POP-EDVP

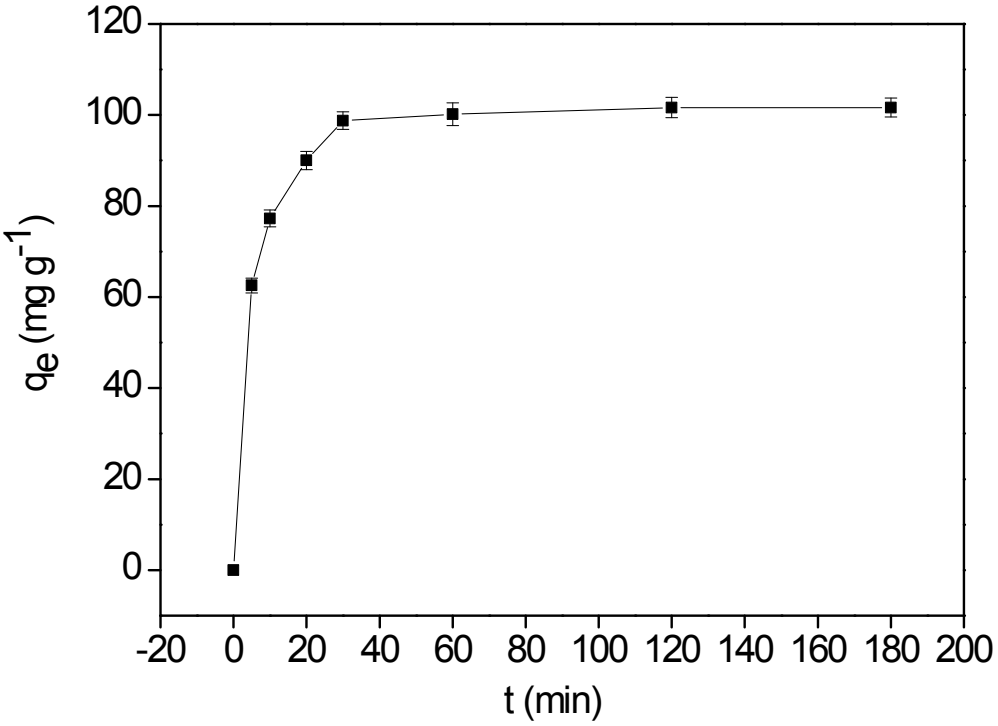

Fig. S7 Effect of contact time for the sorption of uranium onto POP-EDVP (C_0=100 mg L^{-1}, V=25 mL, T=298 K, $c(H^+)$ =4 M, m=10mg)

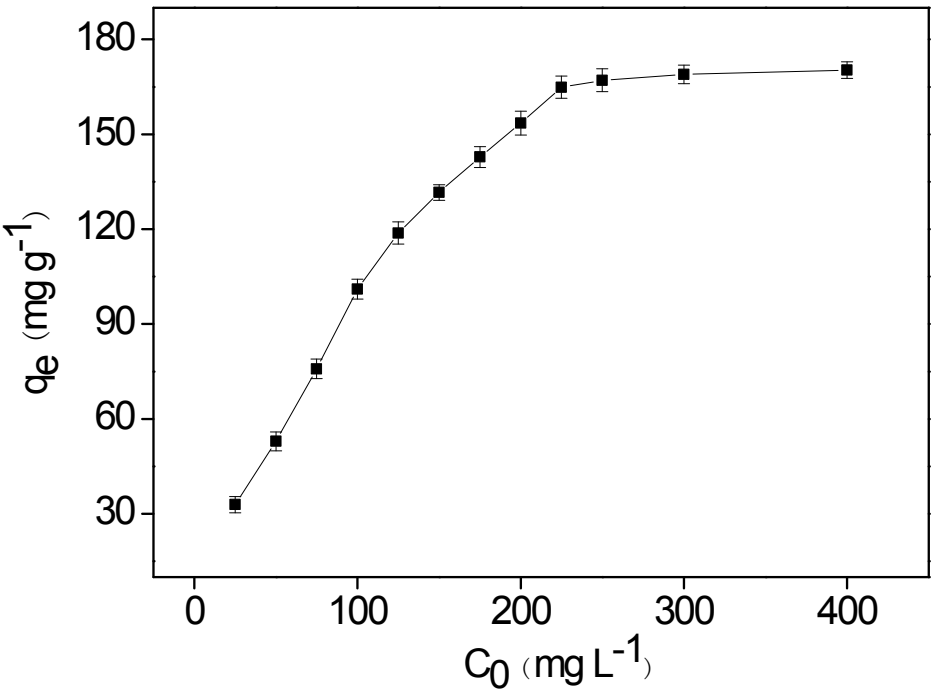

Fig. S8 Effect of initial uranium concentration on the sorption of U(VI) onto POP-EDVP (t = 180 min, c(H+) =4 M, V = 25 mL, T = 298 K, and m = 10 mg)

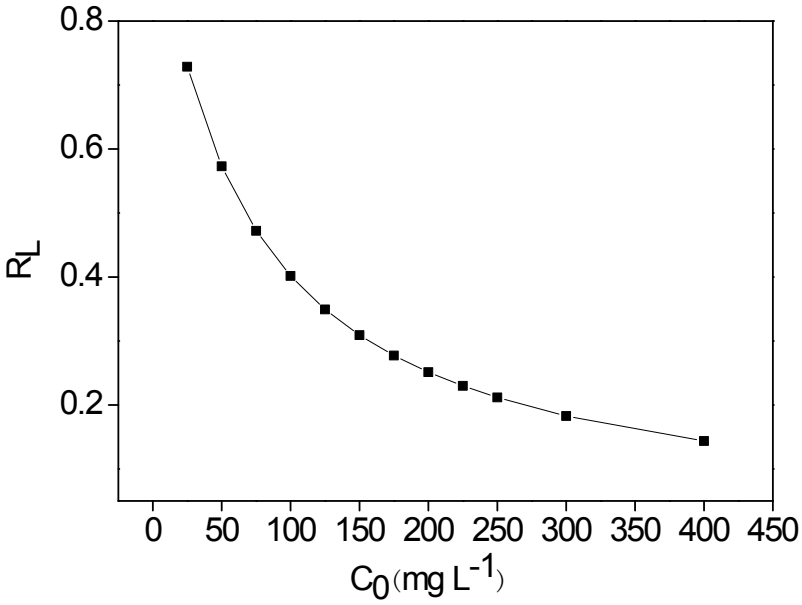

Fig. S9 Effect of initial uranium concentration on the value of R_L (t = 180 min, $c(H^+)$ =4 M, V = 25 mL, T = 298 K, and m = 10 mg)

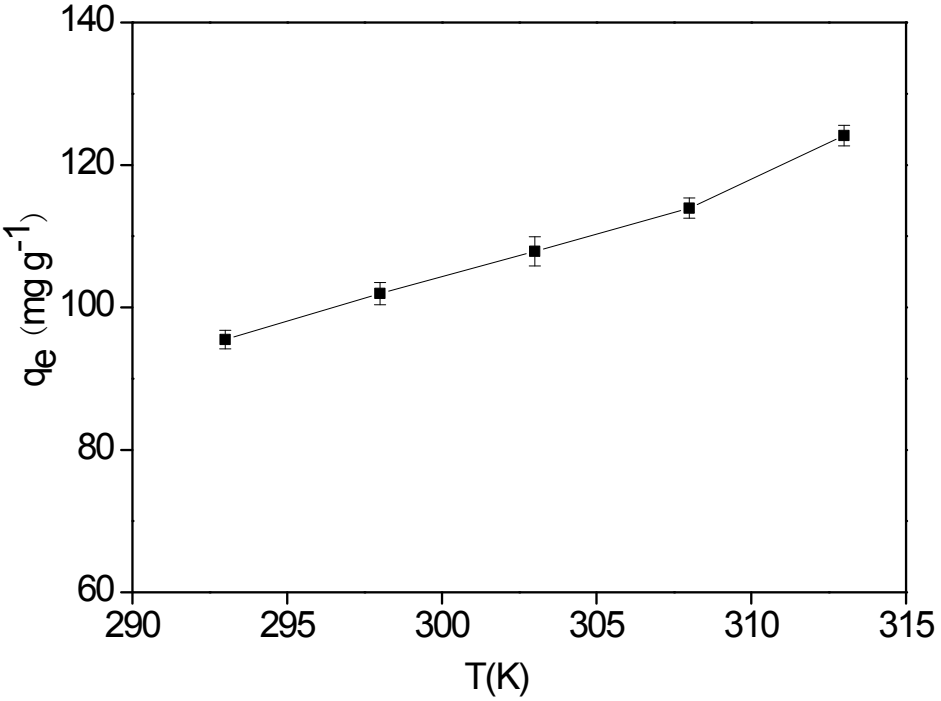

Fig. S10 Effect of temperature on the U(VI) sorption on POP-EDVP (C_0 = 100 mg L^{-1}, *c* (H^+) =4 M, V = 25 mL, t = 180 min, and m = 10 mg)

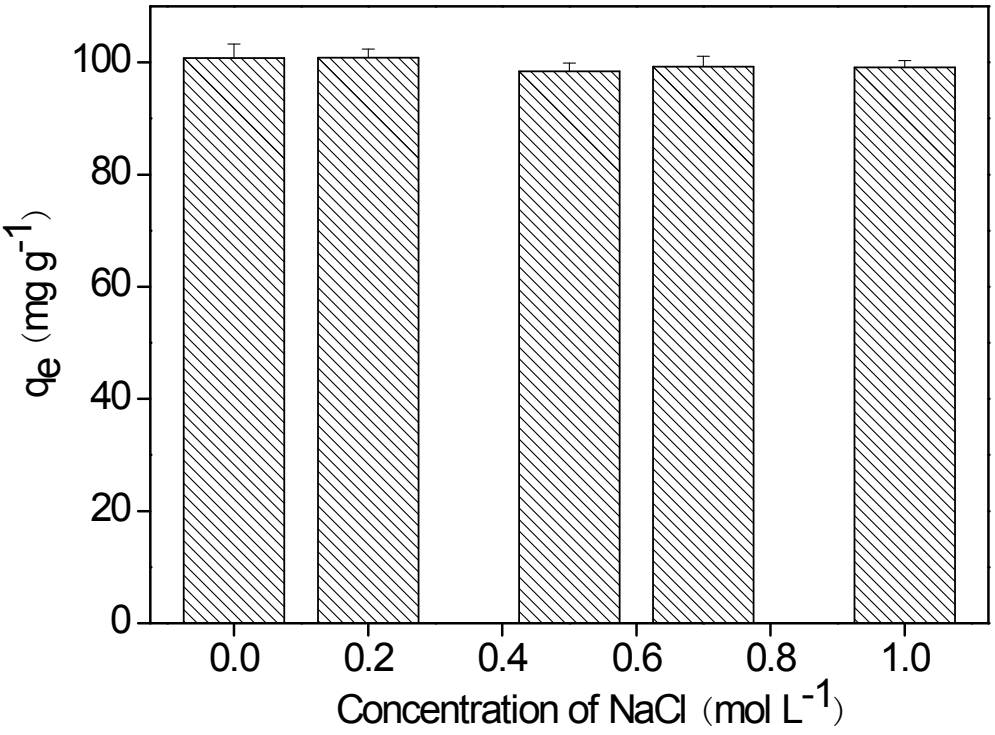

Fig. S11 Effect of concentration of NaCl on the U(VI) sorption on POP-EDVP (C_0 = 100 mg L^{-1}, c (H^+) =4 M, V = 25 mL, t = 180 min, T=298K, and m = 10 mg).

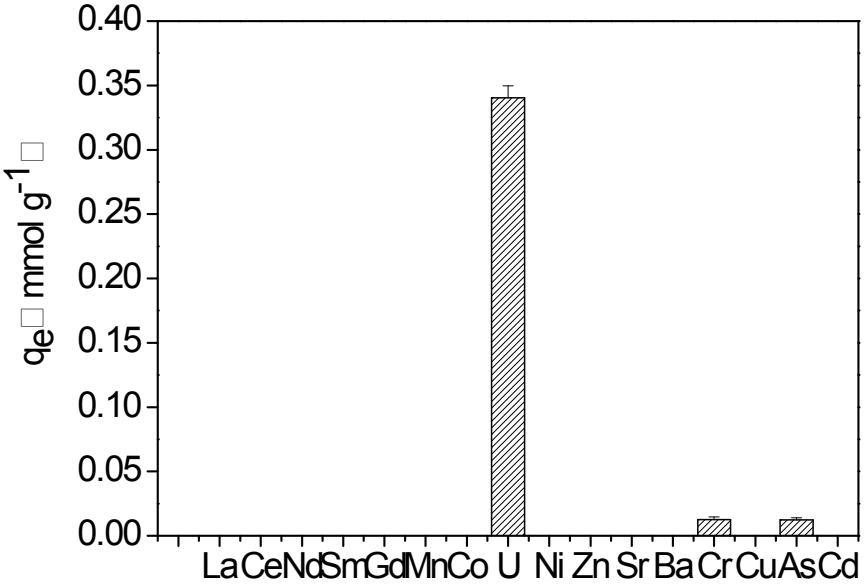

Fig. S12 Competitive sorption capacities of coexistent ions on P4 (C_0=0.5 mmol L^{-1} for all cations, c (H^+) =4 M, T=298 K, V= 25 mL, t=180 min, and m=10 mg).

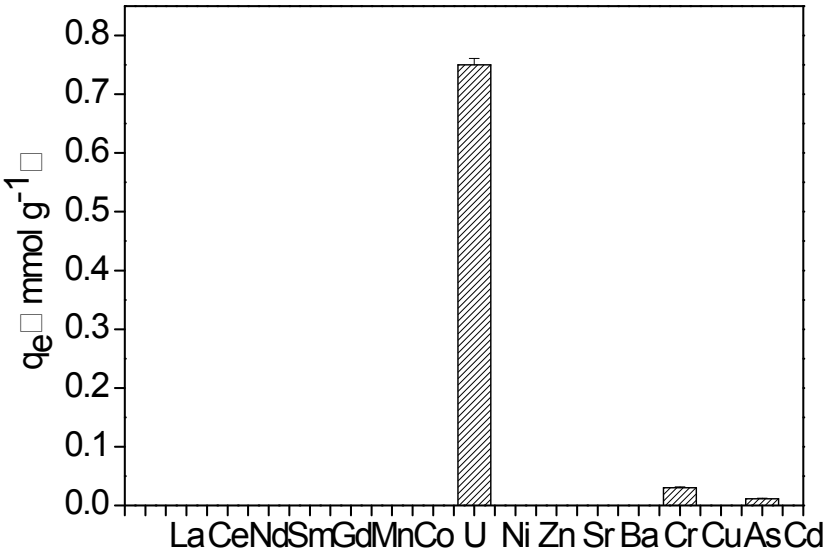

Fig. S13 Competitive sorption capacities of coexistent ions on P5 (C_0=0.5 mmol L^{-1} for all cations, c (H^+) =4 M, T=298 K, V= 25 mL, t=180 min, and m=10 mg).

Table S1

Kinetic parameters for uranium adsorption on POP-EDVP.

Kinetic model	Parameter	Value
Pseudo-first-order	k_1 (min^{-1})	0.03813
	$q_{e.\ cal}$ ($mg\ g^{-1}$)	30.5126
	R^2	0.8705
Pseudo-second-order	k_2 ($g\ mg^{-1}\ min^{-1}$)	0.00388
	$q_{e.\ cal}$ ($mg\ g^{-1}$)	102.45
	R^2	0.9999
Intraparticle diffusion	K_{int} ($mg\ g^{-1}\ min^{-1/2}$)	2.74619
	c ($mg\ g^{-1}$)	71.26477
	R^2	0.77369

Table S2

Adsorption isotherms parameters for uranium on POP-EDVP.

Adsorbent	Kinetic model	Parameter	Value
POP-EDVP	Langmuir	b (L mg $^{-1}$)	0.0149
		q_{max} (mg g^{-1})	215.9
		R^2	0.9882
	Freundlich	K_F (mg g^{-1})	9.76515
		n	1.8448
		R^2	0.96556

Table S3

Thermodynamic parameters of uranium adsorption on POP-EDVP.

△H° (KJ mol $^{-1}$)	△S° (J mol $^{-1}$ K^{-1})	△G° (KJ mol $^{-1}$)				
		293 K	298 K	303 K	308 K	313 K
17.1684	119.58	-17.86854	-18.46644	-19.06434	-19.66224	-20.26014

Table. S4

Comparison of selectivity of POP-EDVP, P1, P2 and P3 in strong HNO_3 media [a]

Adsorbents	S_u	c (H^+) (mol/L)
POP-EDVP	94.2%	4
P1	0	4
P2	0	4
P3	0	4

[a] Competitive sorption capacities of coexistent ions on adsorbents (C_0=0.5 mmol L^{-1} for all cations, c (H^+)= 4 M, T=298 K, V= 25 mL, t=180 min, and m=10 mg).

Table. S5

The porosity of POP-EDVP, P4 and P5

Adsorbents	S_{BET} (m^2/g)	Pore Size (nm)	V (ml/g)
POP-EDVP	61.8	42.7	0.41
P4	114.9	27.8	0.64
P5	0.02	465.2	Not detected

Table. S6

Comparison of selectivity of POP-EDVP, P4 and P5 in strong HNO_3 media [a]

Adsorbents	S_u	c (H^+) (mol/L)
POP-EDVP	94.2 %	4
P4	93.2 %	4
P5	94.7 %	4

[a] Competitive sorption capacities of coexistent ions on adsorbents (C_0=0.5 mmol L^{-1} for all cations, c (H^+)= 4 M, T=298 K, V= 25 mL, t=180 min, and m=10 mg).

Table S7

Calculated interaction energy parameters (in kcal mol^{-1}) for the complexation of $UO_2(NO_3)_2$ with POP-EDVP with two P=O / $UO_2(NO_3)_2$.

Ratio of P=O: $UO_2(NO_3)_2$	ΔE_{gas}
1:1	-48.94
2:1	-40.66