Supporting Information

Scandium-Triflate/Metal-Organic Frameworks: Remarkable Adsorbents for Desulfurization and Denitrogenation

Nazmul Abedin Khan and Sung Hwa Jhung*

Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu 702-701, Korea

*Corresponding Author: Prof. Sung Hwa Jhung

Fax: 82-53-950-6330, Tel: 82-53-950-5341

Email: sung@knu.ac.kr

Experimental:

Syntheis of CuBTC: The synthesis of CuBTC was performed as previously described.[1] In short, an exact amount of H_3BTC (2.0 mmol) and copper (II) nitrate trihydrate (3.65 mmol) was dissolved in 24 mL of a 1:1 (wt./wt.) mixture of H_2O and CH_3CH_2OH, and magnetically stirred for 10 min. The resulting mixtures were loaded into a Teflon autoclave that was sealed and placed in a microwave oven (Mars-5, CEM, maximum power: 1200 W) to exploit the advantage of fast synthesis under microwave irradiations.[2] After heating for 1.0 h at 140 ^{o}C, the autoclave was allowed to cool to room temperature and the products were collected *via* centrifugation. The products were washed with a water/ethanol mixture to remove any unreacted trimesic acid and dried overnight at 100 ^{o}C.

Syntheis of UiO-66: The synthesis of the MOF, UiO-66, was carried out solvothermally under conventional electric heating following a previous report[3] with a few modifications. The detailed procedure for the synthesis of the MOF is as follows: $ZrCl_4$ (1.129 g), TPA (1.626 g), HCl (1.009 g) and DMF (27.04 g) were mixed in a molar ratio of 1:2:2:76. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated in an electric oven for 24 h at 180 °C. After the synthesis, the solid product was filtered, washed, and purified by mixing with DMF and heating at 150 °C for 5 h. For 1 g of MOF, 50 mL of DMF was used in the purification process. The purified MOF was then filtered and dried in a vacuum oven at 150 °C for 12 h to remove the remaining DMF.

Synthesis of MIL-101: MIL-101 was synthesized from $Cr(NO_3)_3 \cdot 9H_2O$, TPA and deionized water similar to a reported method.[4] The reactants composition was 1.0 $Cr(NO_3)3 \cdot 6H_2O$: 1.0 TPA : 300 H_2O. The precursor of 30 g was loaded in a Teflon-lined autoclave and put in a preheated electric oven at 210 ^{o}C for 8 h. After the reaction, the autoclave was cooled to room temperature and solid green-colored products were recovered

2

by filtration. After synthesis, the MOF was purified in three steps.[5] In the first step, 1.0 g MIL-101 was added to 300 mL water and stirred magnetically for 5 h at 70 °C. Then the MOF was filtered and dried overnight in a drying oven. In the second step, the dried MOF was added to 250 mL ethanol; stirred magnetically at 60 °C for 3 h and then filtered. In the third step, the dried MOF from the second step was added to 150 mL 30 mM NH4F solution and stirred for 10 h at 60 °C. After that, it was filtered and washed at least five times with hot water and then dried in a drying oven again. Finally, the purified MIL-101 was dehydrated at 150 °C overnight and stored in a desiccator.

Adsorption experiments: All the adsorption capacities (mg/g) were calculated from the difference between final and initial concentrations of an adsorbate by using following equation:

$$q_t = \frac{(C_i - C_f)V}{m}$$

Where,

q_t = adsorbed amount in time t (mg/g)

C_i = initial concentration of the adsorbate (mg/ml)

C_f = final concentration after adsorption (mg/ml)

V = volume of the solution subjected to a single adsorption (ml)

m = mass of the adsorbent taken during a single adsorption (g)

Calculation of maximum adsorption capacity (Q_0): The maximum adsorption capacity (Q_o) was calculated using the Langmuir adsorption isotherm. The adsorption isotherms for different adsorbents were plotted according to the Langmuir equation[6,7]

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b}$$

Where,

C_e : the equilibrium concentration of the adsorbate (mg/L)

q_e : the amount adsorbed at equilibrium (mg/g)

Q_o : the Langmuir constant (maximum adsorption capacity, mg/g)

b : the Langmuir constant (L/mg)

Therefore, the maximum adsorption capacity, Q_o, could be obtained from the reciprocal of the slope of a plot of C_e/q_e against C_e.

Adsorption kinetics: Kinetics of BT or DBT adsorption has been interpreted by the pseudo-second-order non-linear kinetic model[8,9] which is expressed by the following equation.

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

Where,

q_e (mg/g): amount adsorbed at equilibrium;

q_t (mg/g): amount adsorbed at time t;

t (h): adsorption time;

k_2 (g/mg/h): the pseudo-second-order rate constant.

A trial-and-error procedure[8] was adapted to measure the pseudo-second order kinetic parameters in the case of non-linear method by using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

Separation factor: The separation factor (R_L) was calculated using the following equation that describes the adsorption process:[10-12]

$$R_L = \frac{1}{1 + bC_o}$$

Where,

R_L: separation factor

b: the Langmuir constant (L/mg)

C_o: initial concentration of adsorbate (mg/L)

Adsorbent regeneration: The used adsorbents were reactivated for further utilization following the two consecutive procedure. Firstly, the used adsorbet was soaked into *n*-octane solvent and allowed to stirr 12 h at room temperature. While, the solvent was exchanged three times with fresh n-octane to wash out the adsorbed BT or QUI from the adsorbent. In next step, the solid adsorbent was filtered and dried at 100 ^{o}C for 12 h. Then the dried adsorbent was heated at 230 ^{o}C under evacuation to evaporate the remaining adsorbed materials.

Reference:

[1]   Seo, Y.-K.; Hundal, G.; Jang, I.T.; Hwang, Y.K.; Jun, C.-H.; Chang, J.-S. *Micropor. Mesopor. Mater.* **2009**, *119*, 331-337.

[2]   Khan, N.A.; Jhung, S.H. *Coord. Chem. Rev.* **2015***, 285,* 11–23.

[3]   Kandiah, M.; Nilsen, M.H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E.A.; Bonino, F.; Lillerud, K.P. *Chem. Mater.* **2010,** *22*, 6632–6640.

[4]   Khan, N.A.; Jhung, S.H. *Cryst. Growth Des.* **2010,** *10,* 1860-1865.

[5]   Hong, D.-Y.; Hwang, Y.K.; Serre, C.; Ferey G.; Chang, J.-S. *Adv. Funct. Mater. 19*, **2009,** 1537–1552.

[6]   Hameed, B.H.; Rahman, A.A.; *J. Hazard. Mater.* **2008.** *160,* 576-581.

[7]   Lin, S.-H.; Juang, R.-S. *J. Environ. Manag.* **2009,** *90*, 1336-1349.

[8]   Ho, Y. -S. *Water Res.* **2006,***40*, 119-125.

[9]   Nouri, L.; Ghodbane, I.; Hamdaoui, O.; Chiha, M. *J. Hazard. Mater.* **2007,** *149,* 115–125.

[10]   Weber, T.W.; Chakkravorti, R.K. *AIChE J.* **1974,** *20,* 228-238.

[11]   Önal, Y.; Akmil-Basar, C.; Sarıcı-Özdemir, C. *J. Hazard. Mater.* **2007,** *148*, 727-734.

[12]   Singh, K.P; Mohan, D.; Sinha, S.; Tondon, G.S. *Ind. Eng. Chem. Res.* **2003**, *42*, 1965-1976.

[13]   Khan, N.A.; Jhung, S.H. *Angew. Chem. Int. Ed.* **2012***, 51,* 1198-1201.

[14]   Khan, N.A.; Jhung, S.H. *J. Hazard. Mater.* **2012,** *237-238,* 180-185.

[15]   Khan, N.A.; Hasan, Z.; Jhung, S.H, *Chem. Eur. J.* **2014,** *20,* 376-380.

[16]   Khan, N.A.; Jhung, S.H. *Fuel Process. Technol.* **2012,** *100,* 49-54.

[17]   Hasan, Z.; Jhung, S.H. *ACS Appl. Mater. Interfaces* **2015**, *7*, 10429-10435.

Table S1. Physiochemical properties of virgin and Sc(OTf)₃-supported MOFs.

	S_{BET}, m^2/g	Pore volume (total), cm^3/g	S, wt% [a]	Sc, wt%[a]
CuBTC	1427	0.70	0.0	0.0
CuBTC(1%Sc)	1340	0.68		
CuBTC(2%Sc)	1239	0.63	0.51	0.25
CuBTC(5%Sc)	1218	0.62		
CuBTC(7.5%Sc)	1187	0.61		
CuBTC(10%Sc)	1131	0.57		
MIL-101	2902	1.62		
MIL-101(1%Sc)	2730	1.53		
MIL-101(5%Sc)	2396	1.21		
MIL-101(10%Sc)	1579	0.79		

[a] Based on energy dispersive spectroscopic (EDS) analysis

7

Table S2. Increament% of maximum adsorption capacity (Q_o) for BT with MOFs having various active components at similar adsorption condition.

Adsorbents	Q_o increased %	Reference
Sc(OTf)$_3$/CuBTC	64.7	This work
CuCl$_2$/MIL-47	34.2	[13]
Cu$_2$O/MIL-100-Fe	14.1	[14]
Ionic liquid/MIL-101	70.6	[15]
Phosphotungstic acid/CuBTC	26.3	[16]
Cu-pyrazine/MIL-100-Fe	12.3	[17]

Figure S1. XRD patterns of (a) virgin and Sc(OTf)$_3$-supported CuBTCs; and (b) virgin and Sc(OTf)$_3$-supported MIL-101s.

Figure S2. N$_2$ adsorption isotherms of (a) virgin and Sc(OTf)$_3$-supported CuBTCs; and (b) virgin and Sc(OTf)$_3$-supported MIL-101s.
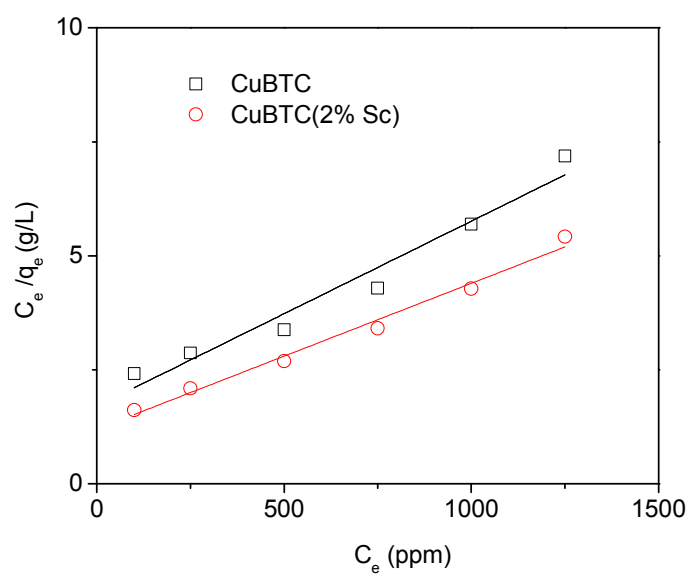
Figure S3. Langmuir plots of the adsorption of DBT over CuBTC and CuBTC(2%Sc).
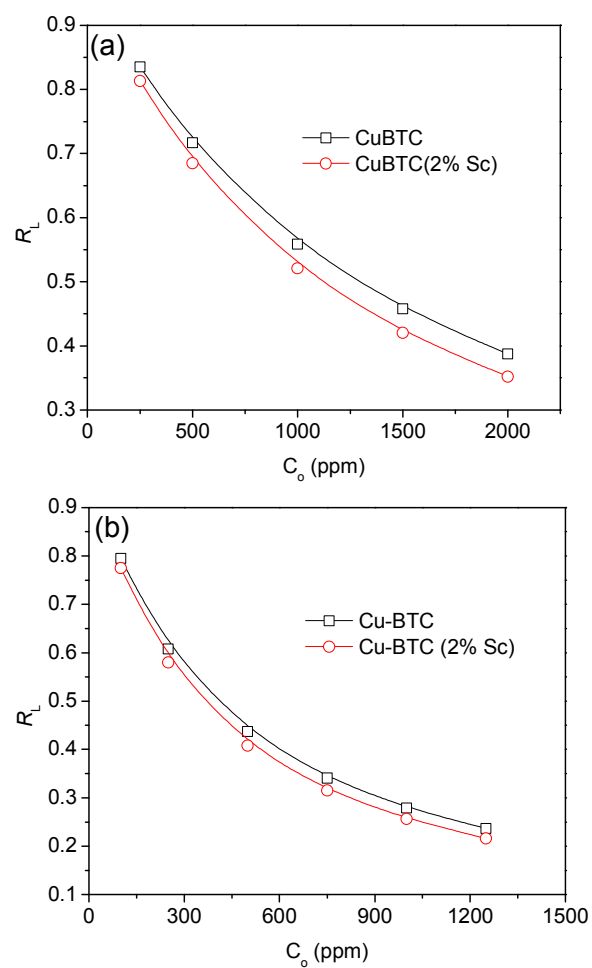
Figure S4. R_L values of the two adsorbents in different initial concentrations of (a) BT; (b) DBT.
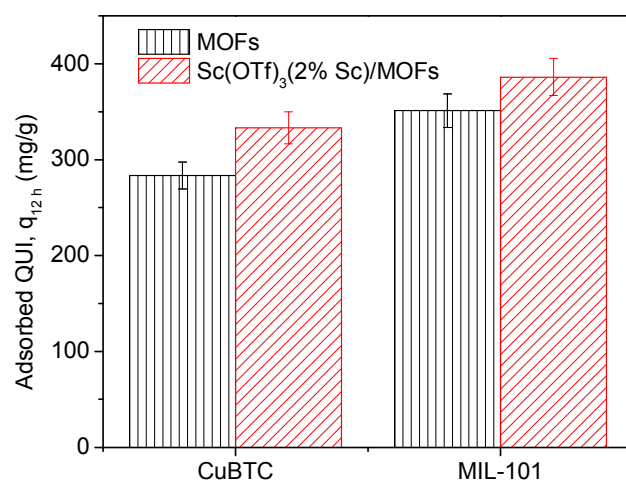
Figure S5. Adsorption of QUI with virgin and Sc(OTf)$_3$-supported adsorbents. The initial QUI concentration in n-octane solvent was 1000 ppm and the adsorption time was 12 h.
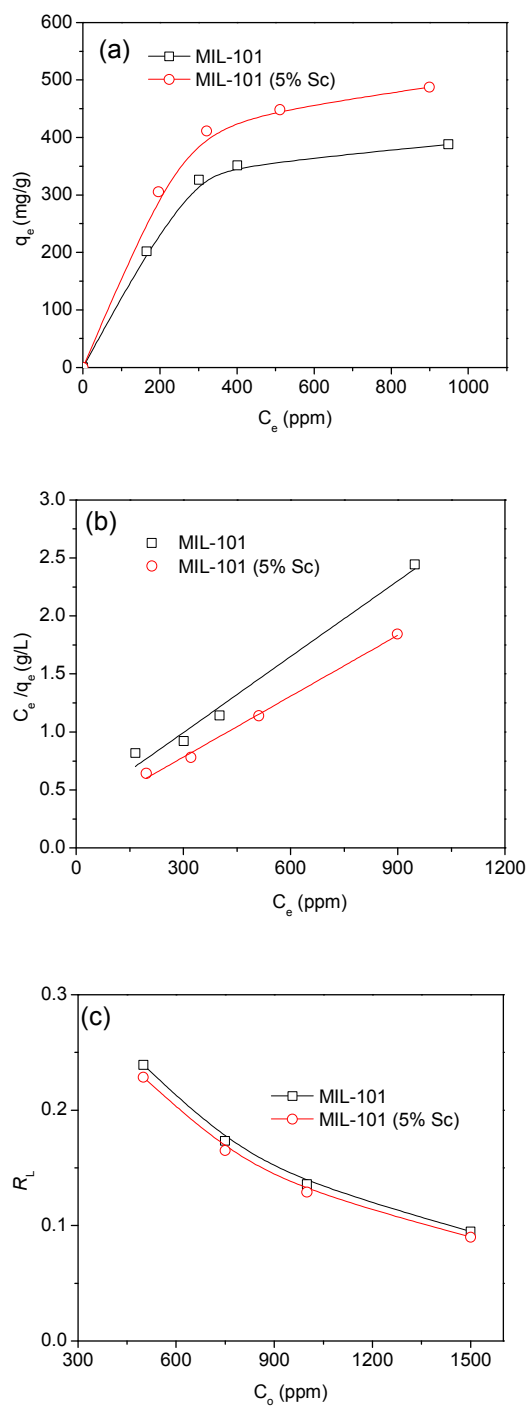
Figure S6. (a) Adsorption isotherms and (b) Langmuir plots and (c) effect of initial QUI concentrations on the separation factor R_L for the adsorption of QUI over MIL-101 and MIL-101(5%Sc).