

1 Supplementary Information

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3 1. Chemicals and the synthesis of adsorbents

4 All of the chemicals utilized in this study were obtained from commercial distributors and used without any
5 additional purification. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%), 1,4-benzenedicarboxylate (terephthalic acid,
6 BDC, 98%), trimethylamine (TEA, 99%), copper nitrate hemi pent-hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, 98%), trimesic acid
7 (H_3BTC , 95%), zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%), and amino terephthalic acid (BDC- NH_2 , 99%)
8 were procured from Sigma-Aldrich (St. Louis, Missouri, USA). Dimethylformamide (DMF, 99.0%) and ethanol
9 (99.5%) were purchased from Samchun Chemicals, Seoul, South Korea. Chloroform (99.5%) was purchased from
10 Daejung Chemical and Metals Co. Ltd., Seoul, South Korea. Hydrochloric acid (HCl, 35.0 – 37.0%) was purchased
11 from Junsei Chemical Co. Ltd., Seoul, South Korea. Activated carbon (granular) was procured from Duksan Pure
12 Chemicals Co. Ltd., Seoul, South Korea.

13 The synthesis of M5 was completed as described in the literature (Dutta et al., 2018). The linker solution for the
14 MOF was made by adding BDC (0.3 g, 1.81 mmol) into a DMF solution (25 mL) and homogenized *via* a mechanical
15 stirrer (hotplate stirrer; DAIHAN Scientific, Seoul, South Korea) at 1,000 rpm using a magnetic bar. In a similar
16 manner, the metal solution was prepared by dissolving $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.4 g, 4.71 mmol) into DMF (25 mL). Both
17 of the prepared solutions were thoroughly mixed by prolonged stirring. Dropwise addition of TEA (2 mL) was added
18 to the solution to reduce the reaction time required for the production of M5 crystals. The resulting solution was
19 covered with aluminum foil and kept at room temperature for 2 h. The precipitate was recovered *via* a 47 mm diameter
20 glass microfiber filter (Whatman™, Little Chalfont, Buckinghamshire, UK) in 5 min by utilizing a mini diaphragm
21 vacuum pump (N86KT.18, KNF, Witney, Oxfordshire, UK) working at a 0.01 bar pressure difference. The DMF was
22 washed twice to remove the excess BDC. The DMF was exchanged with chloroform (40 mL) for a prolonged standing
23 time (12 h) before swapping with fresh chloroform. After 48 h, filtration was carried out to remove the chloroform

24 and the acquired product was dried for 8 h at 90 °C in a universal oven (CO-150, Hanyang Scientific Equipment Co.,
25 Ltd, Seoul, South Korea).

26 The synthesis of M199 was also carried out in accordance with the protocol reported previously (Dutta et al., 2018).
27 A 1:1:1 solvent (250 mL) containing water, ethanol, and DMF was used to dissolve H₃BTC (5 g, 23.7 mmol) and
28 Cu(NO₃)₂·2.5H₂O (10 g, 43 mmol). The prepared solution was subsequently transferred to an airtight glass vessel and
29 heated for 20 h at 85 °C in a universal oven (CO-150, Hanyang Scientific Equipment Co., Ltd, Seoul, South Korea).
30 The obtained blue crystals were washed with DMF (30 mL) twice to remove the excess ligand materials. The
31 undissolved impurities were removed from the crystals by immersing them for 24 h in DMF (30 mL). The produced
32 crystals were recovered *via* a glass microfiber filter with a 47 mm diameter (WhatmanTM, Little Chalfont,
33 Buckinghamshire, UK) for 10 min by utilizing a mini diaphragm-based vacuum pump (N86KT.18, KNF, Witney,
34 Oxfordshire, UK) working at a 0.01 bar pressure difference. The acquired product was dried for 24 h at 170 °C in a
35 universal oven (CO-150, Hanyang Scientific Equipment Co., Ltd, Seoul, South Korea).

36 The synthesis of U6 and U6N was completed by modifying the protocol reported previously (Katz et al., 2013).
37 For U6, 125 mg of ZrOCl₂·8H₂O (0.38 mmol) was dissolved in 5 mL DMF to which 3 mL 37% HCl was added
38 (mixture A). One-hundred twenty-three mg of BDC (0.74 mmol) was dissolved in 10 mL of DMF in another vessel
39 and then mixed with mixture A. The resulting solution was ultra-sonicated for an additional 30 min. The resulting
40 mixture was heated in an oven (CO-150, Hanyang Scientific Equipment Co., Ltd, Seoul, South Korea) for 12 h at 80
41 °C. Solid crystals were obtained by filtration, and the unreacted materials were removed by washing with DMF and
42 ethanol. The solvent was exchanged with 10 mL ethanol for 3 days and dried in an oven for 12 h at 90 °C. U6N was
43 prepared by first dissolving 134 mg of BDC-NH₂ (0.74 mmol) in 10 mL DMF and then adding mixture A before ultra-
44 sonication for 30 min. Afterward, solvent exchange and drying was completed following the procedures as described
45 for U6.

47 2. Characterization of adsorbents

48 The MOFs used in this study were thermally activated for 2 h at 150 °C and subsequently characterized and utilized
49 for the experiments. The powder X-ray diffraction (PXRD) patterns were generated by an HR-XRD diffractometer
50 (Rigaku Corporation, Tokyo, Japan). A 2θ range of 5, step size of 0.02° , and a scan speed of 4° min^{-1} were utilized to
51 record the PXRD data. Thermogravimetric analyses (TGA) were conducted on an SDT Q600, Auto-DSCQ20 system
52 (Eden Prairie, Minnesota, USA). During TGA analysis, the samples were placed in alumina pans and heated from 25
53 to 800 °C at a rate of $10^\circ \text{ C min}^{-1}$ under a 100 mL min^{-1} N_2 . Fourier transform infrared (FTIR) spectroscopy was
54 carried out (to identify the functionalities present on the surface of adsorbents) using a Perkin Elmer L1600400-IR
55 spectrometer (Akron, Ohio, USA) adopting an attenuated reflectance method (ATR) in the range of 400-4000 cm^{-1} .
56 Moreover, a scanning electron microscope (FE-SEM, Hillsboro, Oregon, USA) was used to investigate the surface
57 morphologies of the studied sorbents. The Brunauer-Emmett-Teller (BET) surface areas and pore properties of the
58 applied sorbents were determined using a Micromeritics ASAP 2010 (Norcross, Georgia, USA) surface analyzer
59 operating at 77 K.

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61 3. Gaseous working standard (G-WS) preparation and experimental outline

62 In this study, the gaseous primary standards (G-PS-1) of five CCs (AA (99.6 ppm), PA (20.1 ppm), BA (18.6 ppm),
63 IA (19.6 ppm), and VA (15.1 ppm)) were purchased from RIGAS, Daejeon, South Korea. The FA G-PS-2 was made
64 by injecting 20 μL of aged formalin (FA: $\sim 5\%$ (w/w %) in H_2O with 10-15% methanol) into a 1 L polyester aluminum
65 (PEA) bag (Top trading Co., Seoul, South Korea) filled with ultrapure N_2 (99.99% pure, RIGAS, Daejeon, South
66 Korea) at 1 atm. The PEA bag was left for 24 h at room temperature to allow the formalin to vaporize. The relative
67 humidity of the G-PS was determined to be $<85\%$ at 298 K. To understand the adsorptive removal of CCs under real-
68 world conditions, it is also important to assess the interactions between FA and water vapor.

69 For quantification, the G-PS was pulled (1 L min^{-1} for 5 min) through a 2, 4-dinitrophenylhydrazine (DNPH)
70 cartridge (Sigma-Aldrich, St. Louis, Missouri, USA) for derivatization followed by acetonitrile elution (5 mL) of the
71 DNPH cartridge. A $20 \mu\text{L}$ aliquot of the extract was loop-injected on a high-performance liquid chromatograph
72 equipped with an ultraviolet detector (HPLC-UV, Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA).
73 HPLC calibration was done using a Supelco 14-mix DNPH-hydrazone standard (Sigma-Aldrich, St. Louis, Missouri,
74 USA). The analytical column was a HICHROM RPB (length: 0.25 m, particle size: $5 \mu\text{m}$, diameter: 4.6 mm, Hichrom
75 Limited, Theale, Berkshire, UK). The mobile phase mixture was composed of 70% acetonitrile and 30% distilled
76 water at a flow rate of 1.5 mL min^{-1} for 16 min.

77 After the successful determination of G-WS CC concentrations, the desired gaseous working standards (G-WS)
78 were prepared by the subsequent dilution/mixing of G-PS-1 and G-PS-2 with ultrapure N_2 . The prepared G-WS was
79 subsequently utilized for the purpose of sorption experiments after confirming its concentration by employing the
80 procedure explained above.

81 Quartz tubes (89 mm length with 4 (inner) and 6 mm (outer) diameters: Top Trading Co., Seoul, South Korea)
82 were used for adsorption experiments. The quartz tubes were packed with the adsorbent held in place by quartz wool
83 plugs. At the beginning of each adsorption experiment, any impurities of pre-sorbed guest/target analytes were
84 removed by conditioning the packed sorbent tubes at 150°C for 3 h using ultrapure N_2 as a purge gas (flow rate of
85 200 mL min^{-1}). All of the experiments were conducted in triplicate and the averaged values of the results were
86 reported.

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88 *4. Computational model and method*

89 The interaction mechanisms between the MOFs and the guest molecules were studied by analyzing the DFT
90 calculations. For this purpose, the pseudo-potential code SIESTA model was applied (Kim et al., 2018). All of the

91 calculations were carried out using the generalized gradient approximation (GGA-PBE) with spin-polarization and
 92 the $+vdW$ correction required for the description of weak interactions (Li et al., 2018). A full optimization of atomic
 93 positions was performed. During the course of optimization, the ion cores were described by norm-conserving, non-
 94 relativistic, pseudopotentials with cut-off radii of 2.52, 2.37, 2.08, 1.15, 1.14, 1.45, and 1.25 au for Zr, Zn, Cu, O, C,
 95 N, and H, respectively (Boukhvalov et al., 2018). Moreover, the wave functions were expanded with a double-f plus
 96 polarization basis of localized orbitals for all species and a double-N basis for hydrogen. Optimization of the force
 97 and total energy was performed with accuracy values of 0.04 eV Å⁻¹ and 1 meV, respectively. These calculations were
 98 carried out with an energy mesh cut-off of 300 Ry and a k-point mesh of 4x4x4 for the MOFs within the Monkhorst-
 99 Pack scheme. The electronic structure of all of the molecules was calculated for a single molecule located in the empty
 100 cubic box with sides of 20 Å. This procedure was considered to reflect the realistic atomic structures of M5 and M199
 101 based on the Cambridge Database (CCDC), and of U6N taken from (Valenzano et al., 2011). The DFT-based 0 K
 102 adsorption enthalpy (ΔH_{ad}) was calculated by using Equation 1 as follows:

$$103 \quad \Delta H_{ad} = (E_{(host + guest)}) - (E_{host} + E_{guest}), \quad (1)$$

104 where $E_{host+guest}$ is the total energy of the MOF and the guest analyte, E_{host} is the total energy of the system before the
 105 adsorption of the molecule(s), and E_{guest} is the energy of the guest molecule(s) in the gas phase. In the case of the
 106 adsorption of the first molecule, E_{guest} is the total energy of the pristine MOF molar formula. For the further steps,
 107 E_{guest} is the total energy in the same unit with a single molecule or two molecules of the adsorbed analyte. The
 108 adsorption Gibbs free energy (ΔG_{ad} at 298 K) can be calculated using the 0 K ΔH_{ab} (with no thermal and zero-point
 109 energy corrections) and the estimated adsorption entropy change (ΔS_{ab}) by following the empirical procedure
 110 reported in the literature (Campbell and Sellers, 2012) as follows:

$$111 \quad \Delta G_{ad} = \Delta H_{ad} - T \cdot \Delta S_{ad}. \quad (2)$$

112 We performed the calculation of $T\Delta S_{\text{ad}}$ only for this analyte, and for other CCs we used this value (36.7 kJ mol^{-1}) as an
113 approximate reference point without calculations of ΔG_{ad} , because experimental data of the gas phase entropy used for
114 evaluation of the S_{ad} available was only for formaldehyde. Therefore, we considered adsorption to be unstable in the
115 case of ΔH_{ad} being higher than -20 kJ mol^{-1} .

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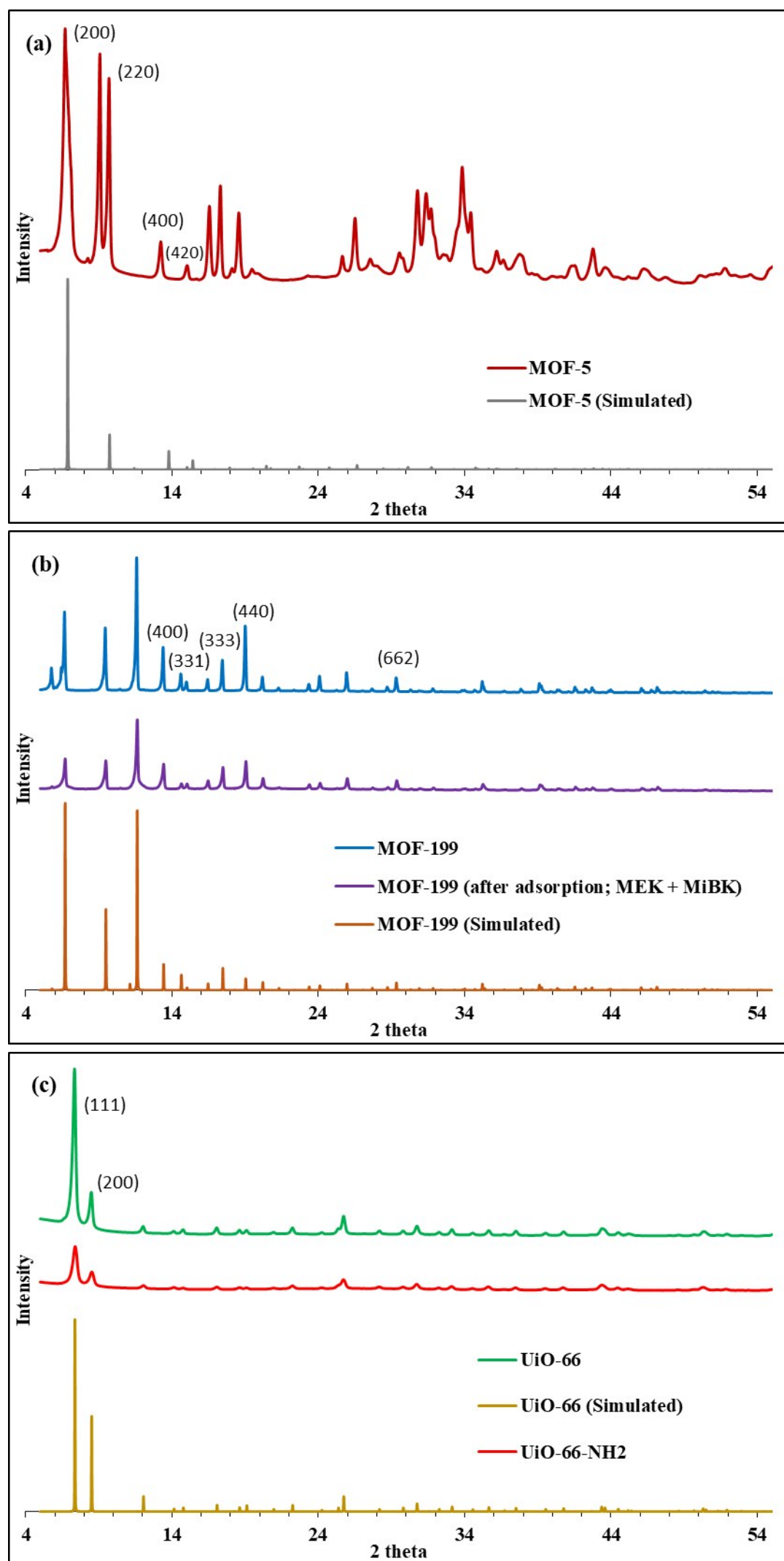


Figure 1S. PXRD patterns of MOFs investigated in this work: (a) MOF-5, (b) MOF-199, (c) UiO-66, and UiO-66-NH₂ (right after synthesis but prior to thermal activation). The simulated PXRD patterns for these MOFs were drawn using suitable crystallographic information files (CIFs) and ‘Visualization for Electronic and Structural Analysis (*VESTA*)’ software (Momma and Izumi, 2008). All the CIFs were obtained from (Furukawa et al., 2013).

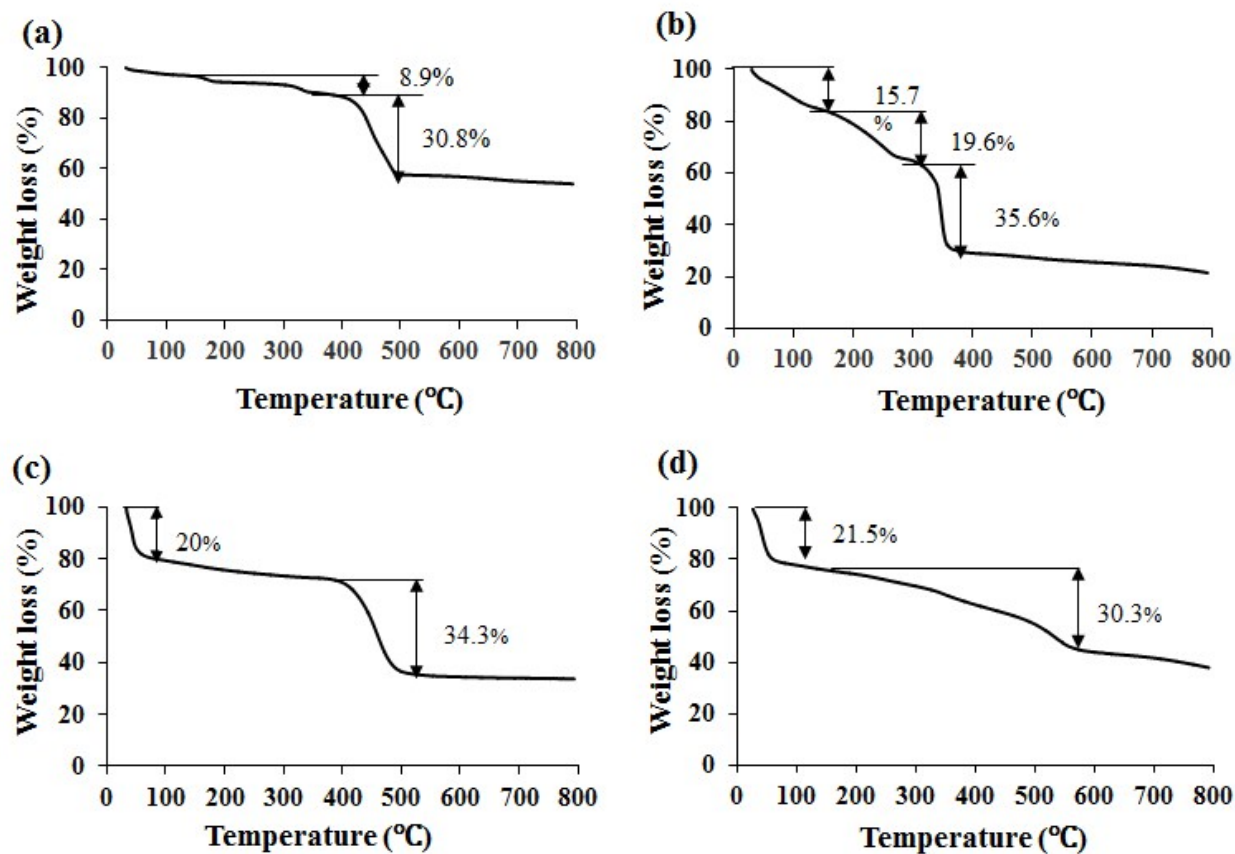


Figure 2S. TGA plots of (a) MOF-5, (b) MOF-199, (c) UiO-66, and (d) UiO-66-NH₂ (in N₂, soon after synthesis prior to thermal activation).

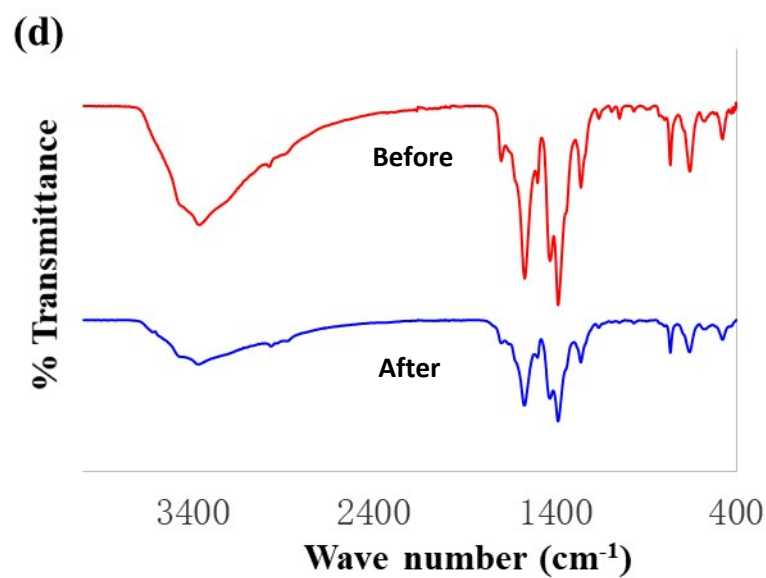
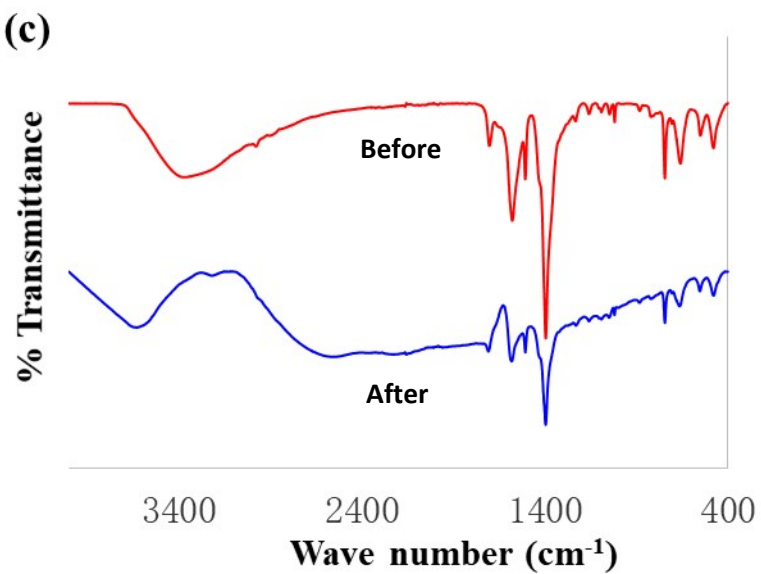
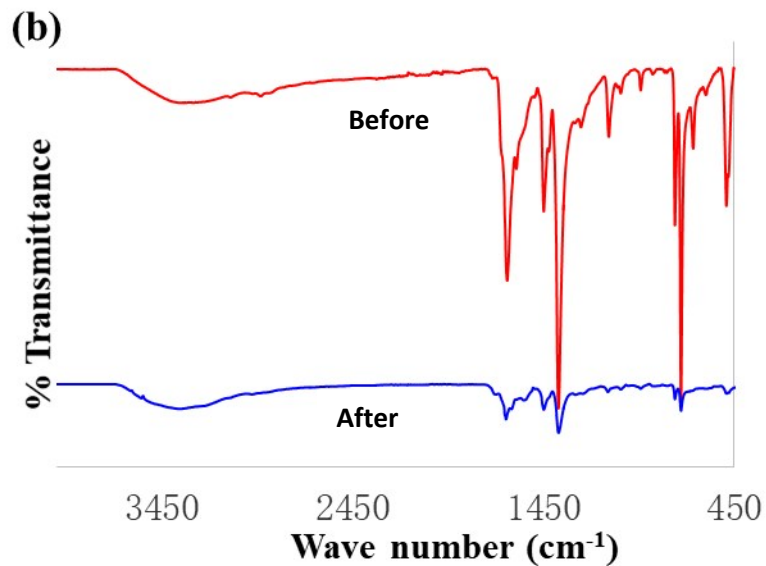
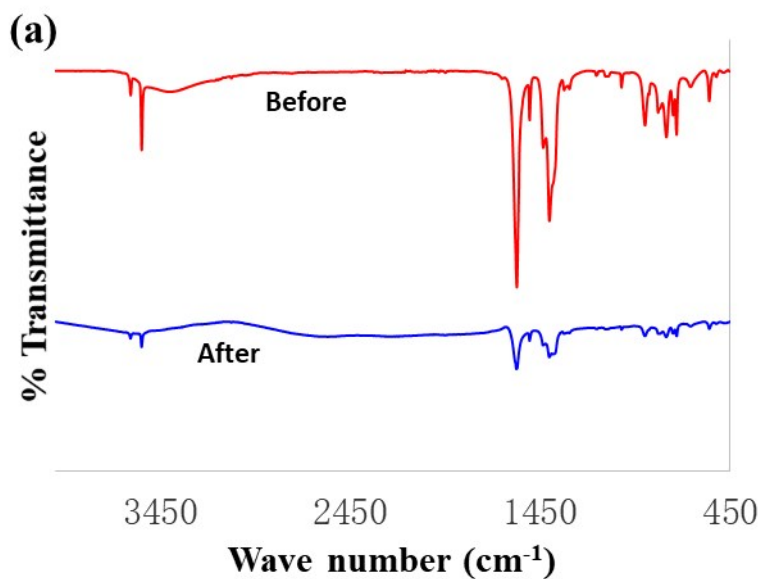


Figure 3S. FTIR spectra before (soon after synthesis prior to thermal activation) and after adsorption of: (a) MOF-5, (b) MOF-199, (c) UiO-66, and (d) UiO-66-NH₂.

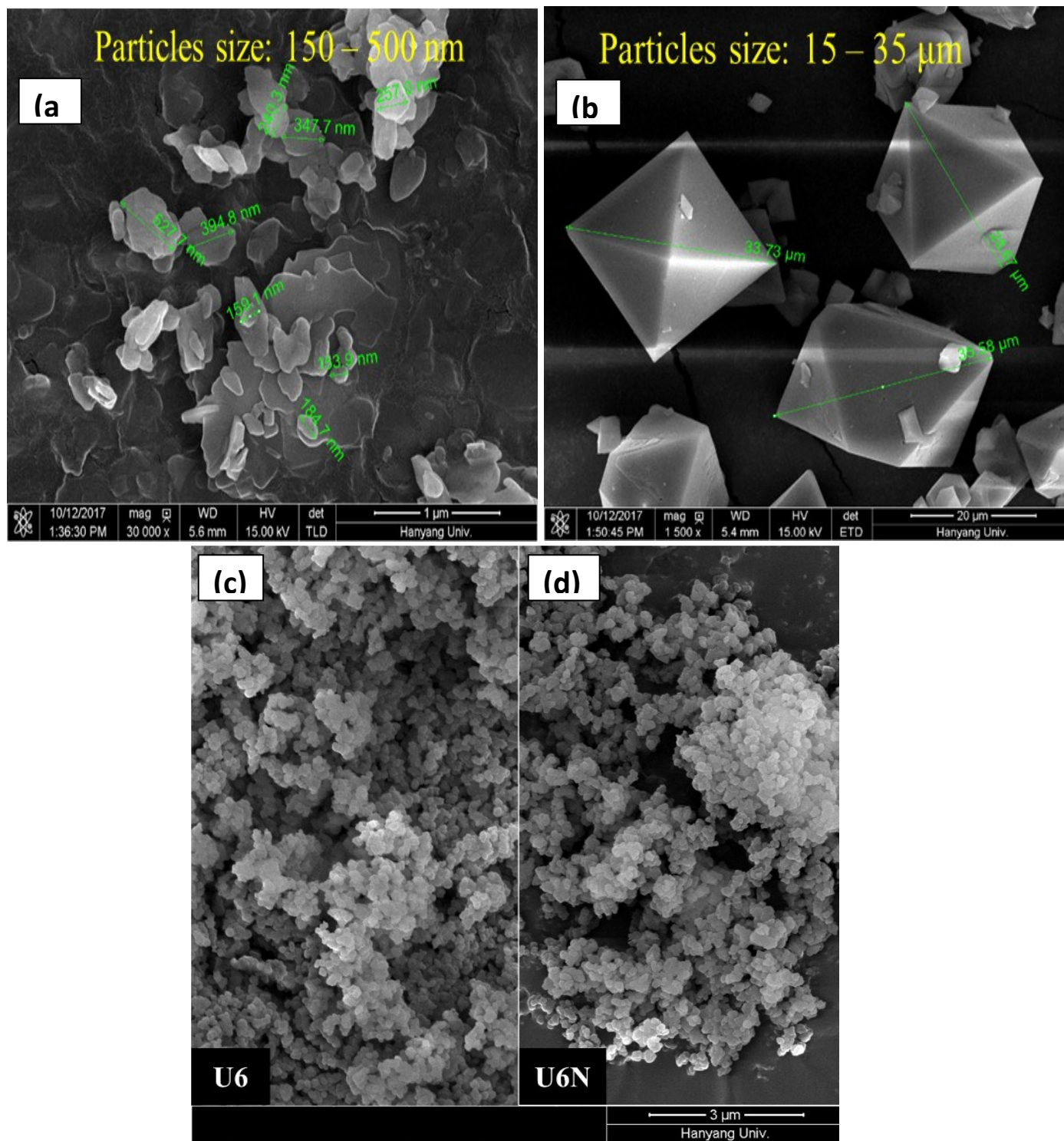
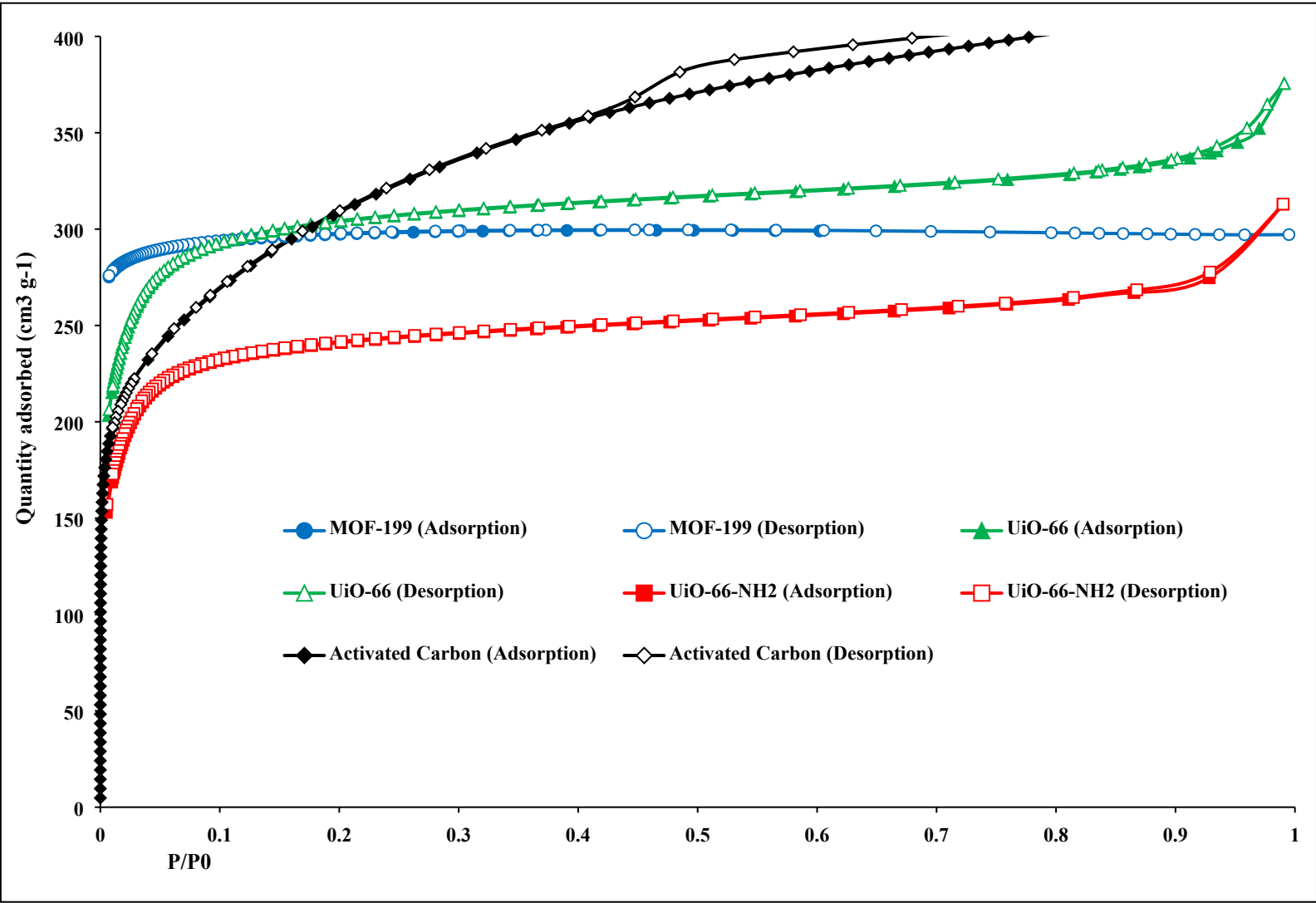


Figure 4S. SEM images of (a) MOF-5 (1 μm scale), (b) MOF-199 (20 μm scale), (c) UiO-66 (3 μm scale), and (d) UiO-66-NH₂ (3 μm scale).



279 **Figure 5S.** Nitrogen adsorption-desorption isotherm plots for the analyzed adsorbents. Data for MOF-5 not
280 shown.

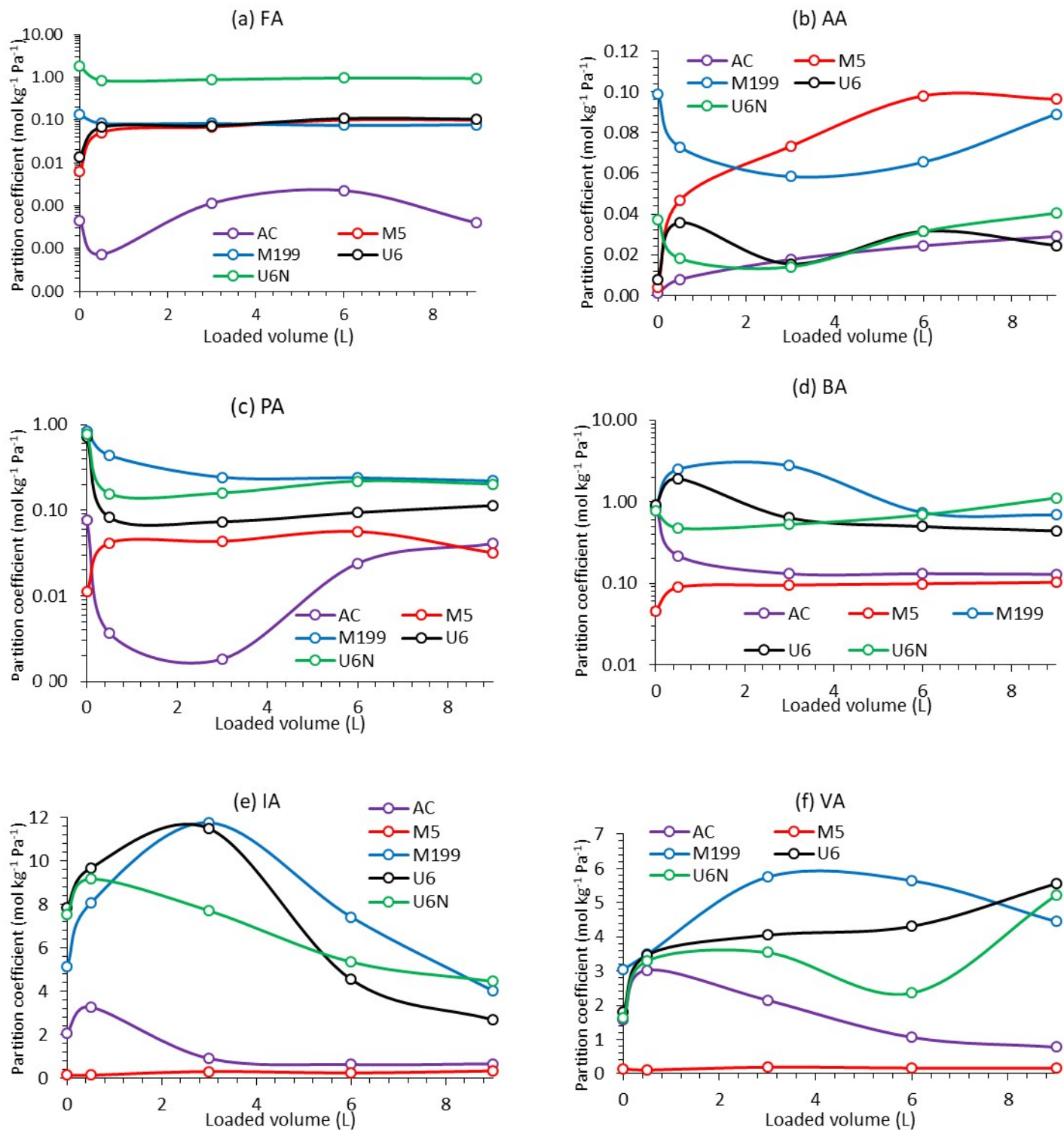


Figure 6S. Partition coefficient values of the tested adsorbents (high partial pressure (1 Pa for FA and AA, and ~ 0.2 Pa for the other CCs), mixture of all of the tested CCs, and 5 mg sorbent). (a) FA and (b) AA. (c) PA, (d) BA, (e) IA, and (f) VA.

314 **Table 1S.** The surface properties of adsorbents used in this study.

Order	Adsorbent	BET surface area	Single point surface area (Calculated using the standard BET model)	Pore volume (Calculated using the standard BJH model)	Adsorption average pore diameter (4V/A by BET)
		m ² g ⁻¹	m ² g ⁻¹	cm ³ g ⁻¹	nm
1	MOF-199	1,212	911	0.46	1.52
2	MOF-5	424	535	0.22	2.07
3	UiO-66-NH ₂	963	749	0.58	1.56
4	UiO-66	1,210	943	0.73	1.58
5	Activated carbon	1,004	831	0.71	1.21

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335 **Table 2S.** Calculated values of the enthalpy of adsorption (kJ mol⁻¹) for step by step loading of CC molecules
336 on various hosts. The numbers corresponding to the maximum energetically favorable loading of molecules
337 are in bold and used for the estimation of the maximum load in mg g⁻¹. The data presented here are derived
338 using the theoretical DFT-based simulations.

Order	Guest	Host	Number of molecules adsorbed per molar formula unit of the MOF			Maximum adsorption capacity (mg g ⁻¹)
			1	2	3	
1	FA	M5	-119.3	-120.7	-119	58.5
2		M199	-26.4	-9.8	-7.1	11.5
3		U6N	-45.7	-3.8	0.8	17.0
4	AA	M5	-143	-143	-144	85.6
5		M199	-31.2	-9.3	-10.4	11.2
6		U6N	-47.1	-2.6	1.2	25.0
7	PA	M5	-146	-146	-139	113.1
8		M199	-53.4	-11.4	-23.4	22.2
9		U6N	-49.8	-12.1	-4.2	33.0
10	BA	M5	-147	-148	-154	140.3
11		M199	-53.4	-10.4	-10.7	27.6
12		U6N	-56.7	-15.4	-9.9	40.9
13	IA	M5	-163	-162	-172	167.6
14		M199	-62.4	-14.1	-28.3	33.0
15		U6N	-56.9	0.68	-10.9	48.9
16	VA	M5	-148	-147	-157	220.3
17		M199	-56.7	-14.8	-24.9	65.0
18		U6N	-56.4	-9.84	-7.04	64.2

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