Supplementary information

Insights into binding manners of a Fe doping MOF-808 in high-

performance adsorption: A case of antimony adsorption

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Section S1

Chemicals

All chemicals in this study were analytical grade. N, N-dimethylformamide (DMF), anhydrous acetone, formic acid (purity >98%), zirconium oxychloride octahydrate (ZrOCl2·8H₂O), Benzenetricarboxylic acid (H₃BTC), and ferric chloride (FeCl₃) were used for the synthesis of MIL-100, MOF-808 and $Zr_xFe_{(1-x)}$ -MOF-808. Sb(V) and Sb(III) stock solutions (1 g L⁻¹) were prepared by dissolving H₆KO₆Sb and C₈H₁₈K₂O₁₅Sb₂ in deionized (DI) water, respectively.

Section S2

MOF-808 Synthesis

 H_3BTC (0.28 g, 1.33 mmol) and ZrOCl₂·8H₂O (1.293 g, 4 mmol) in a solvent mixture of DMF/formic acid (60 mL/60 mL) were placed in a 200 mL Teflon-lined stainless steel autoclaves, which was heated at 130 °C for 2 days. Opalescent liquid were collected and washed three times with 10 mL of fresh DMF. As synthesized MOF-808 was rinsed with 10 mL of anhydrous DMF three times per day for 3 days, and immersed in 10 mL of anhydrous acetone for 3 days, during which time the acetone was replaced three times per day. Acetone exchanged crystals were activated on a vacuum dryer, followed by evacuation at 150 °C for 24 h.

Section S3

Characterization

The crystal structure of the MOFs was analyzed using X-ray diffraction (XRD) analysis (PAN'Alytical X'Pert Alpha 1, using Cu K- α 1, λ = 1.5406 Å). Specific surface areas (BET) of the samples were investigated using a F-Sorb 3400 automatic surface area Gold APP Instrument. The morphology of the adsorbents was examined using a scanning electron microscope (LEO 1530 field emission SEM). Prior to imaging, the sample was sputtered with gold in a vacuum condition for 30 s (Emitech K575 Sputter Coater, Emitech Ltd., Ashford Kent, UK). X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode (Al-K α = 1486.7 eV).

Section S4

Adsorption Isotherms

The adsorption isotherms of Sb(V) and Sb(III) with different materials ($Zr_xFe_{(1-x)}$ -MOF-808 (x=0.2, 0.4, 0.5, 0.8, 0.9) and MOF-808) were conducted by adding 20 mg of MOFs and 20 mL with the different initial concentration of the Sb(V) and Sb(III) solution (range from 100 to 1000 mg L⁻¹) in 100 ml conical flask at 25 °C. All of the suspensions were sealed and stirred at 180 rpm. After shaking for 12 h, the residual concentrations in solution were analyzed. The dosage of adsorbents for all the experiments was 1 g L⁻¹. Then, the supernatant was filtered using 0.22 µm filter. The initial and residual concentrations of Sb were determined using an atomic absorption spectroscopy. The adsorption capacity (q_e) for both Sb(V) and Sb(III) were calculated

according to eq 1, and the data were evaluated by both Langmuir (eq 2) and Freundlich (eq 3) isotherm:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{eq s1}$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{eq s2}$$

$$qe = K_F C_e^{\frac{1}{n}}$$
 (eq s3)

Where $q_e (mg g^{-1})$ is the equilibrium adsorption capacity; C_0 and $C_e (mg L^{-1})$ are the initial and equilibrium concentrations of adsorbents in the solution, respectively; V is the volume (mL) of the Sb aqueous solution; and m is the mass (mg) of the adsorbent used in the experiment. In eq 2, $q_m (mg g^{-1})$ and $K_L (L mg^{-1})$ are the Langmuir parameters; q_m represents the maximum adsorption capacity; and K_L is adsorption equilbrium constant. Meanwhile, in eq 3, $K_F (mg^{1-(1/n)}L^{1/n}g^{-1})$ and 1/n are the Freundlich parameters for values in the range of 0 < n < 1, which indicates favorable adsorption.

Adsorption Kinetics

Adsorption kinetics was conducted at 25 ± 0.2 °C by adding 400 mg of MIL-100, Zr_{0.8}Fe_{0.2}-MOF-808, MOF-808 into a 400 mL solution respectively. The initial Sb(V) and Sb(III) concentrations were 400 mg L⁻¹ and 200 mg L⁻¹ with constantly stirred on the magnetic stirrers. Samples were taken at 20 times. After shaking the sample for 120 min, the sample was centrifuged at 14000 rpm for 10 min to separate the adsorbent. The residual concentrations for both the Sb(V) and Sb(III) ions in the clarified solution were also determined using an atomic absorption spectroscopy. The adsorption kinetic data were analyzed using the pseudo-first-order and the pseudo-second-order models. The pseudo-first-order and the pseudo-second-order are expressed as eq 4 and 5, respectively.

$$q_{t} = q_{e} \left(1 - e^{K_{1}t} \right)$$
 (eq s4)
$$q_{t} = \frac{q_{e}^{2}K_{2}t}{1 + q_{e}K_{2}t}$$
 (eq s5)

Where q_e is the amount of adsorbed at equilibrium (mg g⁻¹); q_t is the amount of adsorbate (mg g⁻¹) at time t (min); and K₁ (min⁻¹) and K₂ (g mg min⁻¹) are the rate constants for the pseudo-first and second-order sorption, respectively.

Section S5

Effect of Interfering ion

In order to evaluate the effect of the interfering ions on both the Sb(V) and Sb(III) adsorption, three different anion (SO₄²⁻, NO₃⁻, PO₄⁻, F⁻) were mixed with Sb(V) or Sb(III) in equal molar amount. 20 mg of $Zr_{0.8}Fe_{0.2}$ -MOF-808 and MOF-808 were added into 20 mL of Sb(V) or Sb(III) , which had an initial concentration of 100 mg L⁻¹ and a specific pH value which maintained between 1.0 to 13.0. The mixture was shaken at 25.0 ± 0.2 °C for 12 h and analyzed in the same way, as described in the adsorption isotherm experiments.

Effect of pH

The pH of the aqueous solution was adjusted and maintained between 1.0 to 13.0 using 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH. 20 mg of $Zr_{0.8}Fe_{0.2}$ -MOF-808 and MOF-808 were added into 20 mL solutions of Sb(V) or Sb(III) , which had an initial

concentration of 400 mg L⁻¹, 200 mg L⁻¹ and a specific pH value. The mixture was shaken at 25.0 ± 0.2 °C for 12 h and analyzed in the same way, as described in the adsorption isotherm experiments.

Recycling experiments

The recycling of the material is not only one of the important indicators in its adsorption performance, but also has a great reference value for its practical application. In order to examine the recycling ability of the materials, four recycling experiments were conducted. 100 mg of adsorbents (MOF-808, $Zr_{0.8}Fe_{0.2}$ -MOF-808) were added to 100 ml of Sb(V) or Sb(III) solution with a concentration of 400 mg L⁻¹ or 200 mg L⁻¹. After the adsorption equilibrium, the two materials were eluted by using 0.1 mol L⁻¹ HCl until the eluate was free of Sb. The adsorption-desorption process was repeated four times under the same condition, finally the change of the adsorption capacity was calculated each time.

Section S6

A plane-wave basis set with a kinetic-energy cut-off of 400 eV was used to expand the wave function of valence electrons. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used for describing the exchange-correlation interactions.¹ The structural relaxations were performed by computing the Hellmann–Feynman forces within the total energy and force convergences of 10^{-4} eV and 0.01 eV/Å, respectively. The Brillouin-zone integration was sampled with $1 \times 1 \times 1$ k-points Monkhorst-Pack mesh.

Figures



Fig. S1. The fitting of isothermal adsorption data of Sb(V) (a,c) and Sb(III) (b,d) to the Langmuir and Freundlich models.



Fig. S2. Adsorption kinetics for Sb(V) (a) and Sb(III) (b) adsorption on $Zr_{0.8}Fe_{0.2}$ -MOF-808 and MOF-808; The fitting of kinetic data of Sb(V) (c, e) and Sb(III)(d, f) to the pseudo-first-order and pseudo-second-order models. The initial Sb(V) and Sb(III) concentration were 400 mg L⁻¹ and 200 mg L⁻¹; adsorbent dose was 1 g L⁻¹; the solution volume was 400 mL; the temperature was 25 °C.



Element	Weight%	Atomic%		
СК	37.25	57.04		
ОК	31.49	36.21		
Fe K	3.53	1.16		
Zr L	27.73	5.59		
Totals	100.00			

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Element	Weight%	Atomic%
СК	40.35	58.90
ОК	31.89	34.95
Fe K	3.22	1.01
Zr L	24.54	5.14
Totals	100.00	

Fig. S3. SEM-EDS of $Zr_{0.8}Fe_{0.2}$ -MOF-808.



Fig. S4. The results of structural optimization. (a) The SBU and adjacent organic ligand of MOF-808; (b) The SBU and adjacent organic ligand of Zr_{0.8}Fe_{0.2}-MOF-808;
(c) Sb(V) and (d) Sb(III).



Fig. S5. The calculated models and adsorption energies for all adsorption methods to Sb(V).



Fig. S6. The calculated models and adsorption energies for all adsorption methods to Sb(III).

Tables

Table S1. Langmuir and Freundlich fitting parameters for Sb(V) (left) and Sb(III)

(right) adsorption on $Zr_{0.8}Fe_{0.2}$ -MOF-808 and MOF-808.

	Adsorbate	Lar	ngmuir model		Freundlich model		
Adsorbents		$Q_e (mg g^{-1})$	$K_L(L mg^{-1})$	R ²	1/n	$K_F(mg^{1\text{-}(1/n)}L^{1/n}g^{-1})$	R ²
Zr _{0.8} Fe _{0.2} -MOF-808	Sb(V)	526.3	0.0599	0.9924	0.182	164.82	0.987
MOF-808		303.1	0.0143	0.9863	0.217	64.714	0.942
Zr _{0.8} Fe _{0.2} -MOF-808	Sb(III)	343.6	0.0131	0.9924	0.330	38.371	0.9610
MOF-808		0.9924	0.0179	0.9828	0.162	65.313	0.9154

Adsorbents	Adsorbate	Pseudo	-first-order n	nodel	Pseudo-second-order model			
		$K_1(min^{-1})$	Q ₀ (mg g ⁻¹)	R ²	K ₂ (g mg min ⁻¹)	Q ₀ (mg g ⁻¹)	R ²	
Zr _{0.8} Fe _{0.2} -MOF-808	Sb(V)	0.06259	219.5	219.5	0.000687	312.5	0.9975	
MOF-808		0.0381	64.88	0.9158	0.0233	136.99	0.9959	
Zr _{0.8} Fe _{0.2} -MOF-808	Sb(III)	0.0339	100.77	0.9646	0.000964	163.93	0.9973	
MOF-808		0.0183	40.54	0.6577	0.00282	80.65	0.9902	

Table S2. Pseudo-first-order model and Pseudo-second-order model kinetics fittingparameters for Sb(V) and Sb(III) adsorption on the $Zr_{0.8}Fe_{0.2}$ -MOF-808 and MOF-808.

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	Connection	Binding energy	Binding energy	Binding energy after adsorption	
Materials	Connection	before	after adsorption		
	mode	adsorption (eV)	of Sb(V) (eV)	of Sb(III) (eV)	
7 . Eo	O=C-O	532.76	532.99	532.65	
$\Sigma r_{0.8} F e_{0.2}$ -	Zr-OH	530.91	531.23	531.24	
MOF-808	Fe-OH	530.09	530.31	530.30	
MOF-808	0=C-O	532.18	532.30	532.58	
	Zr-OH	530.35	530.09	529.94	

 Table S3. Specific data of XPS binding energy.

Chemical bond	Adsorbate	Bond length (MOF-808)(Å)			Bond length (Zr _{0.8} Fe _{0.2} -MOF-808) (
Adsorption model		1	2	3	1	2	3	4
Zr-O (Fe-O)	Sb(V)	1.911	2.092/2.165	2.144/2.247	1.899	2.114/2.174	2.129/2.189	1.723
	Sb(III)	1.962	2.112/2.162	2.095/2.208	1.944	2.108/2.155	2.122/2.196	1.767
Sb-O	Sb(V)	2.012	2.079	2.038	2.028	2.051	2.048	2.076
	Sb(III)	1.994	2.014	2.057	2.004	2.014	2.047	2.024

Table S4. The results of the bond length calculations.

References

1 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 1996, 77(18), 3865-3868.