

Electronic Supplementary Material

A ternary mechanism for the facilitated transfer of metal ions onto metal organic frameworks: implications for the “versatility” of these materials as solid sorbents

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SI-1 Several analogous MOFs and SBU presented in this work

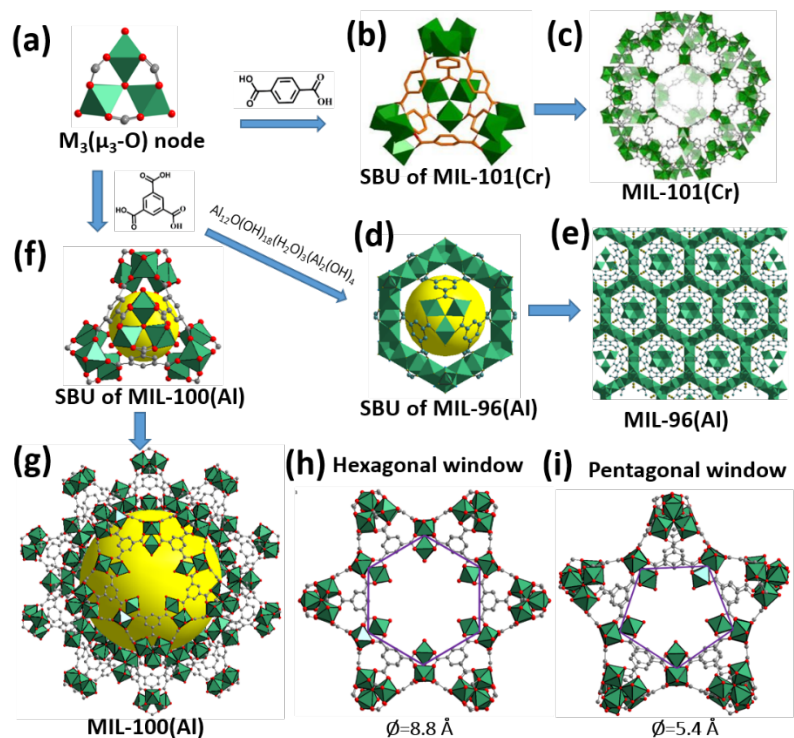


Fig. S1 Several analogous MOFs and SBU derived from M_3O node(a); (h) and (i) represent hexagonal microporous window and pentagonal microporous window of MIL-100(Al), respectively.

SI-2 PXRD and Porosity characterizations

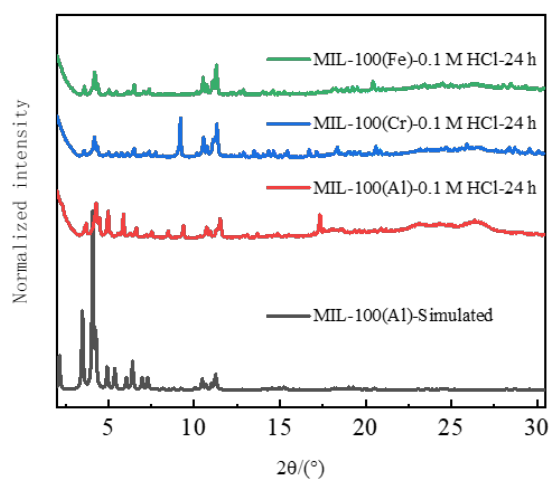


Fig. S2 PXRD patterns of analogous MIL-100s (Al, Fe, Cr) following exposure in 0.1 M HCl solution.

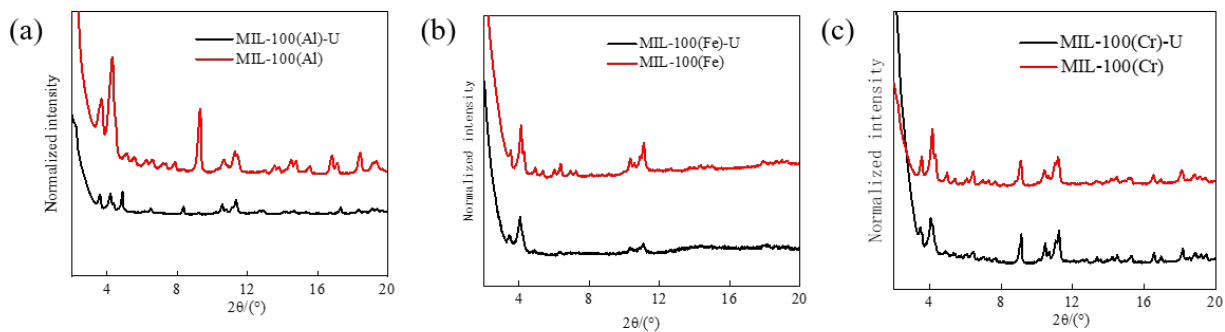


Fig. S3 PXRD patterns of three MOFs before and after uranium adsorption.

Table S1 The surface area, pore volume and pore size of MIL-100.

Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore size (nm)
MIL-100(Cr)	1671.6	0.7848	1.88
MIL-100(Fe)	1980.5	0.9021	1.82
MIL-100(Al)	1825.8	0.8785	1.92

SI-3 The topology dependent U(VI) sorption

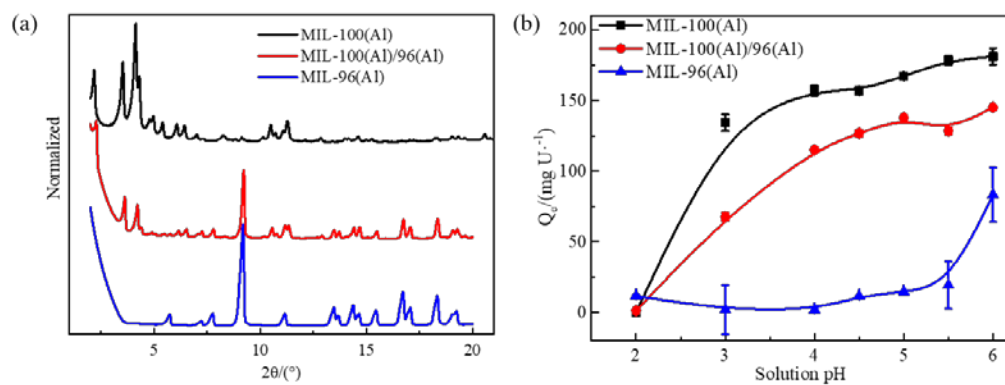


Fig. S4 Comparison of PXRD (Left) of MIL-100(Al) and MIL-96(Al) and uranyl ions adsorption (Right).

SI-4 The species distribution of U(VI)

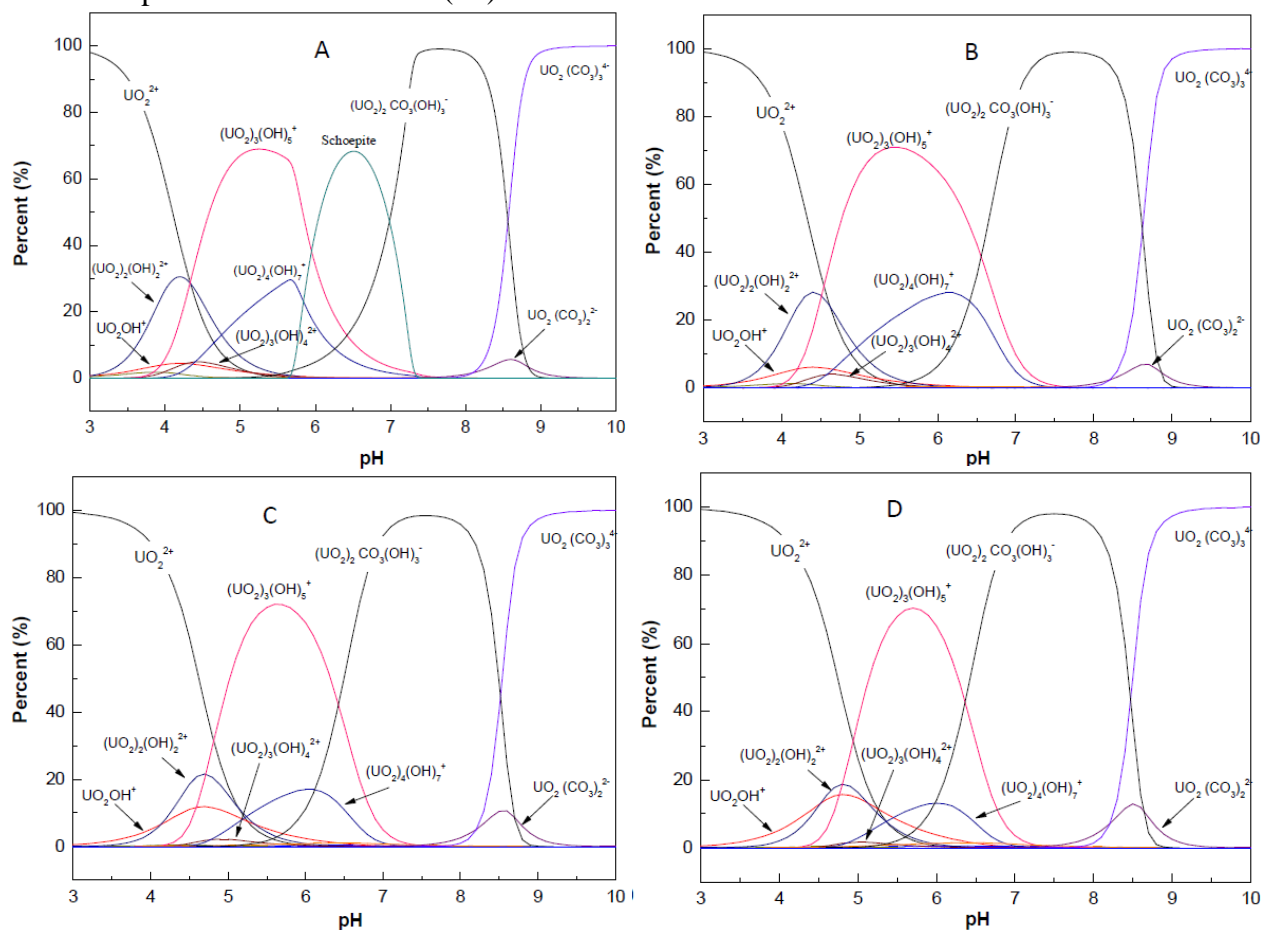


Fig. S5 Aqueous speciation of U(VI) in an open system equilibrated with $p(\text{CO}_2) = 10^{-3.5}$ as a function of pH from reference 1.

A, $[\text{U(VI)}]_{\text{total}} = 1.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$;

B, $[\text{U(VI)}]_{\text{total}} = 5.00 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$;

C, $[\text{U(VI)}]_{\text{total}} = 1.00 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$;

D, $[\text{U(VI)}]_{\text{total}} = 5.00 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in water solution.

(The species less than 1% were not denoted in the figures for clarity)

SI-5 The sorption data fitting by kinetics models

The pseudo-second-order kinetic model and the pseudo-first-order kinetic model were used to fit the dependence of the U(VI) adsorption amount on time. The linear form of the equation is:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}$$

where t is the adsorption time (min), Q_e and Q_t are the amounts adsorbed at equilibrium and at time t , respectively ($\text{mg}\cdot\text{g}^{-1}$), and k_2 is the rate constant for pseudo-second-order adsorption ($\text{g}\cdot(\text{g}\cdot\text{min})^{-1}$). $k_2 = \text{slope}/\text{intercept}$ when t/Q_t is plotted against t . Fig. S5 shows the plots of the pseudo-second-order kinetics of U(VI) adsorption in MIL-100(Al) for different initial U(VI) concentrations. The calculated kinetic constants (k_2) as well as the correlation coefficients (R^2) are listed in Table S2. The value of k_2 decreases with increase of the initial ion concentrations, which can be attributed to the weaker competition of the adsorption surface sites at lower concentrations.

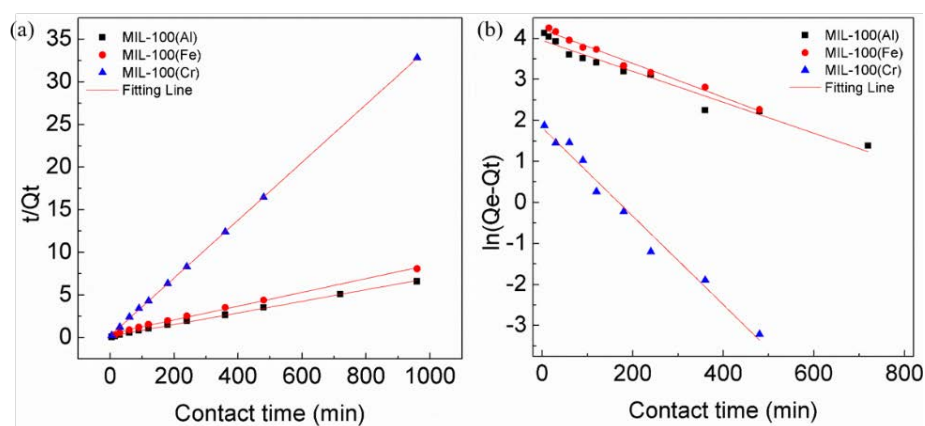


Fig. S6 The pseudo-second-order (left) and pseudo-first-order (right) kinetic linearized plots for U(VI) sorption in MIL-100s

Table S2 Kinetics parameters for U(VI) sorption in MIL-100s (Cr, Fe, Al)

Sample	pseudo-first-order kinetic model			pseudo-second-order kinetic model		
	$q_e(\text{mg}\cdot\text{g}^{-1})$	$K_1(\text{min}^{-1})$	R^2	$q_e(\text{mg}\cdot\text{g}^{-1})$	$k_2(\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	R^2
MIL-100(Cr)	15	0.0108	0.98	30	0.03393	0.999
MIL-100(Fe)	110	0.0414	0.98	120	0.00809	0.99
MIL-100(Al)	130	0.00377	0.96	170	0.00681	0.99

SI-6 The sorption data fitting by isotherm models

The Langmuir model assumes that the removal of metal ions occurs on an energetically homogenous surface by monolayer sorption and there are no interactions between the adsorbates on adjacent sites and the linear form of the equation is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_L} + \frac{1}{Q_L K_L}$$

where Q_e is the amount of adsorbate adsorbed per gram of adsorbent ($\text{mg}\cdot\text{g}^{-1}$), C_e denotes the equilibrium concentration of the adsorbate in solution ($\text{mg}\cdot\text{L}^{-1}$), Q_L is a theoretical limit of adsorption capacity when the monolayer surface is fully covered with the adsorbate to assist in the comparison of adsorption performance ($\text{mg}\cdot\text{g}^{-1}$), and K_L is the separation constant of the Langmuir adsorption isotherm.

The Freundlich equation is an empirical equation based on sorption on a heterogeneous surface. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies. The linear equation can be expressed by:

$$\ln Q_e = \ln k_F + \frac{1}{n} \ln C_e$$

where k_F and n are the Freundlich constants related to the sorption capacity and the sorption intensity, respectively. A linear relationship was obtained by plotting $\ln q_e$ against $\ln c_e$, and the values of k_F and n were calculated from the slope and intercept of the straight line.

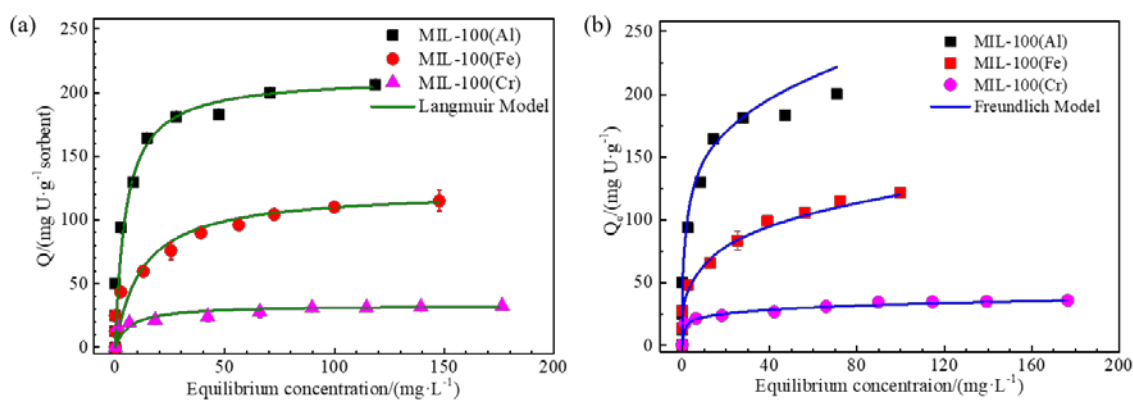


Fig. S7 Langmuir isotherm (left) and Freundlich isotherm (right) for U(VI) sorption on MIL-100(Cr), MIL-100(Fe) and MIL-100(Al)

Table S3 Comparison of parameters of Langmuir and Freundlich isotherms in MIL-100s

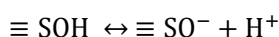
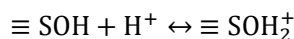
	Langmuir			Freundlich		
	$q_m(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	R^2	$k_F(\text{mg}\cdot\text{g}^{-1})$	n	R^2
MIL-100(Cr)	33.6	0.118	0.99	14.6	6.51	0.99
MIL-100(Fe)	116.3	0.141	0.99	33.6	3.91	0.98
MIL-100(Al)	212.8	0.207	0.99	86	4.926	0.93

Table S4 Number of U(VI) ions adsorbed per node in MIL-100s (Al, Fe, Cr).

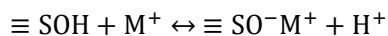
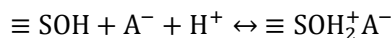
MOFs	MIL-100(Al)		MIL-100(Fe)		MIL-100(Cr)	
	Capacities ($\text{mg}\cdot\text{g}^{-1}$)	Capacities per Node	Capacities ($\text{mg}\cdot\text{g}^{-1}$)	Capacities per Node	Capacities ($\text{mg}\cdot\text{g}^{-1}$)	Capacities per Node
Maximum capacities per node	212.8	0.50	116.3	0.32	33.6	0.09
Actual capacities per node	206.4	0.49	115.1	0.31	32.3	0.087

SI-7 Surface structure and pH_{pzc} value of hydrated MIL-100s(M)

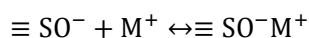
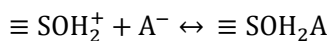
As mentioned in the introduction, MIL-100s present abundant of coordinated unsaturated sites (CUS). Moreover, water molecules present in the solution or atmosphere may cause the hydroxylation of a metal oxide surface. It has been confirmed by solid-state nuclear magnetic aluminum spectroscopy (^{27}Al NMR) that there is no unsaturated coordination site on the surface of the MIL-100 (Al) sample, as shown in Fig. 4b. Amphiphilic surface hydroxyls can be protonated/deprotonated by the surrounding environment:



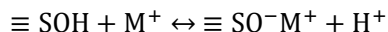
The reactions involving electrolyte (salt) ions can also take place. As a result, the connections of surface complexes or ion pairs are formed. Surface complexes are formed according to the equations:



Moreover, ion pair connections are formed when presence of excess of OH^- with the following way:

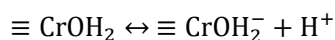


The interactions of positively charged ions with the solid hydroxyl groups (leading to the surface complexes creation) causes formation of negatively charged surface groups according to the reaction:

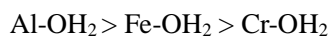


where: S=Al, Fe or Cr atoms, M^+ = other metal ions.

However, for MIL-100(Cr), negatively charged surface groups may formed. Studies have shown that the Cr center metal cluster will dissociate protons from the water ligand (Cr-OH_2) leaving a negatively charged hydroxyl group (Cr-OH^-). Therefore, the insoluble Framework will be the counteranion of the proton or other cations.



From the Zeta potential, it can be seen that the complexing ability of different metal hydrate surfaces with protons (H^+) is not exactly the same, and generally satisfies the following laws:



Therefore, the surface of the MIL-100(Al) shows less negative charge due to the combination of more protons on the surface of Al-metal cluster, followed by the Fe-metal cluster surface. The surface of the Cr-metal cluster is negatively charged due to deprotonation.

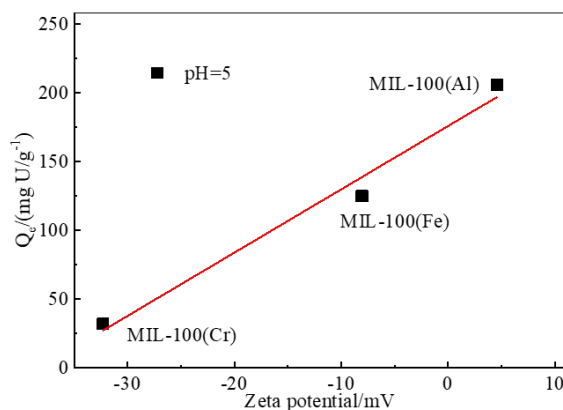


Fig. S8 Correlatons of Zeta potential of analogous MOFs MIL-100s (Al, Fe, Cr) and adsorption for U(VI) at pH=5.0

SI-8 Temperature dependence and adsorption energy

To get further insight into the adsorption mechanism, three basic thermodynamic parameters, standard free energy change (ΔG^0 , $\text{kJ}\cdot\text{mol}^{-1}$), standard enthalpy change (ΔH^0 , $\text{kJ}\cdot\text{mol}^{-1}$) and standard entropy change (ΔS^0 , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) for the adsorption of U(VI) on MIL-100(Al) (Fig. S8 and Table S5) were determined based on the following equations

$$K_d = \frac{C_s}{C_e}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where K_d is the distribution coefficient, C_s the amount of U(VI) adsorbed per mass of MIL-100(M) ($\text{mg}\cdot\text{g}^{-1}$), C_e the U(VI) concentration in solution at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), R is the gas constant, and T is the absolute temperature of aqueous solution.

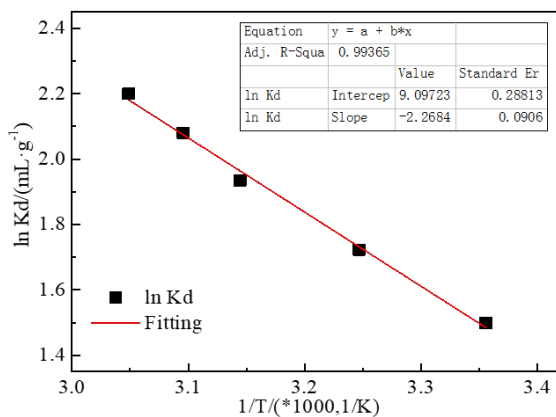


Fig. S9 Effect of adsorption temperature for MIL-100(Al).

Table S5 thermodynamic parameters of U(VI) adsorption by MIL-100(Al).

Condition	ΔH° (KJ·mol ⁻¹)	ΔS° (KJ·mol ⁻¹)	ΔG° (KJ·mol ⁻¹)				
			298 K	308 K	318 K	323 K	328 K
U ₀ =100 ppm; pH=5.	18.86	0.76	-206.53	-214.10	-221.66	-225.40	-229.20

SI-9 Reusability of MIL-100(Al)

Considering that little U(VI) sorption occurred in all the MOF sorbents at lower pH as denoted in Fig. 3a, regeneration of the MOF was performed by eluting the sorbed U(VI) using an acid solution, and the results were given in Fig. S9 and Table S6. It was found that a complete U(VI) leaching (> 99%) for MIL-100(Al) can be easily achieved using a 0.3 mol·L⁻¹ HNO₃ solution, suggesting an apparent reversibility of the U(VI) sorption into the MIL-100(Al).

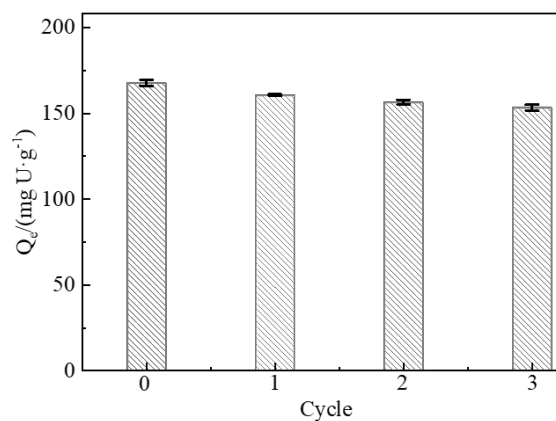


Fig. S10 Reusability of MIL-100(Al).

Table S6 Desorption and reusability of MIL-100s

	Desorption(%)			Reusability(mg · g ⁻¹)	
	0.3	0.1	0.02	Fresh	Reclaimed
[HNO ₃]/ mol/L	0.3	0.1	0.02	Fresh	Reclaimed
MIL-100(Cr)	>99	>99	>99	32	-
MIL-100(Fe)	>99	>99	91	115	-
MIL-100(Al)	>99	86	69	168	158

References

1. Yuan L Y, Liu Y L, Shi W Q, Li Z J, Lan J H, Feng Y X, Zhao X L, Yuan Y L and Chai Z F. A novel mesoporous material for uranium extraction, dihydroimidazole functionalized SBA-15. *Journal of Materials Chemistry*, **2012**, 22: 17019-17026.