

# Supporting Information

## One-pot synthesis of sulfonic acid functionalized Zr-MOFs for rapid and specific removal of radioactive Ba<sup>2+</sup>

Peijia Liu,<sup>a</sup> Pengfei Yang<sup>b</sup>, Jian Yang,<sup>a</sup> and Jinlou Gu<sup>\*,a</sup>

<sup>a</sup>Shanghai Engineering Research Center of Hierarchical Nanomaterials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

<sup>b</sup>Skshu Paint Co., Ltd., Fujian Key Laboratory of Architectural Coating, 518 North Liyuan Avenue, Licheng District Putian, Fujian, 351100, China

**E-mail:** [jinlougu@ecust.edu.cn](mailto:jinlougu@ecust.edu.cn)

Fax: +86-21-64250740; Tel: +86-21-64252599

# Experimental details

## 1.1 Chemicals and materials

Zirconium chloride ( $ZrCl_4$ ) were received from J&K Scientific Ltd., Beijing, China. Mercaptosuccinic acid (SUC-SH) was purchased from Bide Pharmatech Ltd. HCl, NaOH, formic acid (FA), hydrogen peroxide ( $H_2O_2$ ), ethanol, methanol, dichloromethane, acetonitrile, acetone, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were obtained from Shanghai Titanchem Scientific Co.Ltd.  $BaCl_2 \cdot 2H_2O$  and other metal salts were purchased from Aladdin Biochemical Technology Co., Ltd. The applied water used in all the experiments was obtained from an NW Ultrapure Water System (Heal Force, China). All reagents are used directly without further purification.

## 1.2 Synthesis of adsorbents

**Optimized synthesis of Zr-SUC-SO<sub>3</sub>H.**  $ZrCl_4$  (466 mg, 2 mmol) and FA (160  $\mu$ L, 4 mmol) were ultrasonically dissolved in deionized water (2 mL). SUC-SH (100 mg, 0.66 mmol) were ultrasonically dissolved in the  $H_2O_2$  (500  $\mu$ L, 5 mmol) and then added to deionized water (500  $\mu$ L). After mixing the above two solutions, the mixture was allowed to stand for 10 min. to decompose the excess  $H_2O_2$ , and then heated at 80 °C for 8 h. The resulting white powders were collected by centrifugation and washed three times at room temperature with ethanol. Finally, the obtained Zr-SUC-SH was dried in a vacuum oven at 60 °C for 12 h. Other exploration conditions are similar to the above,

but the amounts of reagents were changed. The specific amounts of reagents in the synthesis of Zr-SUC-SO<sub>3</sub>H were summarized in **Table S1**. For the large scale synthesis of Zr-SUC-SO<sub>3</sub>H, all the chemicals used in the above-mentioned procedures were enlarged to 100-fold.

**Synthesis of Zr-SUC-SH.** This synthesis method is based on our previous reports.<sup>1</sup> ZrCl<sub>4</sub> (233 mg, 1 mmol) and SUC-SH (150 mg, 1 mmol) were dissolved in 2 mL water. After ultrasound for 1 min, FA (0.16 mL) was added to the solution, then the mixture was kept in an oven at 80 °C for 2 h. A white powder of Zr-SUC-SH was collected by centrifugation and washed with H<sub>2</sub>O three times. Finally, the resulting Zr-SUC-SH were dried at 80 °C for 24 h in a vacuum oven.

### 1.3 Characterization

Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 instrument with Cu K $\alpha$  radiation (40 kV, 40 mA) at a scan speed of 8° min<sup>-1</sup> over the range of 5°-40°. The N<sub>2</sub> sorption data were recorded on Micromeritics Tristar 3020 porosimeter at 77 K to calculate BET (Brunauer-Emmett-Teller) surface area, and all samples were degassed under vacuum at 80 °C for 12 h before measurements. Fourier transform infrared spectrum (FT-IR) was performed on a Nicolet 7000-C spectrometer with a resolution of 4 cm<sup>-1</sup> using the KBr method. Thermal stability of the as-synthesized MOFs was evaluated by a thermogravimetric (TG) analysis instrument (Perkin-Elmer thermogravimetric analyzer). The VG Micro-MK II instrument was used to measure X-ray photoelectron spectrometer (XPS). Scanning electron microscopy (SEM) images were obtained by the Hitachi S-4800 electron microscope. Intrepid inductively coupled

plasma optical emission spectrometry (ICP-OES) was applied to measure the concentration of Ba<sup>2+</sup>.

#### 1.4 Batch removal of Ba<sup>2+</sup>

Considering the toxicity of radioactive Ba<sup>2+</sup>, all the experiments used nonradioactive Ba<sup>2+</sup> instead of radioactive Ba<sup>2+</sup>. The different concentration of Ba<sup>2+</sup> solutions were prepared by dissolving BaCl<sub>2</sub>·2H<sub>2</sub>O of different masses into the deionized water. The pH values of Ba<sup>2+</sup> solutions were adjusted by 100 mM HCl or 100 mM NaOH aqueous solution. The adsorption experiments were carried out in a reagent vial at 25 °C for certain time. After adsorption, the liquid supernatant was separated by filtration and the concentrations of Ba<sup>2+</sup> in the supernatant were tested by ICP-OES. The equilibrium adsorption capacity ( $q_e$ ) (mg/g) and removal efficiency (R) for Ba<sup>2+</sup> were calculated as following equations:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (S1)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (S2)$$

in which  $q_e$  (mg/g) is the equilibrium adsorption capacity;  $V$  is the volume (mL) of the applied Ba<sup>2+</sup> solutions,  $C_0$  and  $C_e$  are the initial concentration and equilibrium concentration of Ba<sup>2+</sup> (mg/L), respectively; and  $m$  denotes the mass of adsorbent (g).

To further understand the adsorption kinetics of Ba<sup>2+</sup> over samples, the pseudo-first-order (Eqn S3) and pseudo-second-order (Eqn S4) were employed to fit experimental data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (S3)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (S4)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ ) represent the adsorption amounts at any time and at equilibrium, respectively, while  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant.

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 S5):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (S5)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of  $\text{Ba}^{2+}$  solution,  $q_e$  represents the adsorption capacity of  $\text{Ba}^{2+}$  at equilibrium ( $\text{mg g}^{-1}$ ),  $k_L$  means the Langmuir constant ( $\text{L mg}^{-1}$ ) related to adsorption energy and affinity of binding sites, and  $q_{max}$  denotes the maximum adsorption capacity ( $\text{mg g}^{-1}$ ).

Freundlich adsorption equation (Eqn S6) has the linear form as following:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (S6)$$

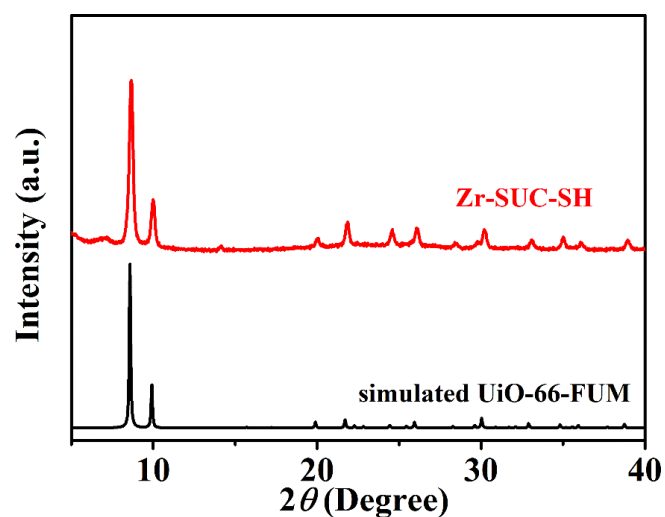
$k_F$  ( $\text{mg}^{1-n} \text{L}^n \text{g}^{-1}$ ) is Freundlich constant related to the adsorption capacity of the adsorbent and  $n$  is an empirical parameter.

### **Recycling experiment.**

The concentrations of  $\text{Ba}^{2+}$  ions and adsorbent dosage were set at 10 and 1000  $\text{mg/L}$ , respectively. We soaked the adsorbed Zr-SUC- $\text{SO}_3\text{H}$  in water ( $\text{pH} = 3$ ) for 6 h to desorb and wash the desorbed adsorbent with water three times, then put it into the next experiment as a new adsorbent and operate it in a cycle.

**Table S1.** The amounts of various reagents in the synthesis of MOFs and phase structure of the products.

Zr/SUC-SH (molar ratio)	Metal solution			Ligand solution			Results
	ZrCl <sub>4</sub> (mg)	H <sub>2</sub> O (mL)	FA (mmol)	SUC-SH (mg)	H <sub>2</sub> O <sub>2</sub> (mL)	H <sub>2</sub> O (mL)	
<b>1</b>	233	2	0	150	0.5	0.5	Unknown crystal
	233	2	1	150	0.5	0.5	Unknown crystal
	233	2	2	150	0.5	0.5	Amorphous phase
	233	2	3	150	0.5	0.5	Amorphous phase
	233	2	4	150	0.5	0.5	Amorphous phase
<b>2</b>	466	2	0	150	0.5	0.5	Mixed crystal
	466	2	1	150	0.5	0.5	Mixed crystal
	466	2	2	150	0.5	0.5	Mixed crystal
	466	2	3	150	0.5	0.5	Mixed crystal
	466	2	4	150	0.5	0.5	Unknown crystal
<b>3</b>	466	2	0	100	0.5	0.5	Amorphous phase
	466	2	1	100	0.5	0.5	Amorphous phase
	466	2	2	100	0.5	0.5	UiO-style crystal
	466	2	3	100	0.5	0.5	UiO-style crystal
	<b>466</b>	<b>2</b>	<b>4</b>	<b>100</b>	<b>0.5</b>	<b>0.5</b>	<b>UiO-style crystal</b>



**Fig. S1** PXRD patterns of the as-synthesized Zr-SUC-SH and simulated UiO type structure.

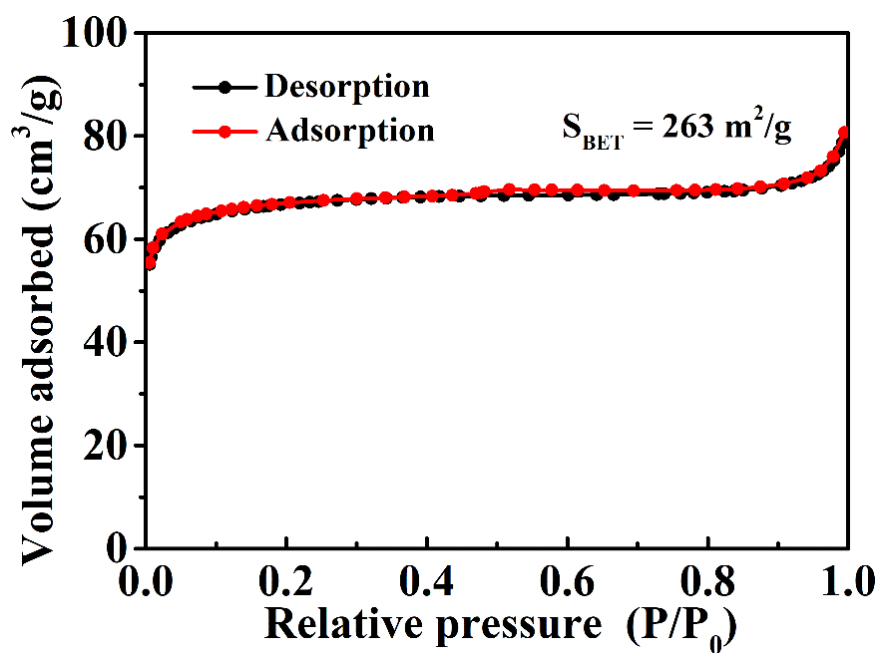


Fig. S2 N<sub>2</sub> sorption isotherms of the as-synthesized Zr-SUC-SO<sub>3</sub>H.

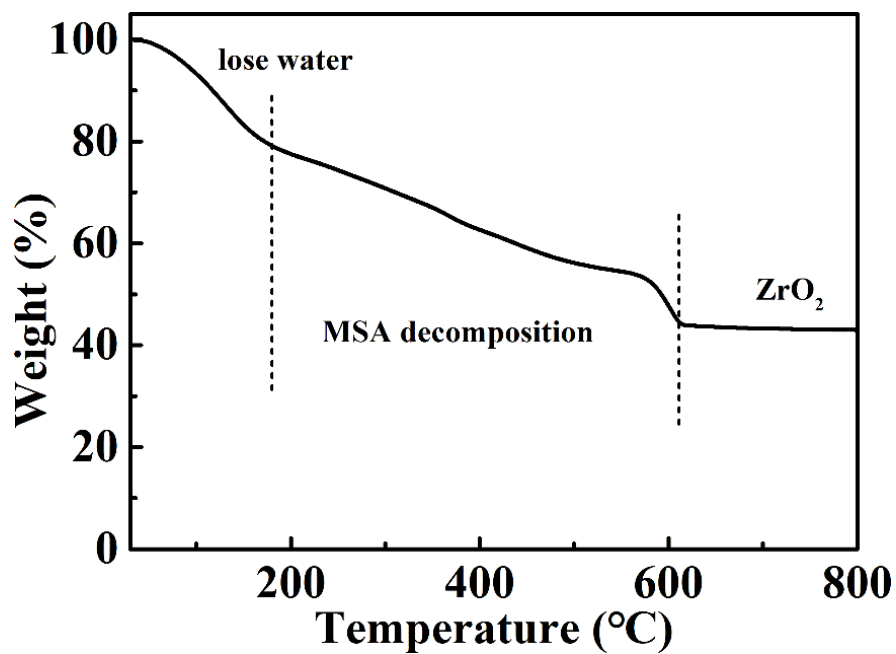
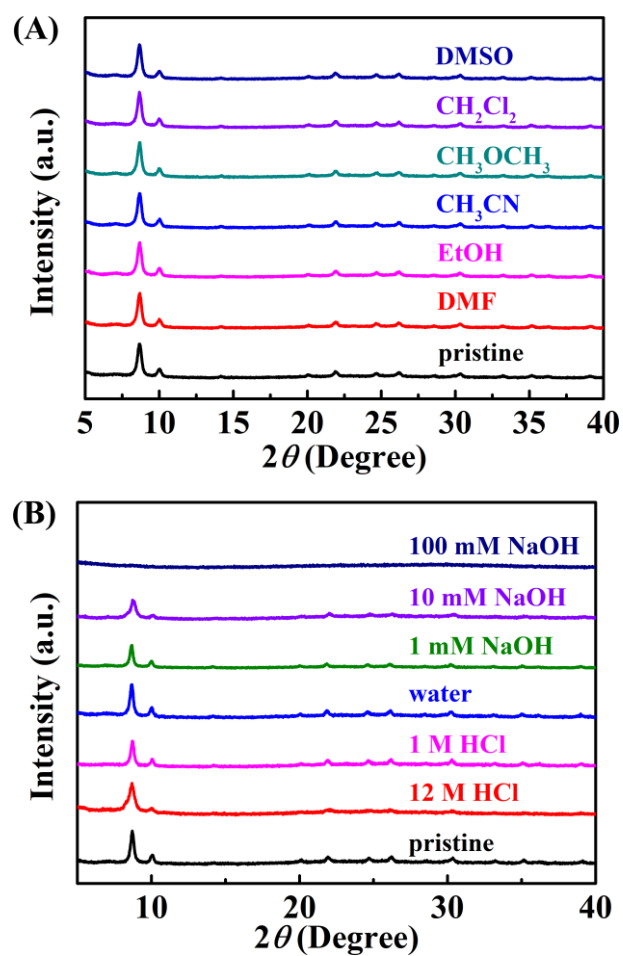
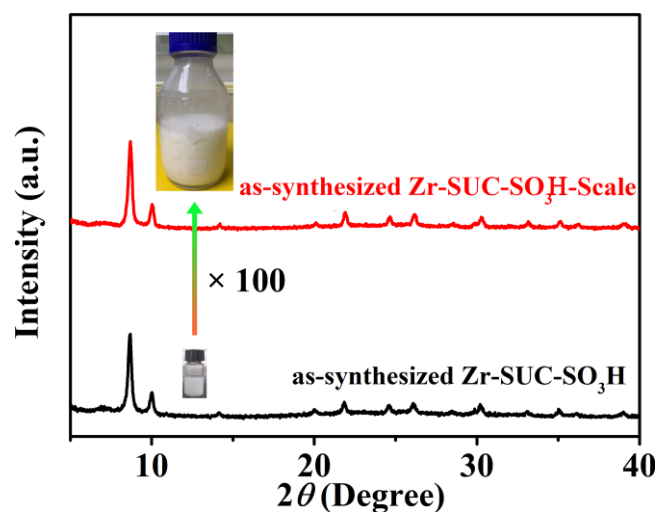


Fig. S3 TGA profile of the as-synthesized Zr-SUC-SO<sub>3</sub>H recorded at air atmosphere.

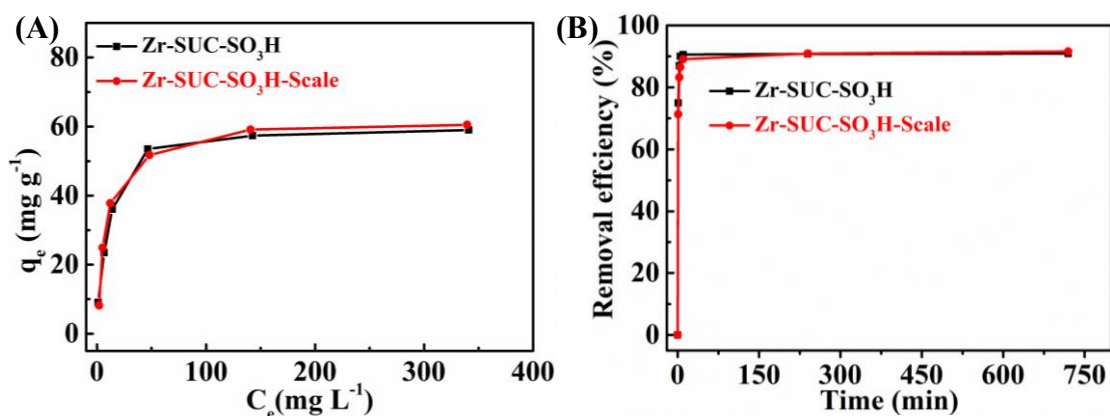


**Fig. S4** PXRD patterns of pristine Zr-SUC-SO<sub>3</sub>H and samples treated with different organic solvents (A), and acidic or basic aqueous solutions (B) for 24 h.



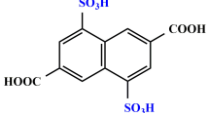
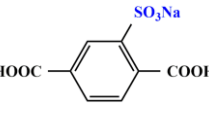
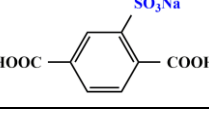
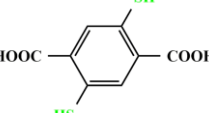
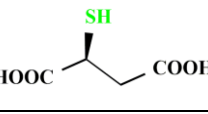
**Fig. S5** PXRD patterns of the as-synthesized Zr-SUC-SO<sub>3</sub>H and Zr-SUC-SO<sub>3</sub>H-Scale.

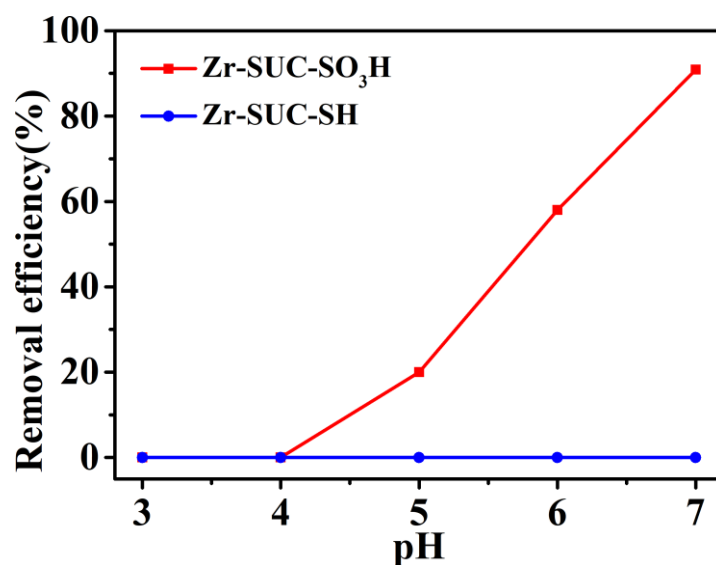




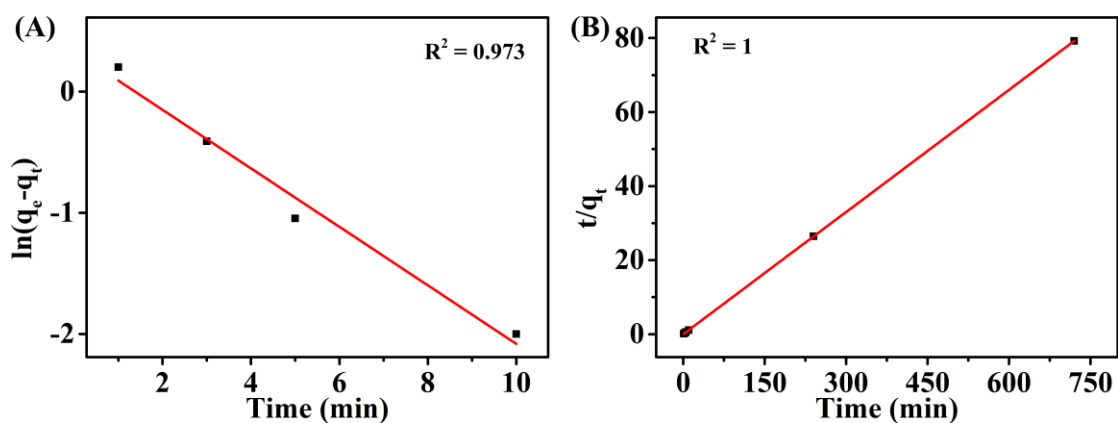
**Fig. S6** The adsorption isotherms (A) and adsorption kinetics (B) of Zr-SUC-SO<sub>3</sub>H produced in large-scale toward Ba<sup>2+</sup> ( $C_{\text{adsorbents}} = 1000 \text{ mg/L}$ ,  $C_{\text{Ba(II)}} = 10 \text{ mg/L}$ ,  $T = 25 \text{ }^\circ\text{C}$ ,  $\text{pH} = 7$ ).

**Table S1.** Comparison of linker availability and MOFs preparation condition of the reported sulfonic acid MOFs. **DMF:** N,N-Dimethylformamide; **DMA:** N,N'-dimethylacetamide; **AA:** acetic acid.

MOFs	Ligand	Ligand source	Solvent and excipients	Reaction Condition	Reference
BUT-8(Cr)		synthetic	DMF/HF	solvothermal 190 °C/24 h	2
MIL-101(Cr)-SO <sub>3</sub> H		commercial 25 g/22 \$ (TCI)	H <sub>2</sub> O/HCl	solvothermal 180 °C/6 d	3
UiO-66-SO <sub>3</sub> H		commercial 25 g/22 \$ (TCI)	DMA/FA	solvothermal 150 °C/24 h	4
UiO-66-(SO <sub>3</sub> H) <sub>2</sub>		synthetic	DMF/AA H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O <sub>2</sub>	Microwave 120 °C/40 min & RT oxidation	5
Zr-SUC-SO <sub>3</sub> H		commercial 25 g/22 \$ (TCI)	H <sub>2</sub> O/H <sub>2</sub> O <sub>2</sub> FA	80 °C/ 2h	This work



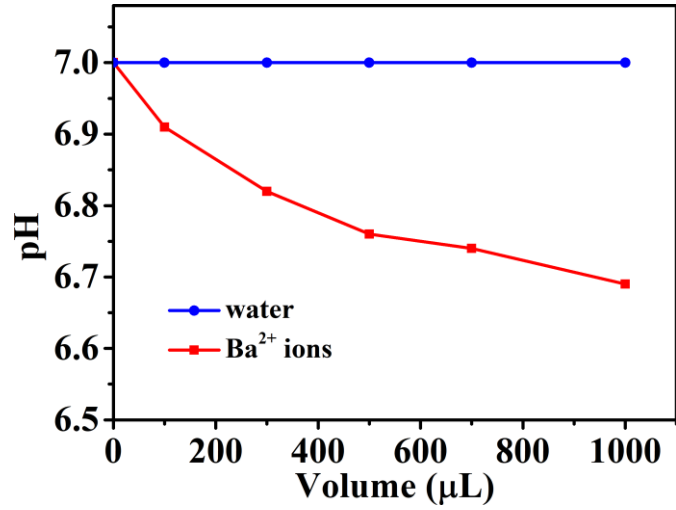
**Fig. S7** Removal efficiency of Ba<sup>2+</sup> (10 ppm) using the newly obtained Zr-SUC-SO<sub>3</sub>H and Zr-SUC-SH under different pH conditions.



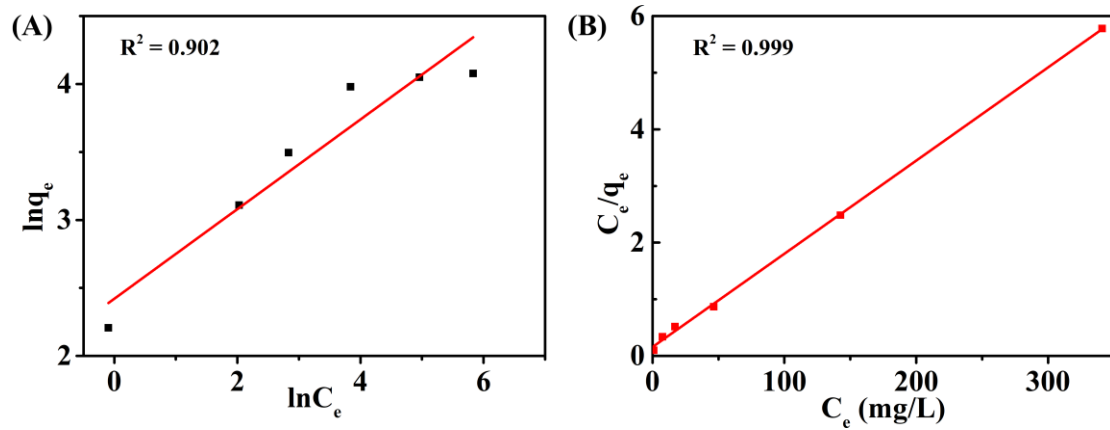
**Fig. S8** Pseudo-first-order (A) and pseudo-second-order kinetic plot of Ba<sup>2+</sup> adsorption onto Zr-SUC-SO<sub>3</sub>H (B).

**Table S2.** Kinetic parameters for the adsorption of Ba<sup>2+</sup> on Zr-SUC-SO<sub>3</sub>H ( $C_{\text{adsorbents}} = 1000 \text{ mg/L}$ ,  $C_{\text{Ba(II)}} = 10 \text{ mg/L}$ ,  $T = 25 \text{ }^\circ\text{C}$ ,  $\text{pH} = 7$ ).

pseudo-first-order kinetic			pseudo-second-order kinetic		
model			model		
$q_e \text{ (mg g}^{-1}\text{)}$	$k_1 \text{ (min}^{-1}\text{)}$	$R^2$	$q_e \text{ (mg g}^{-1}\text{)}$	$k_2 \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	$R^2$
2.15	0.556	0.973	9.09	0.848	1



**Fig. S9** The pH changes of Zr-SUC-SO<sub>3</sub>H solution (10 mL) with the addition of water (pH = 7.0) or Ba<sup>2+</sup> solution (1.0 mg/mL, pH = 7.0).



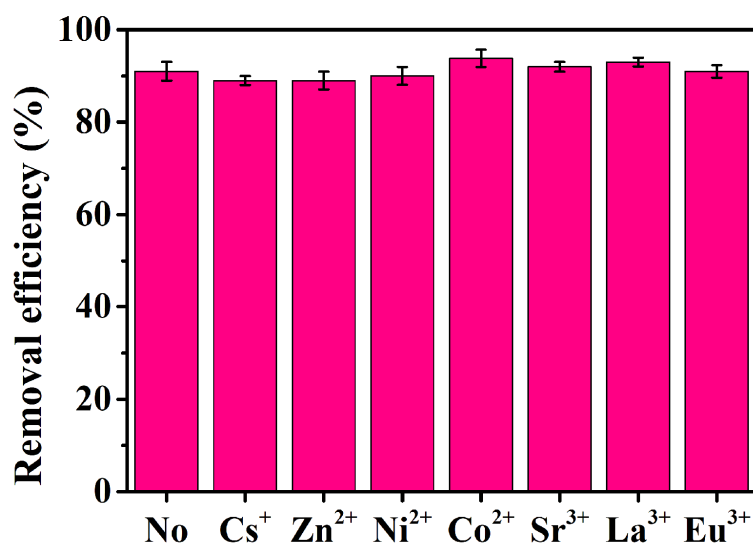
**Fig. S10** Freundlich (A) and Langmuir (B) isotherm model of adsorption of Ba<sup>2+</sup> over Zr-SUC-SO<sub>3</sub>H.

**Table S3.** Adsorption isotherm parameters for the adsorption of Ba<sup>2+</sup> over Zr-SUC-SO<sub>3</sub>H.

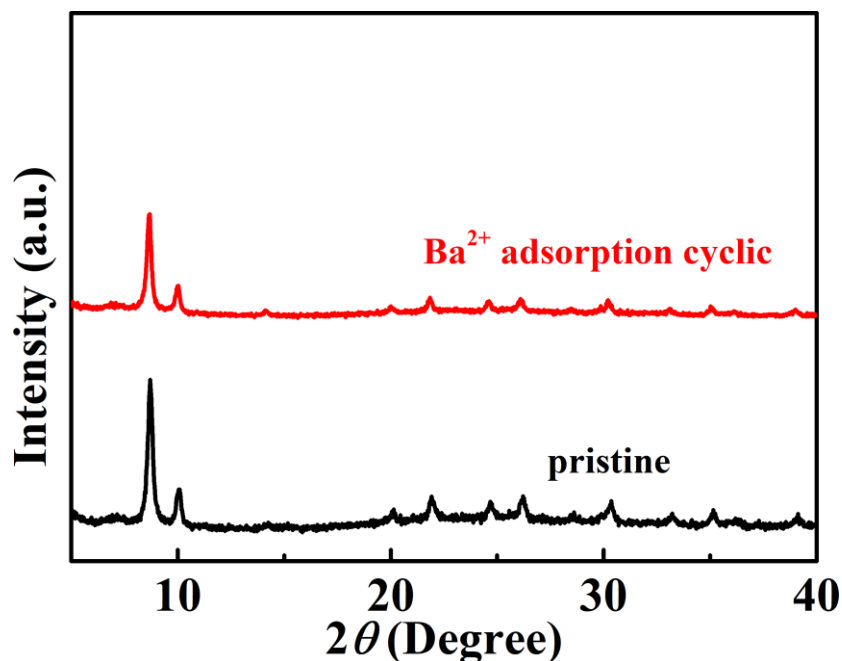
Langmuir			Freundlich		
q <sub>m</sub> (mg g <sup>-1</sup> )	k <sub>L</sub> (L mg <sup>-1</sup> )	R <sup>2</sup>	k <sub>F</sub> (mg g <sup>-1</sup> )	n	R <sup>2</sup>
60.8	0.107	0.999	11.25	3.03	0.902

**Table S4.** Adsorption capacities for the removal of Ba<sup>2+</sup> by different adsorbents.

Materials	Saturated Sorption Capacity (mg/g)	Removal time	Adsorption dosage (mg/L)	References
activated carbon	3.1×10 <sup>-6</sup>	4 h	10	6
expanded perlite	2.5	1.5 h	NA	7
dolomite	3.9	2 h	10000	8
niobate	13.7	48 h	1000	9
zero-valent iron	22.6	4 h	10000	10
montmorillonite clay	36.74	200 h	10000	11
MIL-101-Cr-SO <sub>3</sub> H	70.5	24 h	1000	12
MOF-808-SO <sub>4</sub>	131.1	24 h	1000	12
Zr-BDC-NH <sub>2</sub> -SO <sub>4</sub>	181.8	24 h	1000	13
Zr-SUC-SO <sub>3</sub> H	60.8	1/12 h	1000	This work



**Fig. S11** Effect of possibly coexistent cations on the adsorption of Ba<sup>2+</sup> by Zr-SUC-SO<sub>3</sub>H. The concentrations of initial Ba<sup>2+</sup> and all possible coexisting cations were set at 10 mg/L.



**Fig. S12** PXRD pattern of Zr-SUC-SO<sub>3</sub>H after and before recycling tests.

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