### Selective adsorption of arsenate and the reversible structure

## transformation of the mesoporous metal-organic framework MIL-

## 100(Fe)

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### Supporting Information:

### 1, Experimental Section.

#### **1.1 Preparation of Octahedral Iron Trimesate**

MIL-100(Fe) was prepared according to a modified literature procedure<sup>1,2</sup> by mixing metallic iron (8.0 mmol, 0.45 g), 1,3,5-benzenetricarboxylic acid or trimesic acid (5.4 mmol, 1.13 g), concentrated nitric acid (4.8 mmol), hydrofluoric acid (16 mmol) and deionized water (40 mL) and heating the mixture at 423 K for 12 h in a Teflon-lined autoclave. The light-orange solid product was obtained after filtrated and washed with deionized water. The as synthesized MIL-100(Fe) was further purified by two-step processes using hot water and ethanol to decrease the amount of residual trimesic acid. Typically 15 g of MIL-100(Fe) was treated using 700 mL deionized water at 353 K for 3 h followed by extraction in 700 mL hot ethanol at 333 K for 3 h.

#### 1.2 Characterization

X-ray diffraction (XRD) patterns were performed on Rigaku D/max-2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 40 kV and 200 mA. The morphology and structure of the samples were characterized by field emission scanning electron microscope (FE-SEM, JEOL 6701F) and transmission electron microscope (TEM, JEOL 2100F). The nitrogen adsorption-desorption isotherms were measured on a Quantachrome Autosorb AS-1 instrument and surface areas are measured by Brunauer–Emmett–Teller (BET) method, pore size distributions derived from NLDFT model. Fourier transform infrared spectroscopy (FT-IR) was characterized on Bruker Tensor 27. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K $\alpha$  radiation.

### **1.3 Adsorption Experiments**

Solutions with different concentrations of As(V) were prepared using Na<sub>2</sub>HAsO<sub>4</sub> • 12H<sub>2</sub>O as the sources of heavy metal ions without pH value adjustment. To obtain the adsorption isotherm, 10 mg MIL-100(Fe) was added to 25 mL As(V) (0.4 g/L) solution with different concentration of 10, 20, 50, 100, 150, 200 mg/L and then the mixture was placed on a rotating shaker for 12 h at set temperature (25°C). The solid and liquid phases were then separated by 0.2 µm membranes and analyzed by inductively coupled plasma-optical emission spectroscopy (Shimadzu ICPE-9000) to measure the concentration of remaining meal ions in the clear solution. Adsorption rate curve is tested by adding 10 mg absorbent into 25 mL arsenates solution. At different time interval, certain amount of solution are fetched and filtrated by 0.2 µm membranes and analyzed by ICPE-9000.

For selectivity experiment, 10 mg adsorbent was added in 25 mL mixing solution (As(V) 10 ppm, disturbing ions 50 ppm). Disturbing ions are introduced by using sodium salt NaCl, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub> respectively.

#### **1.4 Desorption Experiments**

For desorption of arsenate from adsorbent, different desorption condition are tested (Table S2). Different dilute HCl concentrations are used from 0.01 M, 0.05 M to 0.1 M. Shaking bed and ultrasound are also evaluated. The optimized desorption condition is 10 mg sample with 25 mL 0.05 M dilute HCl by shaking bed overnight. After the treatment, residual As(V) concentration is detected by ICP-OES.

#### 1.5 Mössbauer Spectroscopy Test

Transmission Mössbauer spectroscopy tests were carried out under room temperature using a conventional constant-acceleration spectrometer and <sup>57</sup>Co source. Velocity calibrations were performed by using  $\alpha$ -Fe foil. All isomer shifts are given relative to that of  $\alpha$ -Fe.



Element	weight	Atom number	
	%	%	
СК	28.60	40.31	
ОК	50.38	53.32	
Fe K	21.02	6.37	
Total	100.00		

Figure S1.	EDS	analysis	and	reports.
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Figure S2. Electron diffraction pattern of MIL-100(Fe) along crystallographical zone axis [001].



**Figure S3.** Adsorption rate curve of MIL-100(Fe) in 10 ppm arsenate solution (0.4 g/L) at room temperature.



**Figure S4.** Pore size distributions (a) before (b) after the adsorption of arsenates from N<sub>2</sub> sorption isotherms (calculated by NLDFT model: N<sub>2</sub> at 77 K on silica (cylindr./sphere. pore, NLDFT ads. model)).



**Figure S5.** FT-IR spectra of HAsO<sub>4</sub><sup>2-</sup> in dissolved species.



Figure S6. TG curve of iron trimesate under air ambience (10  $^{\circ}$ C/min to 600 $^{\circ}$ C, hold at 50 $^{\circ}$ C for 30 min).



Figure S7. Elements dispersion of TEM mapping images after saturated adsorbed in 100 ppm  $AsO_4^{3-}$  solution.

Table S1. Arsenate selectivity experiments of MIL-100(Fe) in 10 ppm arsenate solution with	50
ppm disturbing ions.	

MIL-100(Fe)	Disturbing Ions			
	As(V) Cl <sup>-</sup>	As(V) CO <sub>3</sub> <sup>2-</sup>	As(V) SO <sub>4</sub> <sup>2-</sup>	As(V) NO <sub>3</sub> -
Before adsorb/ppm	10 50	10 50	10 50	10 50
As(V) residual/ppm	1.48	0	1.12	1.31

Desorption Method	Repeat	Initial-concentration /ppm	Equilibrium concentration/ppm	Desorption concentration/ppm	Blank/ppm
Shaking bed	1	10	0.739	2.11	0.118
	2	10	0.725	1.92	0.0949
Ultrasound	1	10	0.686	1.94	0.0343
	2	10	0.687	1.93	0.0139

**Table S2.** Desorption experiments of MIL-100(Fe) in 10 ppm arsenate solution by HCl solution with different concentration.

0.01 mol/L HCl

Desorption Method	Repeat	Initial-concentration /ppm	Equilibrium concentration/ppm	Desorption concentration/ppm	Blank/ppm
Shaking bed	1	10	1.04	7.07	0.226
	2	10	0.926	7.31	0.235
Ultrasound	1	10	1.11	7.22	0.284
	2	10	1.04	7.31	0.269

0.05 mol/L HCl

Desorption Method	Repeat	Initial-concentration /ppm	Equilibrium concentration/ppm	Desorption concentration/ppm	Blank/ppm
Shaking bed	1	10	0.804	8.58	0.846
	2	10	0.757	8.82	0.00
Ultrasound	1	10	0.526	9.52	0.00
	2	10	0.508	8.87	0.00

0.1 mol/L HCl

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