MOF-76: From Luminescent Probe to Highly Efficient U^{VI} Sorption Material

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Experimental

1. Chemicals and reagents

All the solvents and reagents for syntheses were commercially available and used as received. A standard stock solution of U(VI) was prepared by dissolving the appropriate amounts of $UO_2(NO_3)_2 \cdot 6H_2O$ in deionized water. All testing solutions were prepared with Milli-Q water.

2. Synthesis of MOF-76

A mixture of Tb(NO₃)₃·6H₂O (0.23 g, 0.5 mmol) or Y(NO₃)₃·6H₂O (0.191 g, 0.5 mmol), H₃BTC (0.053 g, 0.25 mmol), DMF (4 mL), and H₂O (4 mL) was sealed in a 20 mL of Teflon-lined reactor, and heated at 110 °C for 24 h. The white powder samples with yield of ~ 50 % were obtained. The phase purity was confirmed by powder X-ray diffraction. The as-synthesized samples were treated at 120 °C under

high vacuum for 16 h to obtain the evacuated samples.

3. Luminescent sensing of uranyl cations

The fine grinding sample Tb-MOF of 3 mg was immersed in 3 mL aqueous solution with different concentration of $UO_2(NO_3)_2$ to form stable emulsion before fluorescence study. The photoluminescent (PL) spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The photomultiplier tube voltage was 700 V, the scan speed was 1200 nm min⁻¹, the excitation and the emission slit width were 2.5 and 2.5 nm, respectively.

4. Batch adsorption experiments

All adsorption experiments were conducted by using a batch method in air and at room temperature (~15 °C). The solution pH values were adjusted by adding negligible volumes of HNO₃ or NaOH. Adsorption kinetic of U(VI) on the adsorbent was studied in the range of 1 min to 10 h. Adsorption isotherm studies were conducted within the initial concentrations of U(VI) varied from 20 to 200 mg/L. Determination of U(VI) Concentration by Arsenazo III Spectrophotometric Method The UV-Vis spectra of arsenazo III containing a certain concentration of U(VI) with the reference of arsenazo III alone is shown in Fig. 1A. One can see that there is a strong sorption peak attributed to U(VI)-arsenazo III complex at the wavelength of 656 nm. Then, the absorbance of arsenazo III containing different concentration of U(VI) (0.2-6 mg/L) were measured at the wavelength of 656 nm. The U(VI) standard curve was obtained by plotting the absorbance at 656 nm as a function of U(VI) concentration (Fig 1B), and a high correlation coefficients (R^2 =0.999) was obtained by fitting the curve with a line.

The concentration of U(VI) in the filtrate after sorption was determined by Arsenazo III Spectrophotometric Method at wavelength of 656 nm (the detection limit of the method is below 0.1 ppm). Before the determination, the filtrate was diluted $2.5\sim100$ times to make sure that the absorbance at 656 nm in the dilution was at the scope of the U(VI) standard curve. Then the concentration of U(VI) was calculated by fitting the U(VI) standard curve.



Fig. S1. (A) UV-Vis spectra of arsenazo III containing a certain concentration of U(VI), and (B) the standard curve of U(VI).

The adsorption capacity q_e of U(VI) on adsorbent were calculated from the following equations:

$$q_{e} = \frac{\left(c_{0} - c_{e}\right)V}{m} \tag{1}$$

where c_0 and c_e are the initial and equilibrium concentrations of U(VI) respectively in aqueous phase, V and m are the volume of the solution and the dry weight of adsorbent used in the adsorption experiments.

U(VI) adsorption on MOF-76 at different pH conditions.

рН	2.38	2.77	3.16	3.72	4.19	5.04	5.93
Abs	0.305	0.106	0.063	0.202	0.203	0.442	0.554
q _e (mg U/g)	204.94	301.94	321.97	253.68	254.44	134.37	76.75

U(VI) adsorption on MOF-76 at $pH = \sim 3.0$ conditions for 5 h.

pH 3.04 3.11 3.16 2.91 2.97	nH 3.04 3.11 3.16 2.01 2.07
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<i>q</i> _e (mg U/g) 297.94 30	94 321.97	276.84	289.24
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4.1. Adsorption kinetic

In order to assess the sorption rate of U(VI) onto adsorbent, the effect of different contact time (1 min to 10 h) on the adsorption of U(VI) on adsorbent from aqueous solution with an initial U(VI) concentration of 140 mg/L is studied. To ensure the complete sorption of U(VI), the mixture of the sorbent and the solution was stirred for at least 5 h in subsequent experiments.

In order to investigate the controlling stage of sorption rate, further investigation is needed to find out the effect of intraparticle diffusion to the entire sorption process. Intraparticle diffusion model is given by Weber and Morris¹ and expressed as the following equation:

$$q_t = k_{id} t^{1/2} \tag{2}$$

where k_{id} is the intraparticle diffusion rate constant. If adsorption is controlled by the intraparticle diffusion process, the plot should be linear when plotting q_t as a function of $t^{1/2}$. As shown in Fig. S2, it can be seen that the points are not linear for the whole contact time but give three straight lines with three different slopes, which indicates that the intraparticle diffusion is not the only rate-controlling stage.

4.2. Adsorption isotherms

The adsorption amount of U(VI) as a function of U(VI) concentration in supernatant at the equilibrium state was determined with the U(VI) concentration of 20–200 mg/L and pH of 3.0 ± 0.1 (Fig. S3).

In order to investigate the adsorption mode of U(VI) on adsorbent, the Langmuir isotherm and Freundlich isotherm models were used to model the equilibrium data.

The Langmuir model assumes that the adsorption of metal ions occurs on a homogenous surface by monolayer adsorption and there no interaction between adsorbed ions, with homogeneous binding sites, equivalent adsorption energies. The linear equation of the Langmuir isotherm model is expressed as followed:

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \tag{3}$$

where q_m is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g) and k_L is a constant indirectly related to adsorption capacity and energy of adsorption (L/mg), which characterizes the affinity of the adsorbate with the adsorbent. The linearized plot is obtained when plotted c_e/q_e against c_e (Fig. S4) and q_m and k_L could be calculated from the slope and intercept.

The Freundlich equation is an empirical equation with the assumption of adsorption on a heterogeneous surface. The linear equation can be express by:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \tag{4}$$

where k_F and n are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively. The linear plot obtained by plotting lnq_e against lnc_e (Fig. S4), the values of k_F and n were calculated from the slope and intercept of the straight line.

The Langmuir and Freundlich isotherm models constants are summarized in Table S1. We can see that a high correlation coefficient ($R^2=0.999$) for Langmuir equation

is obtained, which indicates that the Langmuir isotherm can fit the experimental adsorption data perfectly, but the Freundlich isotherm model can not fit the data well.

5. Selectivity test

The U(VI) selective adsorption by adsorbent from the aqueous solution containing a range of competing metal ions, including Zn^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} , Sr^{2+} , Cr^{3+} , and Cs^+ , was performed at pH 2.5 and 3.0, respectively. For comparison, the initial concentrations of the metal ions were selected as the same as the adsorption experiments (0.6 mM) and the residual concentration of tested ion(s) in supernatants was determined by inductively coupled plasma mass spectrometry (ICP-MS).

The selectivity coefficient (S $_{U/M}$) for U(VI) relative to competing ions is defined as:

$$S_{U/M} = \frac{K_d^U}{K_d^M}$$
(5)

where K_d^{U} and K_d^{M} are the distribution ratio of U(VI) and competing ions in adsorbent and solution, respectively.

6. Desorption experiments

The desorption experiments were carried out by using 0.1M/L Na₂CO₃ as the elution solution. After the equilibrium was obtained, the samples were centrifuged and some content volume of supernate were taken out then equal volume of Na₂CO₃ solution was added to get the sample solution of 0.1M/L Na₂CO₃. The desorption samples were stirred for 3 hours to get the desorption equilibrium, then the solution was separated from the solid phase by using a 0.45 µm syringe filter and finally the

U(VI) concentration in the liquid phase were determined. The desorption quantity of U(VI) was calculated from the difference of U(VI) content before and after desorption in the supernatant. Desorption efficiency is calculated from the following equation:

 $Desorption(\%) = \frac{Amount \text{ of } U(VI) \text{ desorbed}}{Amount \text{ of } U(VI) \text{ adsorbed}} \times 100 \%$ (6)

Langmuir			Freundlich			
q _m (mg/g)	k _L (L/mg)	R^2	k _F (mg/g)	n	R^2	
314.5	4.818	0.999	276.9	31.368	0.518	

Table S1. The Langmuir and Freundlich isotherm models constants of U(VI) adsorption onto adsorbent.

Table S2. The selectivity coefficients ($S_{U/M}$) of U(VI) for different metal ions at pH 2.5.

metal ions	Ni ²⁺	Co ²⁺	Sr^{2+}	Cr ³⁺	Cs^+	Pb^{2+}	Zn^{2+}
$S_{U\!/M}$	68.5	15.8	15.6	12.8	10.2	5.1	2.7



Figure S2 The PXRD patterns of MOF-76 under different pH conditions for 5 h.



Figure S3 Intraparticle diffusion kinetics of the sorption of U(VI) on adsorbent.



Figure S4 Adsorption isotherm of U(VI) adsorption on adsorbent, $c_{adsorbent} = 0.4$ g/L, t = 5 h and pH = 3.0 ± 0.1 .



Figure S5. The Langmuir and Freundlich isotherm model linearized plots for U(VI) sorption on adsorbent.



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Fig S6. EDX data of

The atomic ratios of the metal ions are slightly different from the ICP results; in this case, the more accurate ICP data are adopted in the paper.

References

1. Borah, D.; SatoKawa, S.; Kato, S.; Kojima, T. J. Hazard. Mater. 2009, 162, 1269.