Supporting Information for Chemical Communications

Selective Removal of Cesium and Strontium using Porous Frameworks from high level Nuclear Waste

Briana A. Aguila, [ab] Debasis Banerjee, [a] Zimin Nie, [c] Yongsoon Shin, [a] Shengqian Ma[b] and Praveen Thallapally* [a]

[a] Physical and Computational Science Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, United States, [b] *Department of Chemistry, University of South Florida, Tampa, FL 33620, United States,* [c] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, United States

1. Experimental

All chemicals were obtained from Sigma Aldrich, unless otherwise specified, with no further purification required before use. A mixture of monosodium 2-sulfoterephthalic acid (3.35 g, 12.5 mmol), CrO_3 (1.25 g, 12.5 mmol), and concentrated aqueous hydrochloric acid (0.8 mL, 12 M, 25 mmol) was dissolved in deionized water (25 mL) and then transferred to a Teflon-lined stainless steel autoclave. The solution was heated at 453 K for six days under the hydrothermal conditions. The reaction product was harvested by centrifugation and washed three times with deionized water (400 mL) and methanol (100 mL) followed by drying in air at room temperature. The green powder was purified in DMF at 120 °C for 24 hours followed by in a mixed solution of methanol and H_2O at 120 °C for 24 hours. The obtained green microcrystalline powder of MIL-101-SO_3Na(H) was post-synthetically treated in a mixed solution of diluted HCl (0.08 M) in methanol and water, and was further treated in methanol and water to remove additional HCl. The resultant green solid was finally dried overnight at 120 °C under vacuum prior to further use.[1]

2. Characterization of MIL-101-SO_3H

Powder XRD: X-ray diffraction patterns were obtained on a Rigaku MiniFlex II X-ray diffractometer with Cu Kα radiation. Measurements were taken between 2° and 50° at a step size of 0.02°.

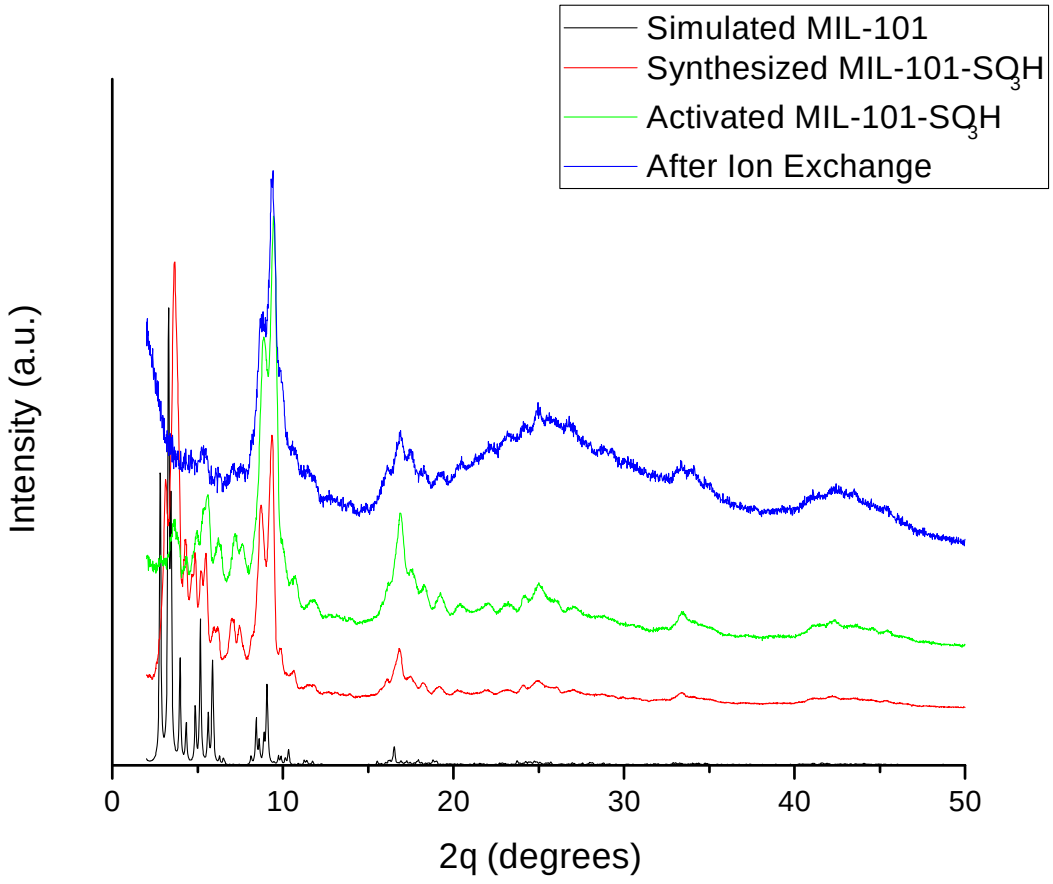

Fig. S1 XRD Pattern of (black) simulated (red) as-synthesized (green) activated (blue) after ion-exchange MIL-101-SO_3H

Surface Area: The N_2 sorption isotherm was collected using a Quantachrome Autosorb-iQ_2 gas sorption analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, with prior degassing at 120°C under dynamic vacuum for 16 hours.

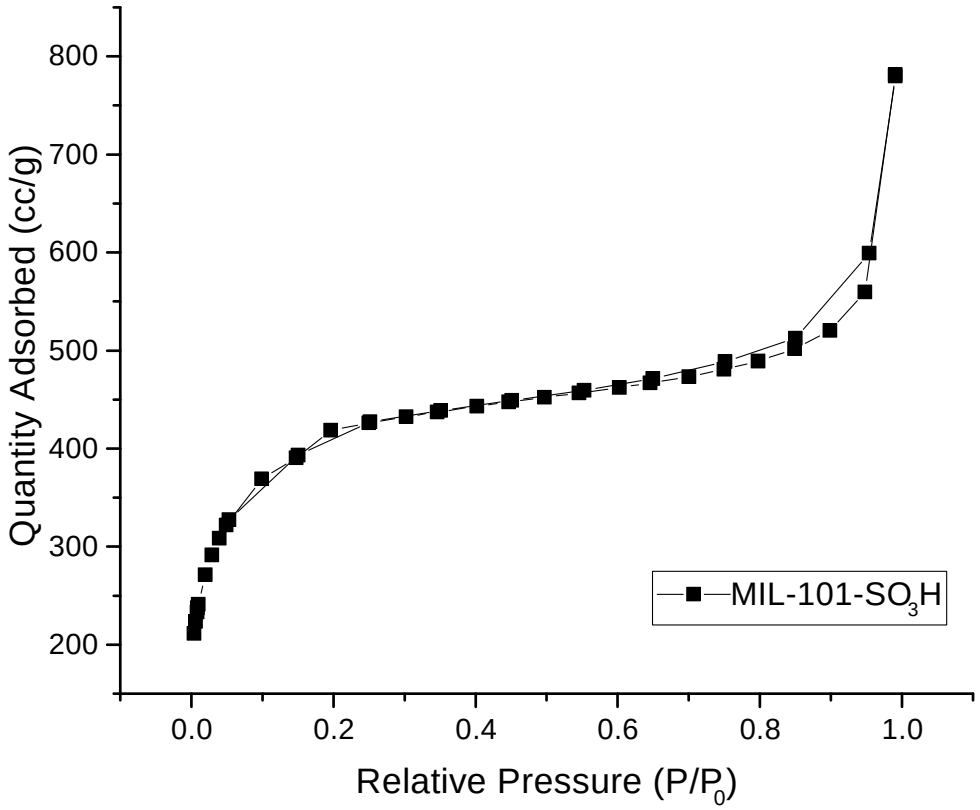

Fig. S2 N_2 Sorption Isotherm of activated MIL-101-SO_3H. The calculated BET Surface Area is 1338 m^2 g^{-1}

3. Solution Preparation

Deionized water used in all the experiments was obtained from a Barnstead Nano pure water purification system.

Table S1. Amounts used for all solutions.

Solution	Concentration (M)	Salt	Mass of salt (g)	Volume of DIW (mL)
1	0.05	$CsNO_3$	0.9767	100
2	0.001	$CsNO_3$	0.0108	50
3	0.001	$SrCl_2$	0.0066	25
4	0.001	$CsNO_3$	0.0019	10
	0.1	NaCl	0.0584	
	0.1	KNO_3	0.1011	
5	0.001	$SrCl_2$	0.0016	10
	0.1	NaCl	0.0584	
	0.1	KNO_3	0.1011	
6	0.001	$CsNO_3$	0.0019	10
	0.001	$SrCl_2$	0.0016	
	0.1	NaCl	0.0584	
	0.1	KNO_3	0.1011	
7	0.001	$SrCl_2$	0.0428	100
	0.01	$Ca(NO_3)_2$	0.242	
	0.01	$Mg(NO_3)_2$	0.264	

4. Ion-Exchange Studies

The concentration of each sample was determined by a Perkin Elmer Optima 7300DV Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES) after appropriate dilution. Three emission lines were chosen for each element as a crosscheck for spectral interference. The calibration standards were matrix-matched in water.

4.1 Contact Time Study on Cs Removal

20 mg of MIL-101-SO_3H was placed in a 20 mL glass vial, to that 5 mL of Solution **1** was added; the vial was then sealed and left undisturbed for the allocated time. After, the solid was filtered out and the solution was kept for ICP/AES analysis.

Table S2. Concentrations of Cs ions at different time intervals.

Time (min)	**Concentration (mg/L)**
C_0	6665
5	6176
20	6100
60	5999
720	5500
1440	5268

4.2 Concentration Ratio Study on Cs and Sr Removal

MIL-101-SO_3H was placed in a 20 mL glass vial, to that 5 mL of Solution **2** was added; the vial was then sealed and left undisturbed for 24 hours. After, the solid was filtered out and the solution was kept for ICP/AES analysis.

Table S3. Cs^+ ion concentrations at varying molar ratios using solution **2**

Molar Ratio	Mass of MIL-101-SO_3H (mg)	Concentration (mg/L)
C_0	0	145.86
1:1	5	68.84
2:1	10	34.7
4:1	20	0
6:1	30	0

Table S4. Sr^{2+} ion concentrations at varying molar ratios using solution **3**

Molar Ratio	Mass of MIL-101-SO_3H (mg)	Concentration (mg/L)
C_0	0	82.55
1:1	5	26.09
2:1	10	3.80
4:1	20	0.89
6:1	30	1.04

4.3 Solution pH Study on Cs Removal

20 mg of MIL-101-SO_3H was placed in a 20 mL glass vial, to that 5 mL of Solution **2** was added; the vial was then sealed and left undisturbed for 24 hours. After, the solid was filtered out and the solution was kept for ICP/AES analysis. For pH 3, a negligible amount (<0.1 mL) of dilute HCl was added to a 10 mL sample of of Solution **2**. For pH 10, a negligible amount of NH_4OH (28-30 wt.% soln. of NH_3 in water, Acros) was added to a 10 mL sample of Solution **2**.

Table S5. Cs ion concentrations at different pH levels.

pH	Concentration of Standard Solution (c_0) (mg/L)	Concentration after Ion-Exchange (c_e) (mg/L)
3	106.10	12.36
6	82.55	0.89
10	147.20	30.53

4.4 Competing Ions Study

20 mg of MIL-101-SO_3H was placed in a 20 mL glass vial, to that 5 mL of Solution **4** was added; the vial was then sealed and left undisturbed for 24 hours. After, the solid was filtered out and the solution was kept for ICP/AES analysis.

Table S6. Cs^+, Na^+, and K^+ ion concentrations (Experiment A)

Metal	Concentration of Standard Solution (c_0) (mg/L)	Concentration after Ion-Exchange (c_e) (mg/L)
Cs	229.50	190.70
Na	2371	2307
K	3744	3716

20 mg of MIL-101-SO_3H was placed in a 20 mL glass vial, to that 5 mL of Solution **5** was added; the vial was then sealed and left undisturbed for 24 hours. After, the solid was filtered out and the solution was kept for ICP/AES analysis.

Table S7. Sr^{2+}, Na^+, and K^+ ion concentrations (Experiment B)

Metal	Concentration of Standard Solution (c_0) (mg/L)	Concentration after Ion-Exchange (c_e) (mg/L)
Sr	130.81	108.23
Na	2248	2248
K	3740	3670

20 mg of MIL-101-SO_3H was placed in a 20 mL glass vial, to that 5 mL of Solution **6** was added; the vial was then sealed and left undisturbed for 24 hours. After, the solid was filtered out and the solution was kept for ICP/AES analysis

Table S8. Cs^+, Sr^{2+}, Na^+, and K^+ ion concentrations. (Experiment C)

Metal	Concentration of Standard Solution (c_0) (mg/L)	Concentration after Ion-Exchange (c_e) (mg/L)
Cs	73.34	70
Sr	134.60	104.40
Na	2244	2165
K	3722	3468

20 mg of MIL-101-SO3H was placed in a 20 mL glass vial, to that 5 mL of solution **7** was added, the vial was then sealed and left undisturbed for 24 hours. After, the solid was filtered out and the solution was used for ICP/AES analysis.

Table S9. Mg^{2+}, Ca^{2+}, and Sr^{2+} ion concentrations. (Experiment D)

Metal	Concentration of Standard Solution (c_0) (mg/L)	Concentration after Ion-Exchange (c_e) (mg/L)
Sr	95	91.08
Ca	280.02	23.65
Mg	496.21	44.59

5. Data Analysis

The % removal, sorption amount, q_e (mg g^{-1}), and distribution coefficient, K_d (mL g^{-1}), were calculated using the following equations:

$$\% \text{ Removal} = \frac{(c_0 - c_e) \times 100}{c_0}$$

$$q_e = \frac{(c_0 - c_e) \times V}{m}$$

$$K_d = \frac{(c_0 - c_e) \times V}{c_e \times m}$$

Where c_0 and c_e are respectively the initial and equilibrium concentration of metal ions (mg L^{-1}). V denotes the volume of the solution (mL) and m corresponds to the quantity of MIL-101-SO_3H (g).

Reference

1. Y.-X. Zhou, Y.-Z. Chen, Y. Hu, G. Huang, S.-H. Yu and H.-L. Jiang, *Chem. Eur. J.*, 2014, **20**, 14976.