Supporting Information

A robust MOFs-based trap with high-density active alkyl thiol for the super-efficient capture of mercury

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Experimental details

1.1 Chemicals and materials.

ZrCl₄, formic acid (FA), hydrochloric acid (HCl, 37%), Hg(NO₃)₂ (1 mg/mL, 2%-5% HNO₃), N,N-dimethylformamide (DMF), ethanol, acetone, acetonitrile, dichloromethane, deuterated water (D₂O), and dimethyl sulfoxide (DMSO) were purchased from J&K Scientific Ltd., Beijing, China. Mercaptosuccinic acid (MSA) were obtained from Bide Pharmatech Ltd. Pb(NO₃)₂, Cd(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Mg(NO₃)₂·6H₂O and NaNO₃ were purchased from Sinopharm Chemical Reagent Co., Ltd, China. The applied water (18.1 MΩ·cm⁻¹) in the experiments was obtained from an NW Ultrapure Water System (Heal Force, China). All the reagents were used as-received without further purification.

1.2 Synthesis of Zr-MSA.

233 mg (1.0 mmol, 1 eq) ZrCl₄ and 150 mg (1.0 mmol, 1 eq) MSA were dissolved in 2 mL water. After ultrasonic for 1 min, different amounts of FA (0, 0.04, 0.08, 0.12, 0.16 and 0.20 mL, 0-5 eq) were added to the solution, then the mixture was kept in an oven at 80 °C for 2 h. A white powder of Zr-MSA was collected by centrifugation and washed with H₂O three times. Finally, the resulting samples were dried at 80°C for 24 h in a vacuum oven. Yield: 256 mg (90.2 %) for 4 eq FA. The Zr-MAS obtained with 4 eq FA could be expressed concretely as $Zr_6O_4(OH)_4(MSA)_{5.61}FA_{0.78}$. Calculated: Zr, 35.39%; C, 18.05%; O, 33.17%; S, 11.63%; H, 1.76%. Found: Zr, 35.57%; C, 18.11%; O, 32.66%; S, 11.88%; H, 1.78%).

1.3 Large-scale synthesis of Zr-MSA.

All raw materials are enlarged 100 times and kept at the same temperature and washing conditions as the low-dose synthesis of Zr-MSA. Finally, a 26.4 g sample with a space-time yield of 1473 kg m⁻³ day⁻¹ was obtained. Yield: 93.0 %.

1.4 Hg²⁺ ions sorption kinetics.

20.0 mg Zr-MSA was dispersed to 40 mL Hg²⁺ ions solution (pH = 2, 10 ppm), then the suspension was placed on a platform shaker and shaken at 200 rpm in a closed vessel at room temperature. At predetermined time intervals (1, 2, 5, 10, 30, 60, 120, and 240 min), 2 mL suspension was filtered through a 220 nm membrane filter, then the remaining Hg²⁺ ions content in filtrates was analyzed by ICP-MS.

1.5 Effect of pH.

10.0 mg Zr-MSA was dispersed to 20 mL Hg^{2+} ions solution (10 ppm) with different pH (0-7), then the suspensions were shaken at 200 rpm at room temperature for 12 h and then were filtered separately through a 220 nm membrane filter. The remaining Hg^{2+} ions content in filtrates was analyzed by ICP-MS.

1.6 Hg²⁺ ions sorption isotherm.

10.0 mg Zr-MSA was dispersed to each 40 mL Hg²⁺ ions solution (pH = 2) with $_3$

different concentrations. The suspensions were shaken at 200 rpm at room temperature for 12 h, and then were filtered separately through a 220 nm membrane filter. The remaining Hg²⁺ ions content in filtrates was analyzed by ICP-MS or ICP-OES.

1.7 Ion selectivity tests.

50.0 mg Zr-MSA was dispersed to 50 mL Hg²⁺ ions solution (pH = 2) containing Pb²⁺, Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Ca^{2+} , Mg^{2+} and Na^+ ions. The concentration of each ion is set at 10 ppm. The suspension was shaken at 200 rpm at room temperature for 12 h, and then was filtered separately through a 220 nm membrane filter. The remaining ions content in filtrates were analyzed by ICP-MS or ICP-OES.

1.8 Regeneration of Zr-MSA.

8 mg Zr-MSA was dispersed to 32 mL HgNO₃ (pH = 2, 540 ppm), and the suspension was shaken at 200 rpm at room temperature for 12 h. The mixture is separated by centrifugation. Hg^{2+} ions content in supernatant was determined by ICP-OES, and the solid was immersed in 6 mL HCl solution (6.0 M) for 6 h to remove Hg^{2+} ions. Then the solid was washed two times with water then put into the next cycle as a new adsorbent.

1.9 Instruments and methods.

Powder X-ray diffraction (PXRD) patterns were measured at a scan rate of 8° min⁻¹ on Bruker D8 equipped with Cu K α radiation (40 kV, 40 mA). N₂ sorption isotherms were recorded on Micromeritics Tristar 3020 porosimeter at -196 °C. All the samples were degassed under vacuum at 80 °C for 12 h before measurements. The surface areas were determined by the Brunauer-Emmett-Teller (BET) method using adsorption data. Thermogravimetric (TG) analysis was performed using a Perkin-Elmer thermogravimetric analyzer under a N₂ flow (50 mL min⁻¹) at a ramp rate of 10 °C/min from 25 to 800 °C. Field emission scanning electron microscopy (FE-SEM) was taken with a Hitachi S-4800 electron microscope. FT-IR spectra were performed with a resolution of 4 cm⁻¹ using the KBr method on a Nicolet 7000-C spectrometer. ¹H nuclear magnetic resonance (¹H NMR) spectra were obtained from a Bruker Avance III 400. The X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VG Micro-MK II instrument. Intrepid inductively coupled plasma optical emission spectrometry (ICP-OES) was employed to determine the concentration of target metals ions. The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for trace metal detection.

The Zr-MSA was digested by NaOH solution for ¹H NMR measurement. Specifically, 20 mg MOFs and 20 mg NaOH were added to 0.6 mL D₂O, the mixture was then dispersed by ultrasound, and was kept at room temperature for 1 h. The supernatant obtained by centrifugation was used for the ¹H NMR measurement. We have added the specific details to the experimental part.

Two traditionally used isotherms including Langmuir and Freundlich models were employed to quantify and compare the performance of the three different adsorbents. The Langmuir model is presented as the following equation (Eqn S1):

$$q_e = \frac{k_L q_{max} C_e}{1 + k_L C_e} \tag{S1}$$

where $C_e \pmod{L^{-1}}$ is the equilibrium concentration of Hg^{2+} solution, q_e represents the adsorption capacity of Hg^{2+} at equilibrium (mg g⁻¹), k_L means the Langmuir constant (L mg⁻¹)

related to adsorption energy and affinity of binding sites, and q_{max} denotes the maximum adsorption capacity (mg g⁻¹).

Freundlich adsorption equation (Eqn S2) has the linear form as following:

$$q_e = k_F C_e^{(n)} \tag{S2}$$

 k_F (mg¹⁻ⁿ Lⁿ g⁻¹) is Freundlich constant related to the adsorption capacity of the adsorbent and n denotes adsorption intensity. The value of n reflects the type of isotherm to be favorable (0 < n < 1), irreversible (n = 0) or unfavorable (n > 1).

The kinetic data were fitted with the pseudo-second-order kinetic model using the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(S3)

where $q_e (mg/g)$ and $q_t (mg/g)$ are the amount of Hg^{2+} ions adsorbed at equilibrium and at time t (min), respectively; t (min) is adsorption time and k_2 (g/mg/min) is the pseudo-second-order adsorption rate constant.

The distribution coefficient (K_d) was also calculated to quantify the affinity of Zr-MSA for Hg^{2+} ions by the following equation:

$$K_d = \frac{\left(C_i - C_f\right)}{C_f} \times \frac{V}{m} \tag{S4}$$

where C_i and C_f represent the initial metal ion concentration and the final equilibrium metal ion concentration, respectively, V (mL) is the volume of the treated solution and m (g) is the mass of sorbent used.



Fig. S1 Power XRD patterns of Zr-MSA synthesized with different formic acid (FA) amount.

FA (eq)	S _{BET} ^(a) (m ² /g)	S _{micro} ^(b) (m ² /g)	S _{ext} ^(c) (m ² /g)	V _t ^(d) (cm ³ /g)	V _{micro} ^(e) (cm ³ /g)
0	165	6.6	158.4	0.155	0.003
1	440	147	293	0.758	0.062
2	448	219	229	0.985	0.089
3	492	296	196	1.200	0.119
4	516	350	166	0.597	0.139
5	497	379	118	0.365	0.150

Table S1. Textural parameters for the Zr-MSA synthesized with different FA amount.

(a) S_{BET} is the BET surface area. (b) S_{micro} is the t-plot micropore surface area calculated from the N₂ sorption isotherm. (c) S_{ext} is the extra surface area estimated by subtracting S_{micro} from S_{BET} . (d) V_t is the single point adsorption total pore volume at P/P₀= 0.99. (e) V_{micro} is the t-Plot micropore volume.



Fig. S2 SEM images (a-f) of Zr-MSA synthesized with different FA amount (a, 0 eq; b, 1 eq;

c, 2 eq; d, 3 eq; e, 4 eq; f, 5 eq). TEM images (g-i) of Zr-MSA synthesized with 4 eq FA.



Fig. S3 PXRD patterns of the as-synthesized Zr-MSA and Zr-MSA-Scale.



Fig. S4 N₂ sorption isotherms of the as-synthesized Zr-MSA and Zr-MSA-Scale.



Fig. S5 TGA profile of the as synthesized Zr-MSA recorded at air atmosphere.



Fig. S6 The photographs of Zr-MSA treated at different temperatures. In particular, the gray-black color of the Zr-MSA at 550 °C indicates that that the organic component of incomplete combustion still exists.



Fig. S7 PXRD patterns of the tetragonal ZrO₂ and Zr-MSA treated at different temperatures.



Fig. S8 PXRD patterns of pristine Zr-MSA and samples treated with different organic

solvents for 24 h.



Fig. S9 PXRD patterns of pristine Zr-MSA and samples treated with different acidic or basic aqueous solutions for 24 h.



Fig. S10 N_2 sorption isotherms of pristine Zr-MSA and the samples treated with concentrated HCl, water and NaOH (pH = 12) aqueous solutions for 24 h



Fig. S11 (A) Hg^{2+} adsorption isotherm for Zr-MSA after 12 h at pH = 2. The equilibrium adsorption data fitted were by Langmuir adsorption model (B) and Freundlich model (C).

Samplas	Langmuir models			
Samples —	k _L (L mg ⁻¹)	$q_{\scriptscriptstyle max}({ m mg~g}^{-1})$	R ²	
Zr-MSA	0.030	734	0.999	

Table S2. Langmuir equation parameters for Hg^{2+} ions adsorption onto the as-prepared Zr-MSA.



Fig. S12 (A) Adsorption curve of Hg²⁺ versus contact time in aqueous solution. (B) Pseudo-second-order kinetic plot of Hg adsorption onto Zr-MSA.

Table S3 Kinetic parameters of pseudo-second-order models for Hg²⁺ ions on Zr-MSA.

Somulas	pseudo-second-order models			
Samples —	k ₂ (g mg ⁻¹ min ⁻¹)	$q_e (\mathrm{mg \ g^{-1}})$	R ²	
Zr-MSA	15.33	20	1	



Fig. S13 PXRD patterns of Zr-MSA samples treated with 10 ppm Hg²⁺ ions solution with different pH.



Fig. S14 Adsorption selectivity of Zr-MSA for Hg^{2+} ions. The concentration of each ion is set to be 10 ppm under pH = 2.



Fig. S15 N₂ sorption isotherms of the as-synthesized Zr-MSA and Hg-adsorbed Zr-MSA.



Fig. S16 Wide scan XPS spectra (A), magnified Hg 4f (B), C 1s (C), O 1s (D), and Zr 3d (E) XPS spectra of Zr-MSA (black) and Hg²⁺-loaded Zr-MSA (red). (F) S 2p XPS spectra of Zr-MSA (black, low panel) and Hg²⁺-loaded Zr-MSA (red, top panel).



Fig. S17 S 2p XPS spectra of Zr-MSA (black, low panel) and Hg²⁺-loaded Zr-MSA (red, top

panel).