Remarkable Adsorptive Performance of a Metal-Organic Framework, Vanadium-benzenedicarboxylate (MIL-47), for Benzothiophene

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Supplementary Information

Experimental procedures:

The MOFs (MIL-53(Al), MIL-53(Cr), MIL-47(V) used in this study were synthesized hydrothermally under autogeneous pressure similar to the reported methods.[1-3]. However, instead of conventional electric heating, microwaves (Mars-5, CEM) were used as a heating source in order to take advantage of rapid synthesis of porous materials under microwave irradiation. For the synthesis of MIL-53(Al), aluminum chloride hexahydrate ($AlCl_3·6H_2O$, Sigma Aldrich, 99%), terephthalic acid (TPA, C_6H_4-1,4-$(CO_2H)_2$; Sigma Aldrich, 98%) and deionized water were mixed in the molar ratio of $1Al:0.5TPA:80H_2O$. The reaction mixtures containing TPA, aluminum chlorides and water were stirred for 5 min, loaded into a Teflon-lined autoclave, sealed and placed in the microwave oven and finally heated for 2.5 h at 200 °C under autogeneous pressure. The MIL-53(Cr) and MIL-47(V) were synthesized similarly from chromium (III) chloride hexahydrate ($CrCl_3·6H_2O$, Sigma Aldrich, 96%) and vanadium (III) chloride (VCl_3, Sigma Aldrich, 97%), respectively. The reaction temperature and time were changed a bit for the syntheses of the two MOFs (MIL-53(Cr): 210 °C, 2 h; MIL-47: 175 °C, 2 h). After the synthesis, the MOF samples were recovered by cooling, filtration, water washing and drying. To remove TPA from the as-synthesized MOFs, purification was carried out with sonication using an ultrasonic generator (VC×750, max. power 750 W, Sonic & materials, Inc.) in the presence of *N,N*-dimethylformamide (DMF) following the reported purification method.[4] Briefly, 0.3 g of a MOF such as MIL-53(Al) was suspended in 20 ml of DMF and sonicated for 1 h at 70 ° C. The purified MOFs were collected after filtration and dried at 150 °C for 5 h.

The phases of purified products were identified by analysis with an X-ray diffractometer (MO3X-HF, Model NO. 1031, Cu_{Ka} radiation) (Supporting Fig. 6). Before X-ray diffraction, MOFs were hydrated for 2 days over saturated ammonium chloride aqueous solution. The porosity of the Me-BDCs is analyzed with the nitrogen adsorption (Supporting Fig. 7). The nitrogen sorption was carried out using Micromeritics Tristar II 3020 adsorption unit at liquid nitrogen temperature (-196 °C) after evacuation at 150 °C for 15 h. Surface area and micropore volume were calculated with the BET equation and t-plot, respectively, using the nitrogen adsorption isotherms.

Before adsorption of benzothiophene, the adsorbents were dried overnight under vacuum at 150 °C and were kept in a desiccator to avoid adsorption of water vapor. The dried adsorbent was put in n-octane solutions having specific BT concentrations. After adsorption for a pre-determined time under magnetic stirring, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.5 μm). After separation, the solutions were analyzed for BT concentration using a GC (DS 6200, DS SCIENCE INC.) equipped with a FID detector and DB-5 column.

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Calculations for kinetic and thermodynamic parameters:

The adsorption rate constant was calculated using pseudo-second order reaction kinetics.[1,2] Namely, the changes of adsorption amount with time are treated with the versatile pseudo-second-order kinetic model[1,2] because the whole data during adsorption time can be treated successfully:

$$dq_t / dt = k_2 (q_e - q_t)^2 \quad [\text{Eq.}1]$$

$$or, \frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \quad [\text{Eq.}2]$$

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

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

t: adsorption time (h).

Therefore, the second order kinetic constant (k_2) can be calculated by

$k_2 = slope^2/intercept$ when the t/q_t is plotted against *t.*

The maximum adsorption capacity was calculated using the Langmuir adsorption isotherm[1,3] after adsorption for 24 h. The adsorption isotherms in various conditions have been plotted to follow the Langmuir equation:[1,3]

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \quad [\text{Eq.}3]$$

Where,

C_e : equilibrium concentration of adsorbate (mg/L)

q_e : the amount of adsorbate adsorbed (mg/g)

Q_0 : Langmuir constant (maximum adsorption capacity) (mg/g)

b : Langmuir constant (L/mg or L/mol)

So, the maximum adsorption capacity Q_0 can be obtained from the *reciprocal of the slope* of a plot of C_e/q_e againt C_e.

To get the thermodynamic parameters of adsorption such as ΔG (free energy change), ΔH (enthalpy change) and ΔS (entropy change) the adsorption was further carried out at 35 and 45 °C. The Gibbs free energy change ΔG can be calculated by the following equation 4: [4,5]

$$\Delta G = -RT \ln b \quad [\text{Eq.}4] \qquad \text{(where, R is gas constant)}$$

The Langmuir constant *b* (dimension: L/mol) can be obtained from the *slope/intercept* of the Langmuir plot. The enthalpy change ΔH and entropy change ΔS can be obtained by using the van't Hoff equation:[4,5]

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad [\text{Eq.}5]$$

The enthalpy change ΔH and entropy change ΔS were obtained from the *(-slope* x *R)* and *(intercept* x *R)*, respectively, of the van't Hoff plot.

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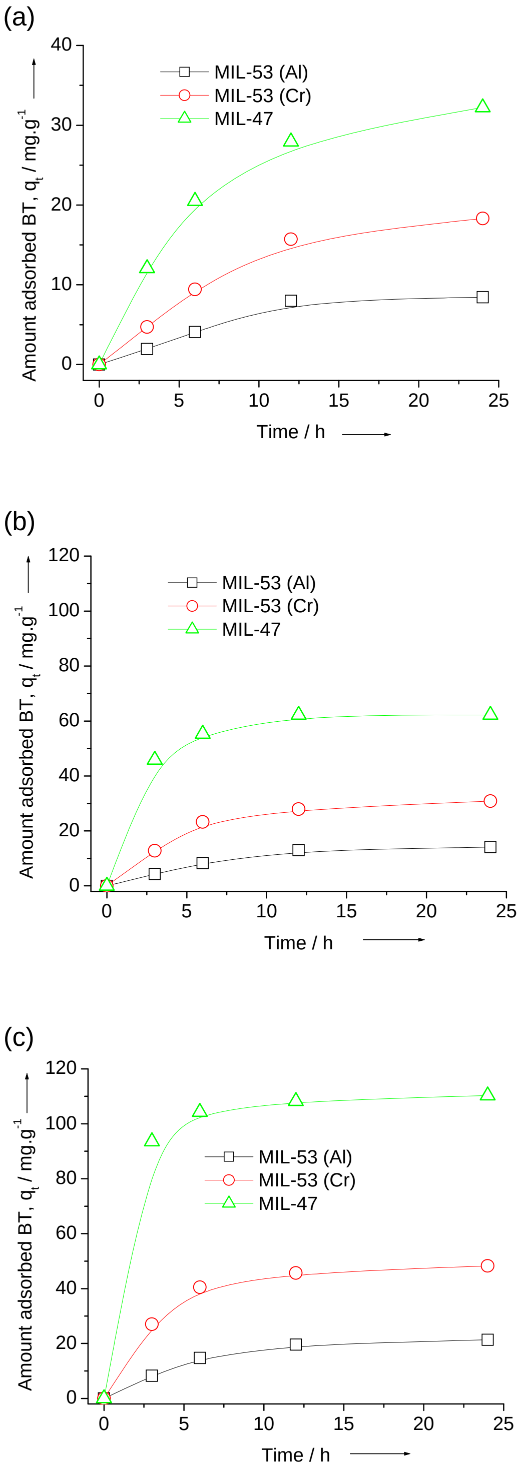
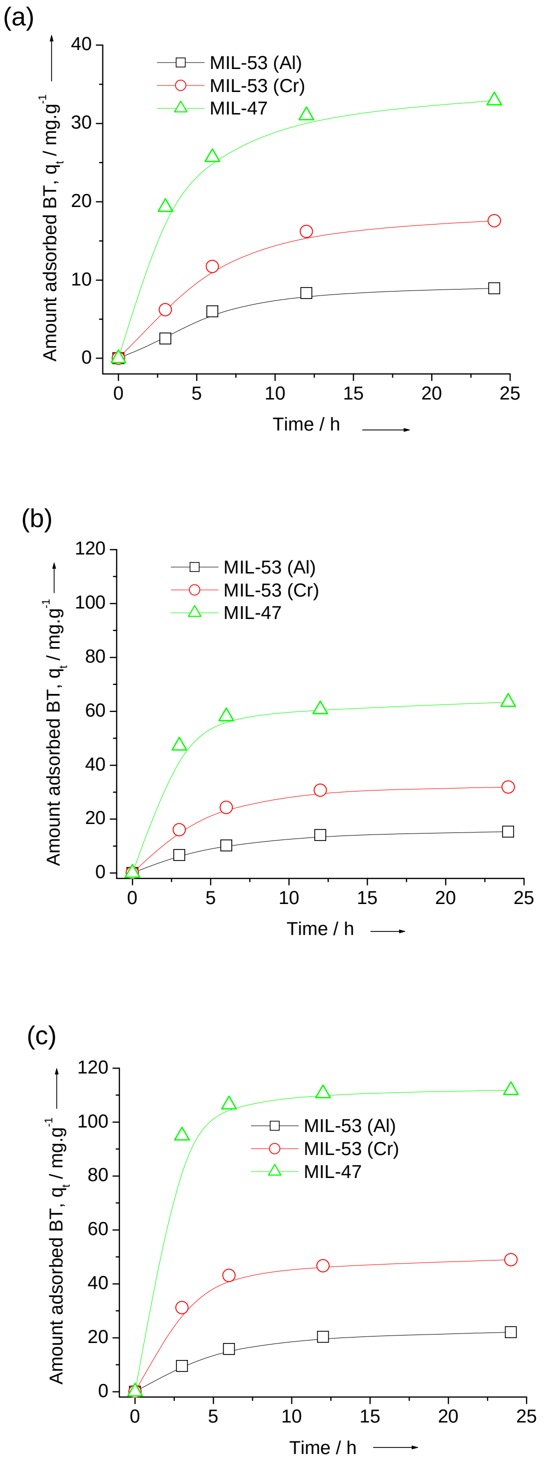
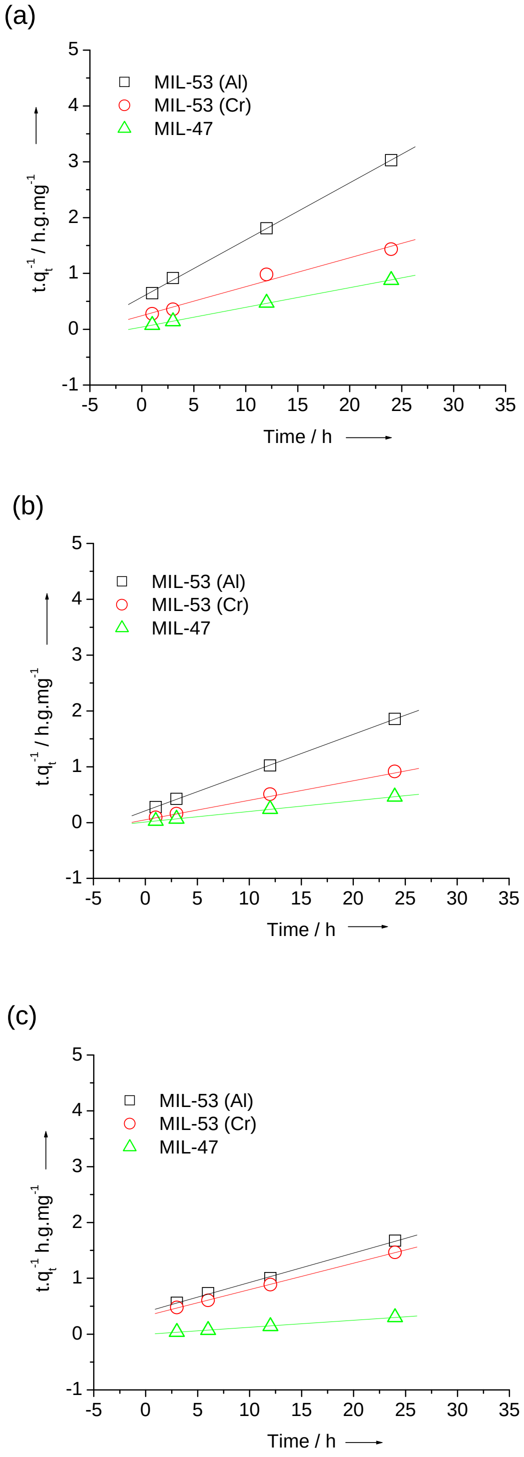


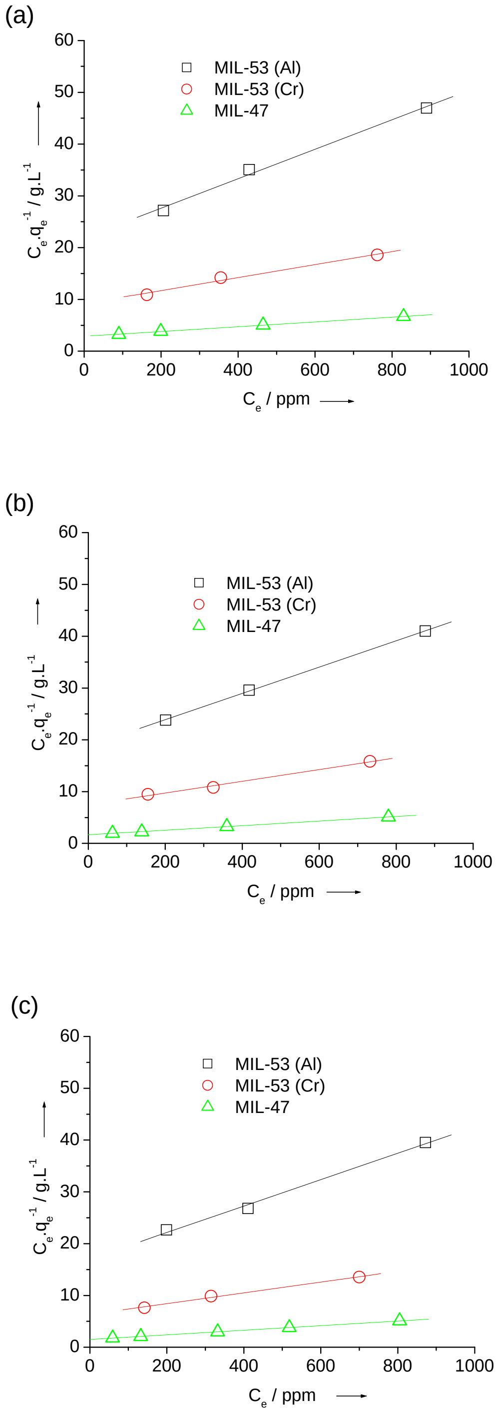
Supplementary Fig. 1. Effect of contact time and initial BT concentration on the adsorption of BT over the three adsorbents at 35 °C: (a) C_i = 250 ppm; (b) C_i = 500 ppm; (c) C_i = 1000 ppm.



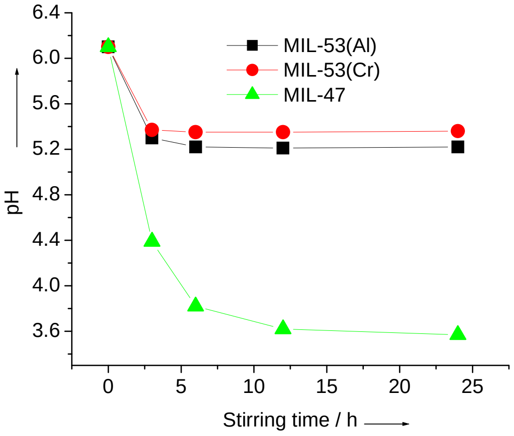
Supplementary Fig. 2. Effect of contact time and initial BT concentration on the adsorption of BT over the three adsorbents at 45 °C: (a) C_i = 250 ppm; (b) C_i = 500 ppm; (c) C_i = 1000 ppm.



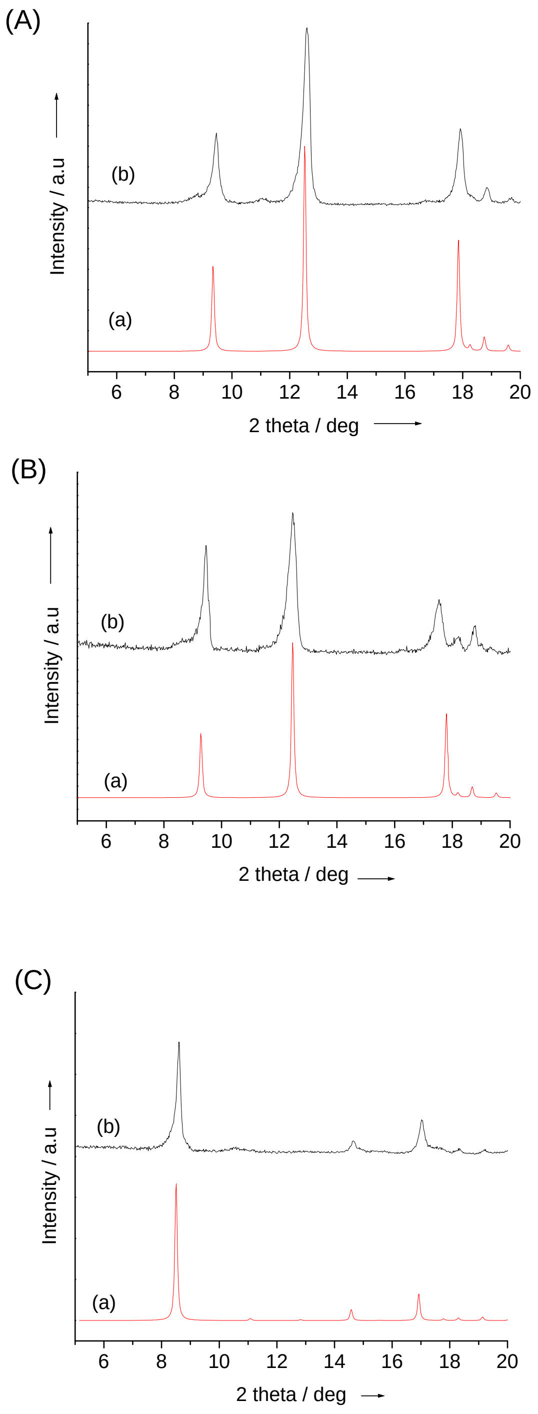
Supplementary Fig. 3. Plots of pseudo-second-order kinetics of BT adsorption over the three adsorbents at 25 ^{o}C: (a) C_i = 250 ppm; (b) C_i = 500 ppm; (c) C_i = 1000 ppm.



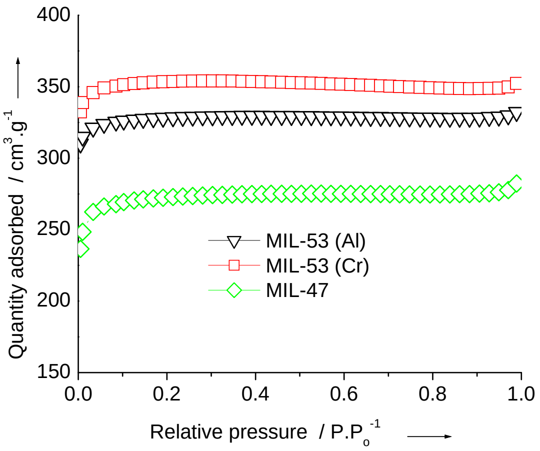
Supplementary Fig. 4. Langmuir plots for BT adsorption over the three adsorbents at (a) 25 ^{o}C; (b) 35 ^{o}C and (c) 45 ^{o}C.



Supplementary Fig. 5. Changes of pH of aqueous slurry (0.02 g of Me-BDCs in 10.0 mL water) of three adsorbents with stirring time.



Supplementary Fig. 6. XRD patterns of the synthesized (A) MIL-53(Al), (B) MIL-53(Cr), (C) MIL-47. Plots (a) and (b) in each case represent the XRD patterns of simulated structure and synthesized sample, respectively. For the XRD measurement, the MOFs were hydrated after purification.



Supplementary Fig. 7. Nitrogen adsorption isotherms of the three adsorbents.