

Imidazole functionalized porous organic polymer for the highly efficient extraction of uranium from aqueous solutions

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Synthesis of polymer adsorbent P (DVB-GMA) bearing epoxy groups

The detailed synthetic experiment was described as follows: the mixture including 1.0 g DVB and 2.0 g glycidyl methacrylate (GMA) was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-GMA).

Synthesis of polymer adsorbent P (DVB-AA) bearing carboxyl groups

The detailed synthetic experiment was described as follows: the mixture including 1.0 g DVB and 2.0 g acrylic acid (AA) was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-AA).

Synthesis of polymer adsorbent P (DVB-HEMA) bearing hydroxyl groups

The detailed synthetic experiment was described as follows: the mixture including 1.0 g DVB and 2.0 g hydroxyethyl methacrylate (HEMA) was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-HEMA).

Synthesis of polymer adsorbent P (DVB-AM) bearing carboxyl groups

The detailed synthetic experiment was described as follows: the mixture including 1.0 g DVB and 2.0 g Acrylamide (AM) was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-AM).

Synthesis of imidazole functionalized polymer adsorbent P (DVB-VIM)-1

The detailed synthetic experiment was described as follows: the mixture including 0.5 g DVB and 2.5 g VIM was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-VIM)-1.

Synthesis of imidazole functionalized polymer adsorbent P (DVB-VIM)-2

The detailed synthetic experiment was described as follows: the mixture including 1.5 g DVB and 1.5 g VIM was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-VIM)-2.

Synthesis of imidazole functionalized polymer adsorbent P (DVB-VIM)-3

The detailed synthetic experiment was described as follows: the mixture including 2.0 g DVB and 1.0 g VIM was dissolved in 5 mL ethyl acetate, followed by addition of 0.05 g AIBN. After stirring for 1 h at 28 °C the solution was transferred into an autoclave with 25 mL of Teon liner and treated at 100 °C for 24 h. The system was cooled to 25 °C and a solid monolith was gained after an evaporation of organic solvent. The solid sample was designated as P (DVB-VIM)-3.

Synthesis of imidazole functionalized polymer adsorbent P (DVB-VIM) by suspension polymerization

The suspension polymerization was performed in a 250 ml three necked round -bottomed glass flask reactor fitted with a mechanical stirrer, reflux condenser and a nitrogen gas inlet tube. The aqueous phase was composed of NaCl saturated solution (150 mL), glutin (0.5 g) and sodium salt of carboxy methyl-cellulose (0.5 g). The organic phase was composed of 1-vinylimidazole (VIM) (2g), Divinylbenzene (DVB) (1g), benzoperoxide (BPO) (0.05g). The above two phases were mixed to form a suspension and the mixture temperature was maintained at 45°C for 30min. Finally, the suspension copolymerization was carried out at 85°C for 8h with a stirring rate of 500 rpm. The reaction mixture was cooled to room temperature and the resulting microspheres were washed with deionized water and ethanol to remove the excess stabilizer and other impurities. Finally, the polymer resin was washed with deionized water, and then dried at 45°C under vacuum for 24h to give white product (abbreviated as P (DVB-VIM)).

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad \text{Eqn (S1)}$$

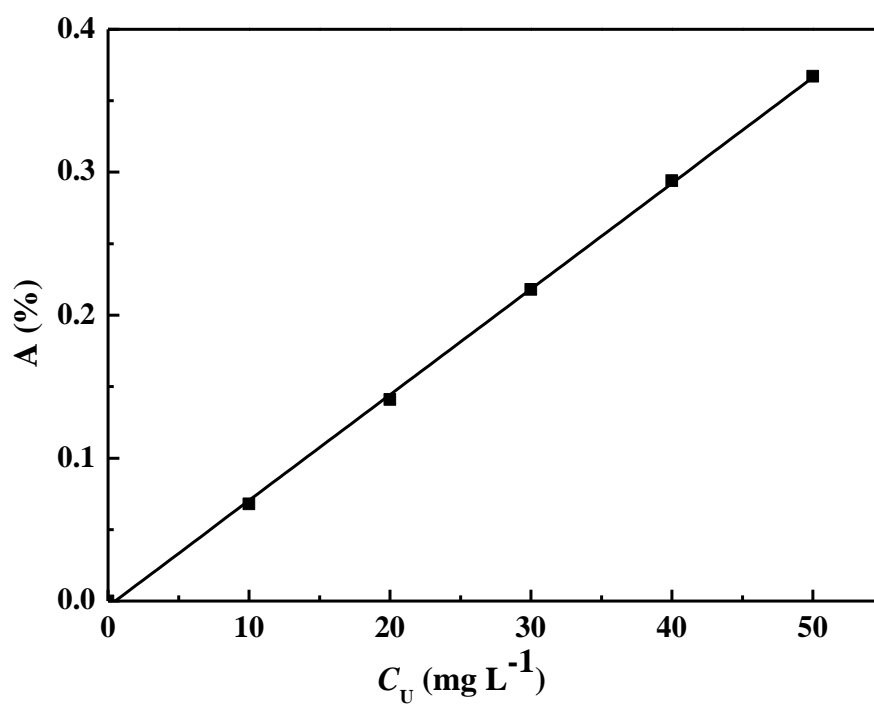


Fig. S1 The calibration curve

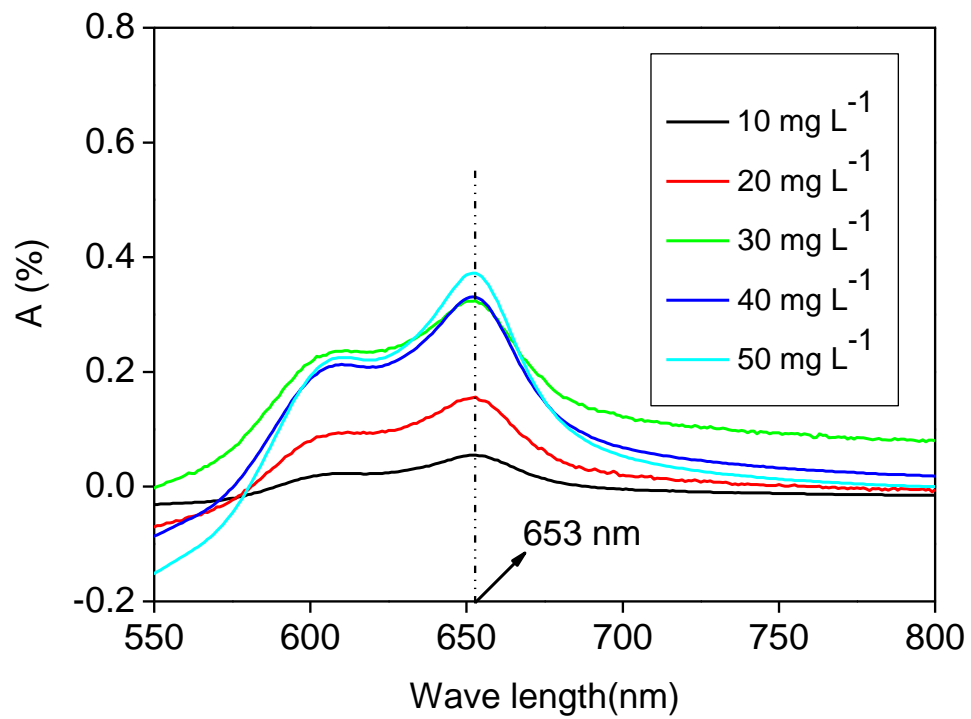


Fig. S2 UV-Vis spectra for standard solutions

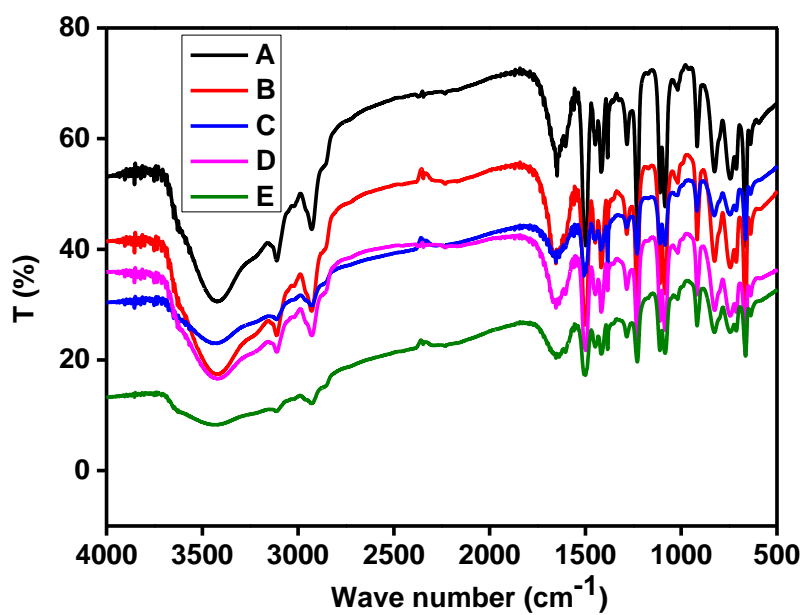


Fig. S3 the FT-IR spectrum of P (DVB-VIM) before (A) and after treated in 3 mol L⁻¹ of NaOH (B), boiling water (C), DMF (D) and 3 mol L⁻¹ of HCl (E) for 12 h, respectively.

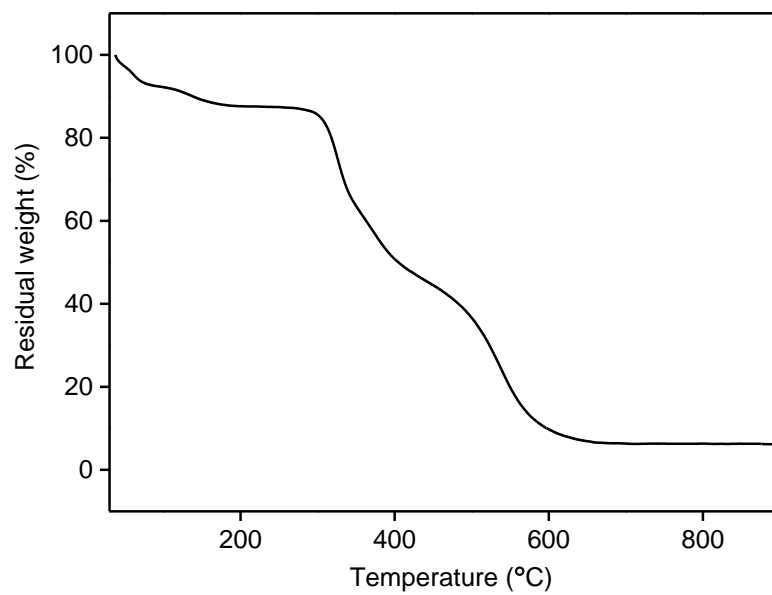


Fig. S4 the TGA curve of P (DVB-VIM) after immersed in DFM for 24 h.



Fig. S5 The measurement of water contact angles for P(DVB-VIM).

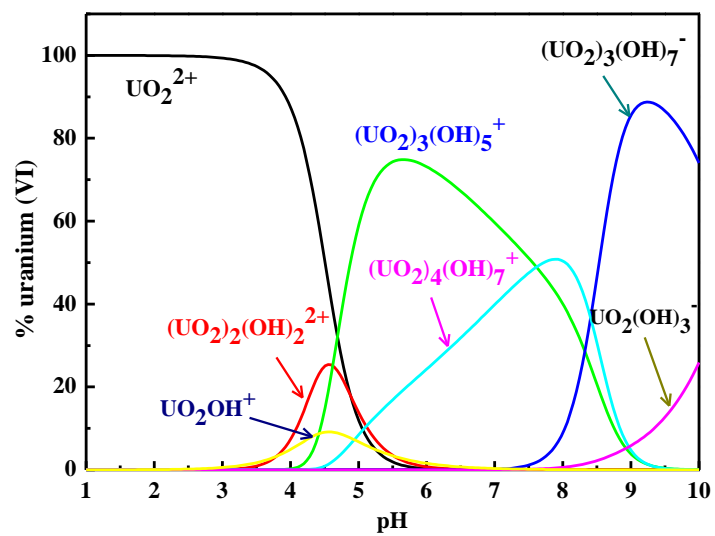


Fig. S6 Distribution of uranium (VI) species in aqueous solution with a total concentration of 100 mg L^{-1} and pH values ranging from 1 to 10. Calculated by using a Medusa program.

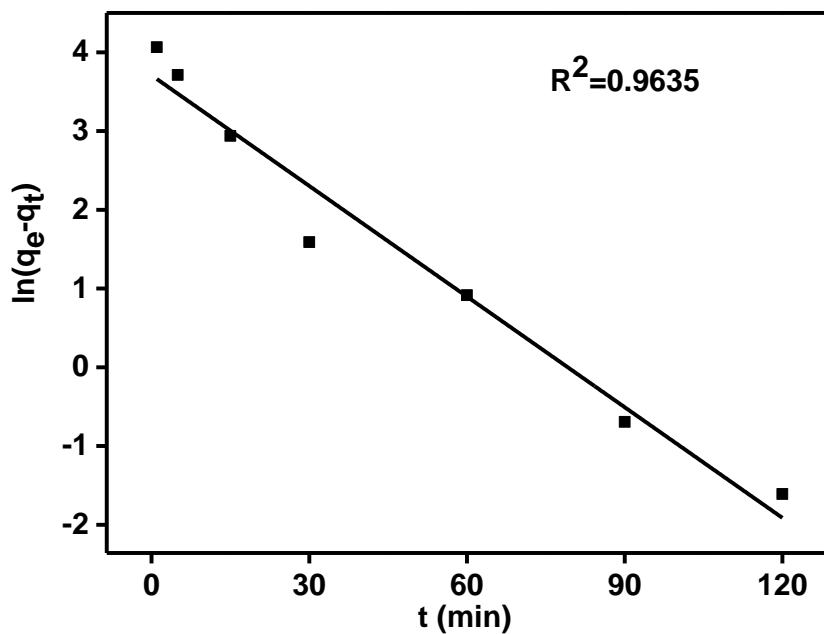


Fig. S7 The pseudo-first-order plot of the sorption

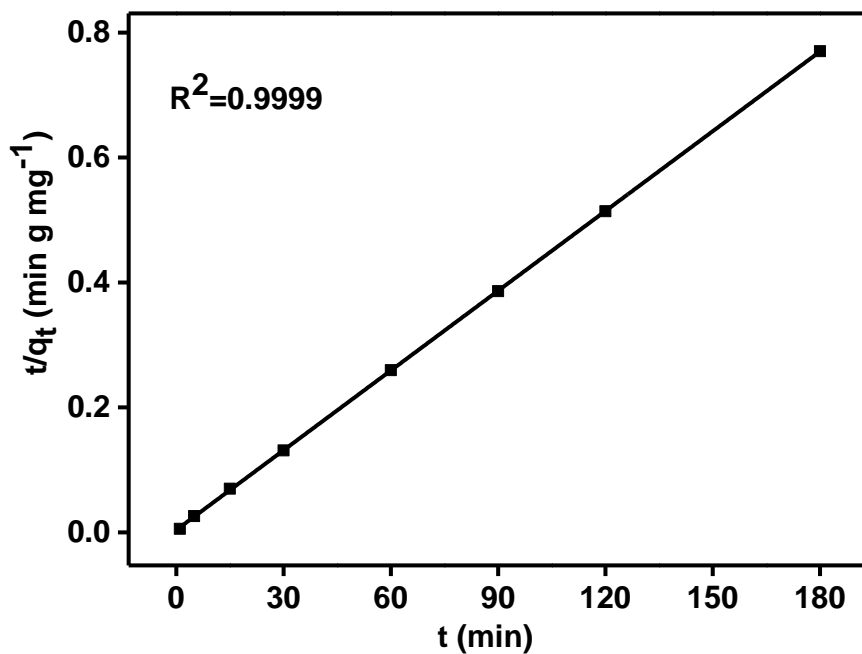


Fig. S8 The pseudo-second-order plot of the sorption

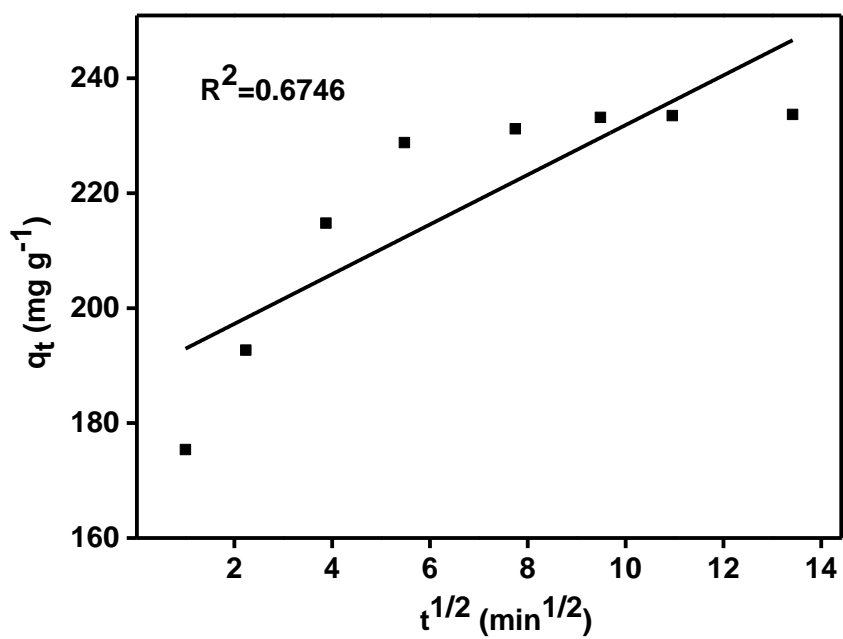


Fig. S9 The Intraparticle diffusion plot of the sorption

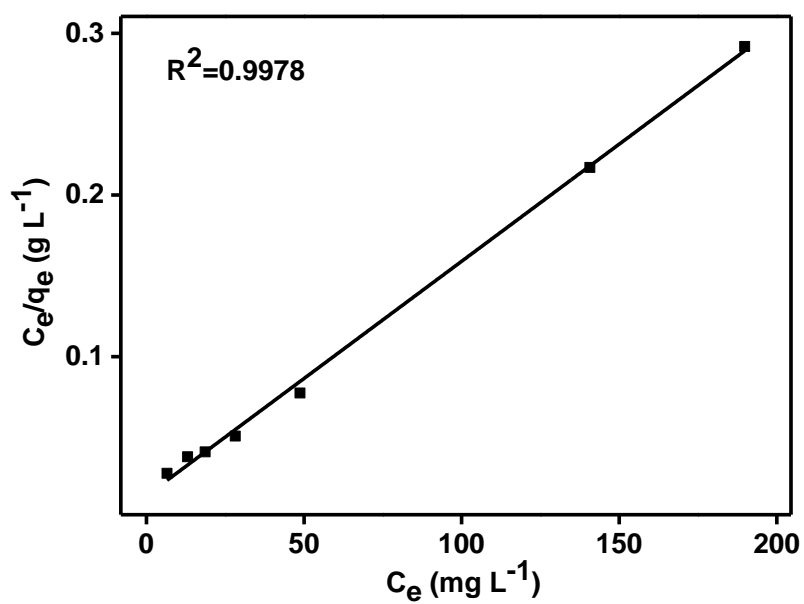


Fig. S10 The Langmuir model fitted the absorption isotherms of uranium

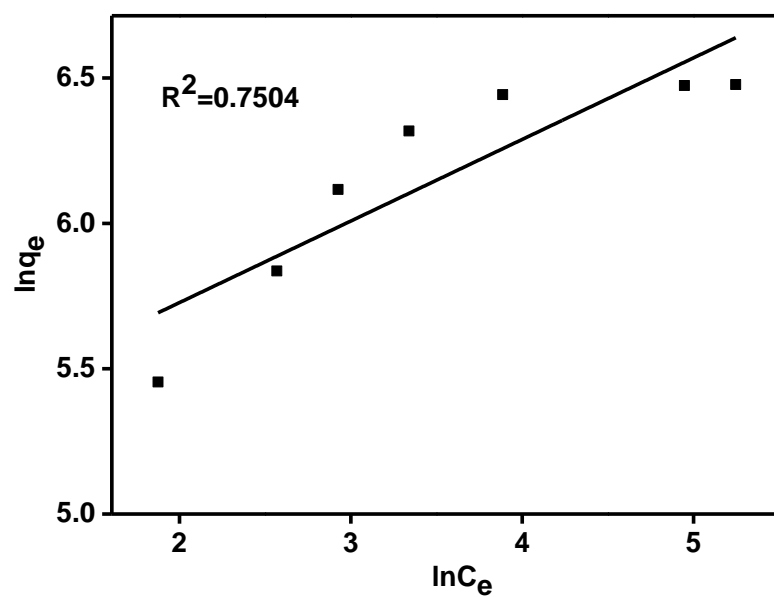


Fig. S11 The Freundlich model fitted the absorption isotherms of uranium

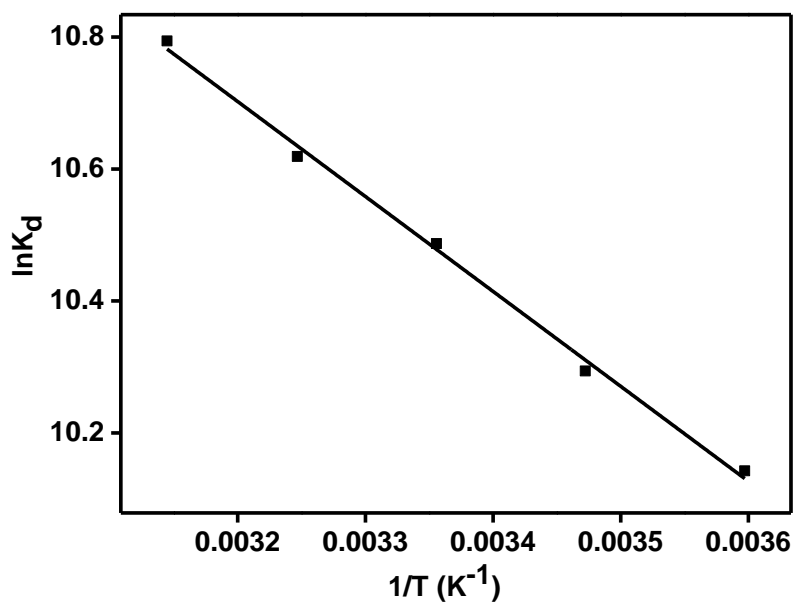


Fig. S12 Variation of $\ln K_d$ with T^{-1} ($C_0 = 100 \text{ mg L}^{-1}$, $\text{pH} = 4.5$, $t = 180 \text{ min}$, and $m/v = 0.4 \text{ g L}^{-1}$).

Table. S1 Comparison of the specific surface area of the adsorbent P (DVB-VIM) before and after immersed in DMF for 24 h.

Adsorbents	S_{BET} (m ² g ⁻¹)
P (DVB-VIM) ^a	67.6
P (DVB-VIM) ^b	65.3

^a before immersed in DMF for 24 h.

^b after immersed in DMF for 24 h.

Table S2 Kinetic parameters for uranium adsorption on P(DVB-VIM).

Kinetic model	Parameter	Value
Pseudo-first-order	k_1 (1 min ⁻¹)	0.03674
	$q_{e. cal}$ (mg g ⁻¹)	40.801
	R^2	0.9635
Pseudo-second-order	k_2 (g mg ⁻¹ min ⁻¹)	0.0048
	$q_{e. cal}$ (mg g ⁻¹)	234.74
	R^2	0.9999
Intraparticle diffusion	K_{int} (mg g ⁻¹ min ^{-1/2})	4.3245
	c (mg g ⁻¹)	188.61
	R^2	0.6746

Table S3 Adsorption isotherms parameters for uranium on P (DVB-VIM).

Adsorbent	Kinetic model	Parameter	Value
POP	Langmuir	b (L mg ⁻¹)	0.1031
		q_{max} (mg g ⁻¹)	689.6
		R^2	0.9978
	Freundlich	K_F [(mg g ⁻¹) (L mg ⁻¹) ^{1/n}]	175.21
		n_F	3.5625
		R^2	0.7504

Table S4 Thermodynamic parameters of uranium adsorption on P (DVB-VIM).

ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (KJ mol ⁻¹)				
		278 K	288 K	298 K	308 K	318 K
11.95	127.0	-23.41	-24.68	-25.95	-27.22	-28.49

Table. S5 Comparison of adsorption of uranium on various adsorbents also developed by solvothermal polymerization ^a

Adsorbents	q_{\max} (mg g ⁻¹)	S_{BET} (m ² g ⁻¹)
P (DVB-VIM)	689.6	67.6
P (DVB-AA)	366.2	79.3
P (DVB-HEMA)	162.2	86.7
P (DVB-GMA)	188.3	91.2
P (DVB-AM)	241.8	76.7

^a Sorption condition (T=298 K, pH=4.5, t=180 min, and m/V=0.4 g L⁻¹).

Table. S6 Effect of the concentration of imidazole group on the uranium adsorption capacity of P (DVB-VIM) ^a

Adsorbent	q_{\max} (mg g ⁻¹)	The concentration of imidazole groups (mmol g ⁻¹)	S_{BET} (m ² g ⁻¹)
P (DVB-VIM)-3	460.2	3.1	444.7
P (DVB-VIM)-2	534.2	4.5	150.2
P (DVB-VIM)	689.6	6.2	67.6
P (DVB-VIM)-1	701.2	7.3	0.58

^a Sorption condition (T=298 K, pH=4.5, t=180 min, and m/V=0.4 g L⁻¹)

Table. S7 Comparison of adsorption of uranium on the adsorbent P (DVB-VIM) developed by suspension polymerization and solvothermal polymerization ^a

Adsorbents	q_{\max} (mg g ⁻¹)
P (DVB-VIM) ^b	689.6
P (DVB-VIM) ^c	275.4

^a Sorption condition (T=298 K, pH=4.5, t=180 min, and m/V=0.4 g L⁻¹).

^b developed by suspension polymerization of DVB (1.0 g) and VIM (2.0 g).

^c developed by solvothermal polymerization of DVB (1.0 g) and VIM (2.0 g).

Table. S8 Calculated interaction energy parameter for the complexation of UO₂²⁺ with imidazole group anchored onto the polymer chain of P (DVB-VIM)

Model	ΔE_{gas} (kcal mol ⁻¹)
1:2 of UO ₂ ²⁺ with the two non-adjacent imidazole groups anchored onto the same polymer chain	-194.0
1:2 of UO ₂ ²⁺ with the two adjacent imidazole groups anchored onto the same polymer chain	-189.0

Table. S9 The comparison of q_{DFT} derived from DFT calculations with the saturated adsorption experimental data q_{max} obtained from the Langmuir model

Adsorbent	q_{DFT} (mg g⁻¹)	q_{max} (mg g⁻¹)
P (DVB-VIM)	737.8	689.6